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Lu Wu, Student

Dr. Dong-Sheng Yang, Major Professor

Dr. Dong-Sheng Yang, Director of Graduate Studies
STRUCTURES AND ELECTRONIC STATES OF SMALL GROUP 3 METAL CLUSTERS

DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Arts and Sciences at the University of Kentucky

By
Lu Wu
Lexington, Kentucky

Director: Dr. Dong-Sheng Yang, Professor of Chemistry

Lexington, Kentucky
2014

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ABSTRACT OF DISSERTATION

STRUCTURES AND ELECTRONIC STATES OF SMALL GROUP 3 METAL CLUSTERS

Group 3 metal clusters are synthesized by laser vaporization in a pulsed cluster beam source and identified with laser ionization time-of-flight mass spectrometry. The adiabatic ionization energies and vibrational frequencies of these clusters are measured using mass-analyzed threshold ionization (MATI) spectroscopy. Their structures and electronic states are determined by combining the MATI spectra with quantum chemical calculations and spectral simulations. This dissertation focuses on the study of several small molecules, which include LaO$_2$, La$_2$, M$_2$O$_2$, M$_3$O$_4$, M$_3$C$_2$, and La$_3$C$_2$O, where M = Sc, Y, and La. Except for La$_2$, these molecules exhibit strong ionic characters between the metal and oxygen or carbon atoms and can be described as [O$^-$][La$^{2+}$][O$^-$], [M$^{2+}$]$^2_2$[O$^2-$]$_2$, [M$^{8/3+}$]$^3_3$[O$^2-$]$_4$, [M$^{2+}$]$^3_3$[C$^3-$]$_2$, and [La$^{8/3+}$]$^3_3$[C$^3-$]$_2$[O$^2-$]. The interactions between the metal atoms form covalent bonds, which can be described by a triple bond in La$_2$, a two-center two electron bond in M$_2$O$_2$, a three-center one electron bond in M$_3$O$_4$, and a three-center three electron bond in M$_3$C$_2$. In addition, the electron in the non-bonding highest occupied molecular orbital (HOMO) is localized in the La 6s orbital in LaO$_2$ and La$_3$C$_2$O. The ground states of these molecules are all in low electron-spin states with the spin multiplicities of 1 or 2. Although the ground electronic state of LaO$_2$ is a linear structure, the excited quartet state of the molecule is determined to be a bent structure. M$_2$O$_2$ and M$_3$O$_4$ have the planar rhombic and cage-like structures, respectively; whereas M$_3$C$_2$ has a trigonal bipyramid structure. La$_3$C$_2$O is formed by oxygen binding with two La atoms of La$_3$C$_2$. Ionization removes a metal-based (n+1)s electron in all
neutral molecules, and the resultant ions have similar geometries to those of the corresponding neutral states. In the case of La$_2$, additional ionization of a La 5d electron is also observed.

KEYWORDS: MATI spectroscopy, metal oxides, metal carbides, adiabatic ionization energy, quantum mechanical calculations
STRUCTURES AND ELECTRONIC STATES OF SMALL GROUP 3 METAL CLUSTERS

By

Lu Wu

Dong-Sheng Yang
Director of Dissertation

Dong-Sheng Yang
Director of Graduate Studies

4/18/2014
Date
STRUCTURES AND ELECTRONIC STATES OF SMALL GROUP 3 METAL CLUSTERS

Lu Wu

The Graduate School
University of Kentucky
2014
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<td>photoelectron spectroscopy</td>
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<td>TPES</td>
<td>threshold photoelectron spectroscopy</td>
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<td>MATI</td>
<td>mass-analyzed threshold ionization</td>
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<td>VUV</td>
<td>vacuum ultraviolet</td>
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<tr>
<td>UV</td>
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</tr>
<tr>
<td>EUV</td>
<td>extreme ultraviolet</td>
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<tr>
<td>EA</td>
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<td>AIE</td>
<td>adiabatic ionization energy</td>
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<td>Franck-Condon factor</td>
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<td>CCSD (T)</td>
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<td>Complete active space SCF</td>
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CHAPTER 1 INTRODUCTION

The concept of clusters was introduced by Cotton in the 1960s to distinguish the compounds containing metal-metal bonds from the Werner complexes.\textsuperscript{1-3} Because of a wide range of the metal-metal bond lengths, identification of a true metal-metal bond is often difficult. To circumvent this problem, the concept was then modified by Mingos in the 1990s to describe the compounds having "a group of two or more metal atoms with a direct and substantial metal-metal bond".\textsuperscript{4} With the development of the cluster science, more and more clusters have been synthesized. Nowadays, a cluster no longer necessarily contains metal-metal bonds and may consist of nonmetal elements, such as carbon or boron. Instead, the concept of clusters is expanded to describe a state of aggregation between atoms and bulk. In 2002, Johnston defined a cluster in his book as "an aggregate of countable number (2-10\textsuperscript{n}, where n can be as high as 6 or 7) of particles (i.e. atoms or molecules)\".\textsuperscript{5} Mass spectrometry has widely been used to study the stability of different clusters. In the 1970s, French Physicists observed the M\textsuperscript{n+/−} (M = metal) clusters when conducting secondary molecular ion emission measurements in the gas phase. Their measurements included the clusters of the main group elements, such as C, Si, Li, Al, Be, and Mg\textsuperscript{6-8}, and some of the transition metals, such as Ag and Cu\textsuperscript{6,7}. They found that the intensities of the secondary ion signals, which indicated the stability of the clusters, are related to their sizes (n). The ion signals either regularly decreased with n (i.e., Be, Mg), oscillated with the parity of n (i.e., Cu), or showed maxima at some particular n values (i.e., Al). These mass spectrometric studies were extended to rare-gas atomic clusters, including He\textsubscript{n} (n<32)\textsuperscript{9},
Ne$_n$ (n<90)$^{10}$, Ar$_n$ (n<60)$^{11}$, Kr$_n$ (n<60)$^{11}$ and Xe$_n$ (n<150)$^{9,12}$ The mass spectra of these clusters exhibited high-intensity peaks with a size of so-called “magic numbers”. The magic numbers were also observed in the mass spectra of alkli-metal clusters.$^{13}$ The exceptional relative stability of these clusters was attributed to the completely packed geometric shells, similar to the closed-shell electronic structure of the rare gas elements.$^{14}$

In 1984, Kroto and co-workers examined the mass spectra of carbon cluster beams produced by laser vaporization and supersonic expansion.$^{15}$ They proposed a buckyball structure for C$_{60}$ to explain its intense cation signal,$^{15,16}$ which is now known as fullerene. Due to the huge potential applications, fullerene analogs have been widely studied in the size range of 20 to 1000 atoms.$^{17}$ Met-car clusters, typically with a formula of M$_8$C$_{12}$, were discovered by Castleman et al. as another group of stable clusters$^{18-21}$ and studied by Duncan and others.$^{22}$ These clusters also showed size-dependent adiabatic ionization energies (AIEs), electron affinities (EAs), chemical reactivity and other properties.$^{5,14,19,23,24}$

Metal clusters in the gas phase have been prepared with Knudsen cell effusive$^{25-28}$, ion sputtering$^{29-31}$, and laser ablation methods among others.$^{32-34}$ The Knudsen cell effusive method involves the heating of a solid or liquid sample in an oven with a small orifice and is commonly used to study the thermodynamic properties of the clusters. The ion sputtering method involves the bombarding of the solid sample surface by high-energetic inert gas ions and is usually used for the surface analysis of solid materials. Laser ablation coupled with supersonic expansion, introduced by Smalley and co-workers in 1981, is the most widely used method to prepare metal clusters in the gas phase.$^{35-39}$ It can be used for any metal elements and can generate a wide range of the cluster sizes in neutral
or ionic states with low internal temperatures. Because of these advantages, I used the laser ablation method to prepare the transition metal clusters of interest in this work.

The transition metal clusters have been extensively studied in the gas phase. The studies of the cationic clusters have been reported on their reactivity, UV-Vis photofragmentation, and infrared (IR) multiphoton photodissociation or single-photon vibrational predissociation. The studies of the anions have largely been carried out with photoelectron spectroscopy, and additional investigations have been reported about their reactivity and IR photodissociation. The neutral clusters are more challenging to study experimentally because they are difficult to select. Their formation and properties have usually been investigated by ionization techniques, including multiphoton IR and single-photon UV and vacuum UV laser ionization. In addition, the neutral clusters have been studied by matrix-isolation IR spectroscopy. In spite of the extensive studies, the current knowledge about the electronic states and molecular structures of the polyatomic transition metal clusters is largely derived from the theoretical predictions. However, the reliable prediction of the electronic and geometric structures is often complicated by the presence of many low energy structural isomers and many low-lying electronic states of each isomer. Inconsistent theoretical results have been reported on the ground electronic states and minimum energy structures of the polyatomic neutral clusters and ions. Therefore, a reliable identification of the molecular structures and electronic states for the transition metal clusters and their ions generally requires the confirmation by spectroscopic measurements, especially by high resolution spectroscopic techniques.
This work focuses on the spectroscopy, bonding, and structures of the rare earth metal oxide, carbide, and carboxide clusters. These clusters are synthesized by the laser ablation technique and cooled by the supersonic expansion. Their AIEs and vibrational frequencies are measured by mass-analyzed threshold ionization (MATI) spectroscopy. Their geometric structures and electronic states are investigated by combining the spectroscopic measurements with quantum chemical calculations and spectra simulations.

In the following sections, I will briefly describe the spectroscopic and computational methods. Because the MATI technique is derived from photoelectron spectroscopy (PES), I will first describe the photoelectron technique.

1.1 PES MEASUREMENTS

The PES technique is based on the photoelectric effect, which was first observed by Heinrich Hertz in 1887. In 1902, Philipp Lenard quantitatively studied the photoelectric effect and discovered the 'stop voltage' in a photoelectric experiment. His work was explained by Albert Einstein with the following equation:

$$E_k = h\nu - W$$

Where $E_k$ is the kinetic energy of emitted electrons, and $\nu$ is the frequency of light, $W$ is the work function of the sample surface.

Although the photoelectric phenomena were studied for a long time, the first photoelectron spectrometer was not built until 1957 by Kai Siegbahn to study the energy levels of atomic core electrons. His work focused on the characterization of solid surfaces with the X-ray light source. The PES was also applied in the extreme ultraviolet (EUV),
vacuum ultraviolet (VUV), and ultraviolet (UV) energy regions to study valence electrons. The first gas-phase PES spectrometer was developed by Turner and coworkers in the VUV region and modified by Smalley and coworkers to measure the valence electron binding energies. In this dissertation, the term of PES will be restricted to the gas-phase PES unless otherwise noted.

1.1.1 Conventional PES

In a PES measurement, a molecule absorbs a photon and emits an electron. According to the energy conservation rule, the photon energy ($h\nu$) is transferred to the kinetic energy ($E_k$) of the emitted electrons and the internal energy change ($\Delta E$) of the molecule, as expressed by Equation (1.2):

$$h\nu = \Delta E + E_k$$

(1.2)

The internal energy of a molecule is the summation of its electronic, vibrational, rotational, and translational energies. Because the mass of an electron is negligible compared to that of the molecule, the kinetic energy change of the nuclear frame is approximately zero. The energies and the angular distributions of the incident photon and the ejected photoelectron reveal the electronic, vibrational, and rotational information of the molecule.

Conventional PES is used to study the neutral molecules and anions. It provides the IEs for the neutral molecules and the EAs for the anions. As shown in Figure 1.1(a), a molecular beam is bombarded with light of the fixed wavelength. The electrons are ejected when the energy of light exceeds their binding energies. For a neutral molecule, the AIE is obtained by recording the kinetic energies of the ejected electrons. It is convenient to
build an apparatus for the conventional PES measurements because a fixed-wavelength laser and an electron energy analyzer can simply meet the requirements. However, the application of this technique is limited by the resolution of the electron energies. Because the neutral molecules are converted to the cations at different energy levels when the photon energy exceeds their AIEs, their vibrational and rotational information can be derived from the energy distribution of the electrons. However, the rotational structures of the most molecules and the vibrational structures of polyatomic metal-containing molecules have rarely been resolved using the conventional PES, because its resolution is generally no better than 10 meV (~80 cm\(^{-1}\)).

Threshold photoionization (TPES) spectroscopy was developed by Schlag and co-workers to improve the spectral resolution. As shown in Figure 1.1(b), tunable pulsed laser is used to ionize the molecules, and an electron filter is employed to remove the electrons with high kinetic energies. A photoelectron spectrum is measured as a function of the signal intensity of the near-zero kinetic energy electrons, instead of the energy distribution of the emitted electrons. With this scheme, the spectral resolution has been improved to a few meV, which is significantly higher than that of the conventional PES. However, the separation of the near-zero energy electrons from other kinetic energy electrons is still difficult with this method. To further improve the spectral resolution, pulsed-field ionization zero electron kinetic energy (PFI-ZEKE or ZEKE) spectroscopy was developed by Müller-Dethlefs, Sander, and Schlag in 1984.

1.1.2 PFI-ZEKE and MATI spectroscopy

The PFI-ZEKE technique relies on the delayed pulsed field ionization of the long-lived, high-lying Rydberg states (principal quantum number n > 150), which are prepared
by photoexcitation. Because the Rydberg series of the neutral molecule converge to various eigenstates of the cation, the energies of the high-lying Rydberg states are close to the ionization threshold. Thus, the energy of the excitation light source is a good approximation of the AIEs. The electrons which are generated directly from the photoionization process (direct electrons) are separated spatially from the Rydberg molecules by a discrimination electric field. A small time-delayed pulsed electric field is used to ionize the high-lying Rydberg molecules and generate the zero kinetic energy electrons. A spectral resolution of a small fraction of cm\(^{-1}\) has been obtained by using this method\(^{106,107}\), and it can further be improved by decreasing the linewidth of the light source and the strength of the ionization field.\(^{108}\)

The Rydberg states can be described as the energy levels of single electron weakly bounded to an ionic core by the Coulomb force. The energies of a Rydberg series are calculated by Rydberg formula: 

\[
E_{nlm} = -\frac{R_M}{(n-\delta_l)^2},
\]

where \(n, m,\) and \(l\) are the principle, angular, and magnetic quantum numbers, \(\delta_l\) is the \(l\)-dependent quantum defect, and \(R_M\) is the Rydberg constant. The Rydberg constant depends on the mass of the atomic or molecular core and can be estimated by \(R_s = 109737\text{cm}^{-1}\) for heavy atoms or molecules. The high-lying Rydberg states are not fully understood yet, due to the difficulties of theoretical calculations and experimental measurements. The challenges arise from the high density of the energy states and their subtle response to the perturbations from even a weak electric field. The long life time of the high-lying Rydberg states are commonly explained by the strong \(l\)- and \(m_l\)-mixing in the stray field caused by the nearby charged particles. These perturbations remove the high energy degeneracies and generate closely
packed Stark levels.\textsuperscript{108-116} The effects of the electric field on high Rydberg states were extensively studied experimentally and theoretically.\textsuperscript{108-110,117,118} In the presence of an electric field, the AIE from the PFI-ZEKE measurements is red shifted due to the Stark effect. This field effect is predicted by the equation $\Delta IE = c \cdot \sqrt{F}$ ($\Delta IE$ is the IE shift in cm$^{-1}$, $F$ is the strength of the electric field in V/cm, $c$ is a constant) on the basis of the classic atomic model.

PFI-ZEKE provides the accurate AIEs of the neutral species and vibrational information of the cations. It has the advantages over the conventional PES and some of the optical spectroscopic methods. In the gas phase, the optical spectroscopic methods, such as infrared absorption and Raman scattering techniques, are generally less applicable to measure the vibrational frequencies of cations. One of the reasons is that the Coulomb repulsive force between the cations makes it difficult to prepare the samples with high molecular densities. Secondly, the infrared and Raman transitions generally have smaller cross sections than the electronic transitions. Moreover, the vibrational frequencies of metal-ligand complexes and metal clusters are typically less than a few hundred wavenumbers, while the tunable IR light source below 500 cm$^{-1}$ is much more difficult to generate than the UV lasers.

As a sister technique of ZEKE, MATI spectroscopy was developed by Zhu et al.\textsuperscript{119} Instead of detecting electrons, a MATI measurement records the ion signals. MATI spectroscopy provides similar information to ZEKE, yet has the advantage of the mass selection. If multiple clusters exist in the molecular beam and have similar AIEs, the identification of the ZEKE electron carrier becomes less straightforward and MATI measurements are preferred. On the other hand, because the ions are much heavier than...
the electrons, the separation of the ions produced by the delayed filed ionization from those by direct photoionization requires a stronger discrimination electric field and a longer delay time of the ionization field than those in the ZEKE experiment. To increase the lifetime of the high-lying Rydberg states, an AC scrambling field is often used in the MATI experiment.120

1.2 THEORETICAL CALCULATIONS

The spectroscopic measurements are generally analyzed with the help of the theoretical calculations. Ab initio calculations are used to find the minimum energy structures and calculate vibrational frequencies of the neutral and ionic clusters. Franck-Condon factor (FCF) calculations and spectral simulations are used to calculate the intensities of the MATI spectra. The comparison of the spectral measurements and theoretical calculations is used to determine the molecular structures and electronic states of the neutral and ionic clusters.

Although the structure of a molecule is defined by the position of each atom, the internal motions of the molecule are commonly described by the normal coordinates. The potential energy surface of the molecule is calculated by the single-point energies of different structures as a function of their coordinates. Geometry optimization aims to find the stationary points on the potential energy surface. A stationary point is reached when the first derivatives of the potential energy with respect to all the coordinates are zero. If the energy of the molecule increases with an arbitrary small displacement from the stationary point, the stationary point is called a local minimum. If the energy of the molecule increases with a small displacement along all but one of the normal coordinates,
this stationary point is called a transition state. The local minimum with the lowest energy is called the global minimum, which is the ground state of the most stable structure.

The vibrational frequencies are calculated from the second derivatives of the potential energy surface with respect to the normal coordinate. The calculated frequency is a positive real number if the second derivative is positive and an imaginary number if the second derivative is negative. Thus, the number of imaginary frequencies is another way to characterize a stationary point of the potential energy surface. The number of imaginary frequencies is zero for a local minimum and one for a transition state. If the number of the imaginary frequencies is \( n \), it is called the \( n \)th-order saddle point. The transition state is also called the first-order saddle point.

Computational methods are distinguished by the approaches they use to perform the single-point energy calculations. The energy calculations can be performed by molecular mechanics, semi-empirical, and \textit{ab initio} methods. Among all these methods, the \textit{ab initio} methods are the most popular, systematic, and reliable, especially for small molecular systems. Various \textit{ab initio} methods are briefly introduced in this section.

1.2.1 \textit{ab initio} calculations

The Schrödinger equation (Equation (1.3)) is the foundation of the quantum mechanics. By solving the Schrödinger equation, the \textit{ab initio} calculations can provide its eigenvalues as the possible energy levels and eigenfunctions for the status of a system.

\[
\hat{H}\Psi = E\Psi
\]  

(1.3)
Where \( E \) is the total energy, \( \Psi \) is the wavefunction, and \( \hat{H} \) is the Hamiltonian operator.

For a polyatomic molecule under a field-free condition, the Hamiltonian operator can be expressed as

\[
\hat{H} = \sum_{\alpha} \left( -\frac{1}{2} \nabla_{\alpha}^2 \right) + \sum_{r} \left( -\frac{1}{2} \nabla_{r}^2 \right) + \sum_{\alpha > \beta} \frac{Z_{\alpha}Z_{\beta}}{R_{\alpha\beta}} + \sum_{i<j} \frac{1}{R_{ij}} - \sum_{\alpha} \sum_{i} \frac{Z_{\alpha}}{r_{\alpha i}} + V(R, r) \tag{1.4}
\]

In this equation, only the kinetic energies of the nuclei and electrons and the static electric potential are expressed. All other factors, such as relativistic effect and the spin-orbit coupling, are included in the \( V(R, r) \) term.

If the expression of the Hamiltonian can be found, the total energy can be accurately predicted by mathematics. Unfortunately, few systems can be solved analytically and accurately. In most cases, Equation 1.4 is solved numerically with approximations. In the following subsections, I will briefly describe the Hartree-Fock theory and several correlation methods. Strictly speaking, density functional theory (DFT) is not an \textit{ab initio} method because it depends on the empirical density functionals. In this chapter, I will include DFT in the \textit{ab initio} methods.

1.2.2 Hartree-Fock theory

The fundamental difficulty of solving the Schrödinger equation is the separation of the variables. This difficulty is circumvented by the Hartree-Fock theory, which offers a numerical solution. The Hartree-Fock theory solves the Schrödinger equation iteratively and is workable by computer programing. It is also called called self-consistent field method (SCF) and transfers the Schrödinger equation of a multiple-electron system into
equations of single-electron systems with several approximations. First, it ignores the term \( V(R,r) \) in Equation (1.4) because this term is typically small for not very heavy elements. Second, it treats the coordinates of the electrons as variables but freezes the nuclei by applying the well-known adiabatic approximation (also called Born-Oppenheimer approximation or 'frozen core' approximation). \(^{121}\) This is reasonable because the electrons are moving much faster than the nuclei and the nuclear kinetic energy can be considered to be zero. Thus, the nuclear repulsion energy becomes constant and can be removed during the calculations. More importantly, the only variables we need to consider in the Schrödinger equation are the coordinates of the electrons. The Hamiltonian operator can then be simplified as

\[
\hat{H} = \sum_{i} \left(-\frac{1}{2} \nabla_i^2 \right) - \sum_{\alpha} \sum_{i} \frac{Z_{\alpha}}{r_{ai}} + \sum_{ij} \frac{1}{r_{ij}} \\
= \sum_{i} \left(-\frac{1}{2} \nabla_i^2 \right) - \sum_{\alpha} \frac{Z_{\alpha}}{r_{ai}} + \sum_{ij} \frac{1}{r_{ij}} 
\]

The first term in Equation (1.5) is the summation of the one-electron operators, and the second term is the summation of two-electron operators.

The basic idea of the Hartree method is to deal with the electrons separately. By solving the single-electron equations in Equation (1.6), the wavefunctions \((\phi_i(r_i), i = 1, 2, 3 \ldots)\) of individual electrons are used to calculate the wavefunction and the energy of the molecule by Equation (1.7) and (1.8), respectively.

\[
\hat{H} \phi_i(r_i) = \varepsilon_i \phi_i(r_i) 
\]

\[
\Psi = \phi_1(r_1) \phi_2(r_2) \cdots \phi_N(r_N) 
\]
\[ E = \langle \Psi | \hat{H} | \Psi \rangle \]  

(1.8)

In order to calculate the energy contribution of each electron separately, Hartree assumed that each electron is in a spherically averaged electric field of all other electrons. The potential energy of the \( i \)-th electron is expressed in Equation (1.9).

\[
\hat{V}_i(r_i) = \frac{\sum e^2 \int_0^\pi \sin \theta d \theta \int_0^{2\pi} d \varphi \int \left| \phi_j \right|^2 \frac{1}{r_{ij}} dr_j}{\int_0^\pi \sin \theta d \theta \int_0^{2\pi} d \varphi_i}
\]

(1.9)

Where \( \phi_j \) is the wavefunction of the \( j \)-th electron.

The single-electron operator can be modified as:

\[
\hat{H}_i = -\frac{1}{2} \nabla_i^2 - \sum_{\alpha} Z_i \frac{1}{r_{i\alpha}} + \hat{V}_i
\]

(1.10)

Thus, starting from a set of known orbital functions (typically from the atomic orbitals), the single-electron wavefunctions can be solved iteratively from Equations (1.6), (1.9) and (1.10). The wavefunction and energy of the molecule can be calculated from Equations (1.7) and (1.8). The potential energy of the single electron is evaluated by the wavefunction of the molecule in Equation (1.11)

\[
V_i = \sum_{j \neq i} J_{ij} = \sum_{j \neq i} \langle \Psi | \frac{1}{r_{ij}} | \Psi \rangle = \sum_{j \neq i} \langle \phi_i \phi_j | \frac{1}{r_{ij}} | \phi_i \phi_j \rangle
\]

(1.11)

Where \( J_{ij} \) is called Coulomb energies. The operator in Equation (1.11) can be rewritten as the summation of so-called Coulomb operators, which are defined as
\[ \hat{J}_j \phi_i(1) = \left[ \int \phi_j(2) \frac{1}{r_{12}} \phi_i(2) d\tau_2 \right] \phi_i(1) \quad (1.12) \]

Where \( \phi_i \) is the wavefunction of the \( i \)th orbital, 1 and 2 represent the coordinates of two electrons.

Fock modified this algorithm by using the Slater-type orbital in Equation (1.13) to substitute the one in Equation (1.4).

\[
\Psi(r_1, r_2, \ldots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \ldots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \ldots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \ldots & \phi_N(N) \end{vmatrix} \quad (1.13)
\]

The Pauli's exclusiiive principle is considered in the Slater-type orbital, which is ignored in the Hartree's theory. The total Hamiltonian and the single-electron operator are rewritten as the Fock operator in Equation (1.14) and (1.15)

\[
\hat{H} = \sum_i \hat{F}_i \quad (1.14)
\]

\[
\hat{F}_i = -\frac{1}{2} \nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha i}} + \sum_{j=1, j \neq i}^{M} (\hat{J}_j - \hat{K}_j) \quad (1.15)
\]

Where \( \hat{K}_j \) is the exchange operator, which is defined in Equation (1.16)

\[ \hat{K}_j \phi_i(1) = \left[ \int \phi_j(2) \frac{1}{r_{12}} \phi_i(2) d\tau_2 \right] \phi_i(1) \quad (1.16) \]

The Hartree-Fock method considers the Pauli's principle and naturally includes the electrons as fermions. However, it ignores most of the correlation energies from the interaction of the electrons. The correlation energy is typically less than 1\% of the total
energy, but it plays important roles in chemistry because it has the same magnitude as the typical reaction or activation energies.

There are two types of the electron correlations. The first one is called the dynamic correlation. It is due to the instantaneous repulsions of the electrons, which is assumed to be the averaged electron field in Equation (1.3). The Hartree-Fock theory includes the exchange energy by using the Slatter-type orbitals, but ignores the fact that two electrons cannot occupy the same position at the same time. This effect can be corrected to various extents by different single reference methods. The second type is called the static correlation, which is due to the near degeneracy of the electronic states. When the two reference states have the comparable energies, the single reference wavefunction is not able to describe the system precisely. This effect is treated with the multi-reference theories. The single- and multi-reference theories are briefly described below.

1.2.3 Configuration interaction (CI) theory

CI is one of the most successful methods to calculate the electron correlation energies.\textsuperscript{122,123} The orbitals derived by solving the Hartree-Fock equations are used to form the configuration state functions (CSFs). The CSFs are classified as single, double, triple, and higher order excited state configurations according to the number of the electrons that are excited from the ground electronic state. The molecular orbital in the CI calculations is written as a linear combination of the CSFs of the same symmetry, and the molecular wavefunction and energy are calculated by the variation theory.

The computational accuracy and cost of the CI calculations increase rapidly with the number of the CSFs. Thus, the selection of the reasonable size of the CSFs becomes
an important issue. For example, the full CI calculation including all the possible CSFs is so expensive that it is only applicable for a few small molecules, such as N\textsubscript{2} and O\textsubscript{2}. The CSFs are generally selected on the basis of the compromise of the computational cost and accuracy. Because the singly and doubly exited CSFs account for a large part of the correlation interaction energies, the configuration interaction method with the single and double excitations (CISD) is commonly used.

1.2.4 Møller-Plesset perturbation (MPn) theory

MPn theory\textsuperscript{124,125} considers the deviation of the two-electron energy in the Hartree-Fock calculations as a perturbation term. The Hamiltonian in MPn is expressed as

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$$ \hspace{1cm} (1.17)

Where $\hat{H}^{(0)}$ is expressed in Equation (1.14) and solved by the Hartree-Fock method, $\hat{H}^{(1)}$ is the perturbed term and expressed as

$$\hat{H}^{(1)} = \sum_{j \neq i} \frac{1}{r_{ij}} - \sum_{j \neq i} (\hat{J}_j - \hat{K}_j)$$ \hspace{1cm} (1.18)

The MPn methods use the molecular orbitals and energies from the HF calculations as the unperturbed term and treat the perturbed term successively to higher orders. The calculated energy will be closer to the true value with high order calculations. Comparing to variational theory-based methods (i.e., CI), MPn calculations converge much faster. They are commonly used to treat the correlation effect near the equilibrium point. However, unlike the variational theory calculations, the calculated energies by the MPn methods are not necessarily higher than the true energies. The MPn methods cannot predict the precise
energy of a structure that is far away from the equilibrium and also do not work well for the excited states. Moreover, in the unrestricted calculations, the wavefunctions from the UHF calculations are not the eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$ (called spin contamination effect). In such cases, MPn may produce serious errors due to the spin contaminations.

1.2.5 Density functional theory (DFT)

DFT\textsuperscript{126,127} is more efficient than the traditional wavefunction-based \textit{ab initio} methods. In DFT calculations, the ground state energy, wavefunction, and other electronic properties are assumed to be the functionals of the ground state electron densities. The total energy of the molecule is expressed as

\[ E[\rho] = T[\rho] + U[\rho] + V[\rho] \]

In Equation 1.19, $\rho$ is the electron density as a function of the position. $T[\rho]$, $U[\rho]$ and $V[\rho]$ are the kinetic energies, electron-electron correlation energies, and the energies due to the external fields, respectively. Operators T and U are called universal operators because they are only related to the electrons and don't depend on the nuclei in the system. On the other hand, V is a system-dependent term.

DFT can determine the properties of the ground electronic states quite well. In the DFT calculations, the kinetic energies are determined precisely; the exchange-correlation energies are unknown and empirically estimated by different functionals of the electron density. Many exchange-correlation functionals have been developed. The accuracy of a DFT calculation can be greatly improved if a better approximation for the exchange and correlation interactions is available. The combinations of the exchange functionals from
the Becke’s three parameter hybrid functional (B3)\textsuperscript{128} with the gradient-corrected correlation functionals derived by Lee, Yang, and Parr (LYP)\textsuperscript{129} and by Perdew (P86)\textsuperscript{130,131} are two of the most popular hybrid functionals. The calculations with these functionals are sufficiently accurate for most molecular systems. The DFT calculations can provide comparable energy accuracy with the MP2 method at a much lower cost. Thus, they are used to study some of the larger molecules reported in this dissertation.

Similar to the MPn methods, the DFT methods are not based on the variational theory, and the calculated energy could be higher or lower than the true ground state energy. Unlike the wavefunction-based methods, the accuracy of the DFT methods does not only depend on the levels of methods and the size of the basis sets, but also on the exchange-correlation functionals. There is no obvious way to improve the accuracy of the DFT calculations systematically.

1.2.6 Coupled-cluster (CC) theory

The CC method\textsuperscript{132-134} was introduced in 1958 to deal with the systems of interacting particles. The basic idea is to write the molecular orbital as

\[
\varphi = e^T \Phi_0
\]  

(1.20)

Where \( \Phi_0 \) is the normalized ground state wavefunction from the Hartree-Fock calculations.

The operator is expanded into a Taylor-series

\[
e^T = 1 + T + \frac{T^2}{2!} + \frac{T^3}{3!} + \ldots\]

(1.21)
And the cluster operator is

\[ T \equiv T_1 + T_2 + T_3 + \ldots + T_n \]  \hspace{1cm} (1.22)

Where \( n \) is the number of the electrons, and \( T_n \) is the linear combination of the \( n^{th} \)-excited states from the ground state. Similar to the CI method, the coupled cluster calculations with the single and double excitations (CCSD) and sometimes with the perturbed triple excitation (CCSD (T)) are commonly used as a compromise of the computational accuracy and expense.

1.2.7 Multi-reference theories

The complete active space self-consistent field (CASSCF)\(^{135}\) method also uses the CSFs, as the CI and CC methods do. In a CASSCF calculation, the coefficients of LCAO (linear combination of atomic orbital) molecular orbitals and the CSFs are optimized. With the same space of the CSFs, the CASSCF method normally gives a more precise energy than the CI method. Typically, not all configurations contribute significantly to the correlation energies. By considering only the configurations with large coefficients, the multi-configuration self-consistent field (MCSCF) method reduces the number of CSFs and the computational cost without a significant loss of accuracy.

The multi-reference configuration interaction (MRCI)\(^{136,137}\) calculations can be carried out by combining MCSCF with CI. In a conventional CI method, the calculation starts with the SCF orbitals (which are called reference functions) and then generates the CSFs with the ground and excited electron configurations. The molecular orbital is the linear combination of the CSFs of the proper symmetry. In a MRCI calculation, the
MCSCF calculation is first performed to find the MCSCF wavefunctions, which are then used to form a linear combination of the CSFs.

A complete active space with the second order perturbation theory (CASPT2)\textsuperscript{138} calculation also starts with the MCSCF calculation and treats the reference CSFs as the basis functions of the molecular orbitals. The CASPT2 method combines the MCSCF calculation with the MP2 method and treats the system with the perturbation theory.

1.3 SPECTRAL SIMULATIONS

1.3.1 Franck-Condon principle

The intensity profiles of ZEKE/MATI spectra can be predicted by the Franck-Condon (FC) principle.\textsuperscript{139-141} On the basis of the FC principle, the intensity of a vibronic transition is proportional to the square of the transition moment integral, which is expressed as

\[ M_{ev} = \int \Psi_{ev}^* \mu \Psi_{ev} d\tau \]  

(1.23)

Where \( \Psi_{ev} \) and \( \Psi_{ev'} \) are the vibronic wavefunctions of the initial and final states, and \( \mu \) is the molecular dipole moment operator. The molecular dipole moment is determined by the positions of the charges. Specifically, the nuclei and electrons are separated as

\[ \mu = \sum q_i \bar{r}_i = \mu_e + \mu_N \]  

(1.24)

Where \( q_i \) and \( r_i \) are the charges and their positions.
From the Born-Oppenheimer approximation, the wavefunctions of the electrons and nuclei can also be separated. Thus, the transition moment integral can then be expressed as

\[ M_{ev} = \int \Psi'^*_{e} \Psi^*_v (\mu_e + \mu_N) \Psi'_e \Psi_v d\tau \]

\[ = \int \Psi'^*_{e} \mu_e \Psi'_e d\tau_e \int \Psi'^*_v \Psi_v d\tau_N + \int \Psi'^*_{e} \Psi_e d\tau_e \int \Psi'^*_v \mu_N \Psi_v d\tau_N \] (1.25)

Because the wavefunctions of different electronic states are orthogonal, \( M_{ev} \) can be simplified as

\[ M_{ev} = \int \Psi'^*_{e} \mu_e \Psi'_e d\tau_e \int \Psi'^*_v \Psi_v d\tau_N \]

\[ = M_e \int \Psi'^*_v \Psi_v d\tau_N \] (1.26)

Where \( M_e \) is the electronic transition moment and can be considered to be a constant for a specific electronic transition. Then, the intensity of the vibronic transition can be expressed as

\[ I_{\nu'\nu - \nu\nu} \propto \left| \int \Psi'^*_v \Psi_v d\tau_N \right|^2 \] (1.27)

From this expression, the intensity of a vibronic transition is calculated by the square of the vibrational integrals, which is called Franck-Condon factor (FCF).

Most of the electronic transitions observed from our ZEKE/MATI measurements follow the Franck-Condon principle. Thus, the intensity profile of a ZEKE/MATI spectrum tells the structural differences of the neutral molecules and ions and the bonding feature of the removed electrons. A strong 0-0 transition and short vibrational progressions indicate a small structural change upon ionization. In this case, the ejected electron is
weakly attached to the ionic core. In cases where a strongly bonding electron is removed, the molecular structure exhibits a significant change from the neutral molecule to the ion, and a weak 0-0 transition is typically observed with long vibrational progressions in the spectrum. More quantitative information may be obtained by comparing the observed spectra with spectral simulations.

1.3.2 Calculation of multidimensional FCF

The calculation of multidimensional Franck-Condon factors is the key step to simulate the vibronic transitions of the experimental spectrum. Prior to the simulations, the equilibrium geometries, harmonic frequencies of the vibrational modes, and the normal coordinates of each mode are obtained from the \textit{ab initio} calculations. However, the displacements of vibrational modes may be distorted from the neutral state to the ion state. This is so called the Duschinsky effect.\textsuperscript{142} To treat this effect, the Eckart rotational matrix is used to transform the neutral normal coordinates so that they can match the direction of those of the ions.\textsuperscript{143-145} More mathematical and computational details can be found in Shenggang Li's Ph. D. dissertation.\textsuperscript{146} The FCF program used for this study is improved by Li\textsuperscript{146} from the original version.\textsuperscript{147,148}

The PreFCF program is used to extract the geometric and vibrational information from the output files of the neutral and ions from the \textit{ab initio} calculations and to generate the input file for the FCF calculations. In the input file, the energy range, temperature, band width, and step-size are manually entered according to the individual ZEKE/MATI spectra. The Boltzmann distribution is considered to account for the hot transitions, and the Lorentzian line shape is used to describe the ZEKE/MATI band shape.
1.4 OVERVIEW OF THESIS

The accurate AIEs of several metal oxide and carbide clusters are characterized using MATI spectroscopy. By combining the spectroscopic measurements with the *ab initio* calculations and spectral simulations, the molecular structures, electronic transitions, and electron configurations of these clusters are identified. Chapter 2 describes the details of the experimental setups and theoretical calculations. Chapter 3 presents the results and discussion of LaO$_2$. Chapter 4 and 5 discuss about the dimetal clusters (La$_2$ and M$_2$O$_2$). Chapters 6 and 7 are about the trimetal clusters, including M$_3$O$_4$, M$_3$C$_2$ and La$_3$C$_2$O. Finally, Chapter 8 summarizes the AIEs, binding characters, structures, electronic states, and some of the vibrational frequencies of all clusters studied in this work.
Figure 1.1 Schematic diagram for the conventional PES (a), threshold PES (b), and PFI-ZEKE/MAIT (c).

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CHAPTER 2 METHODOLOGY

2.1 EXPERIMENTS

2.1.1 Experimental setups

The schematic of the home-built spectrometer is illustrated in Figure 2.1.\textsuperscript{149} It consists of two vacuum chambers, the source chamber for synthesis and the main chamber for spectroscopy. The source chamber is pumped by an oil diffusion pump (2200 L/s, DP, Edwards, Diffstak 250/2000 M), and the diffusion pump is backed by a two-stage mechanical rotary pump (Edwards, E2M40). The pressure is well-maintained at $10^{-8}$-$10^{-7}$ Torr when the instrument is on standby (standby pressure) and $10^{-5}$-$10^{-4}$ Torr when it is in operation (working pressure). The pressure in the foreline is kept below $10^{-3}$ Torr. An active inverted magnetron gauge (Edwards, AIM-S-NW25) and a linear active pirani gauge (Edwards, AGP-M-NW16) are used to monitor the pressures of the source chamber and the foreline, respectively. The main chamber is evacuated by two turbomolecular pumps (400 L/s, Seiko Seiki, STP-400), and each turbomolecular pump is backed by a two-stage rotary mechanical pump (Edwards, E2M40). The standby and working pressures are typically $\sim 10^{-9}$ Torr and $10^{-7}$-$10^{-6}$ Torr, respectively, as monitored by an ionization gauge (Varian, 571). The backing pressure in the foreline is $\sim 10^{-4}$ Torr as measured by a linear active pirani gauge (Edwards, APG-L0NW16). The gate valve is electrically controlled and will close when an unexpected high pressure is detected by the ion gauge in the main chamber (i.e. beyond the threshold pressure set for the ion gauge). This mechanism works as a protection for the detector and the turbomolecular pumps in the main chamber.

The source chamber houses a Smalley-type cluster source. Metal clusters are generated from a metal rod by laser vaporization. The laser pulses (Lumonics YM-800 Nd:
YAG, 532 nm, ~ 12 mJ) are focused to a ~ 0.5 mm diameter spot on the surface of the metal rod by a focal lens (f = 30 mm). The metal rod is translated and rotated by a motor-driven mechanism (Micro Motor Electronics 1516E012S) to ensure that each laser pulse ablates on a clean and fresh surface and produces stable metal vapor pulses. The rotating speed of the motor is changed by a variable resistor to optimize the ion signal, since the movement of the metal rod may affect the stability and density of the metal vapor. He, Ar, (Ultra High Purity, Scott-Gross) or He/Ar mixtures with an appropriate ratio are used as carrier gases, and the backing pressures of these gases are varied from 20 to 100 psi.

Other reagents can also be introduced to the molecular beam if they are needed. Two methods are commonly used to introduce the gaseous reagents. One is to dope the reagent in the carrier gas with different concentrations. This method can control the concentration of the doped reagent, but it is not convenient to change the concentration continuously. The other method is to introduce the reagent through a stainless-steel tube to a small collision chamber at or downstream the ablation zone, prior to expansion into the vacuum chamber. The pressure of the inert gas is carefully controlled by a main gas valve (NUPRO, SS-4BK or Swagelok, SS-1RS4-A) and a needle valve (Swagelok, SS-SS4-VH). This method can control the amount of the reagent to optimize the ion signal by adjusting the valves. It is easy for operation, but does not tell how much reagent is used each time. The vapor of a liquid ligand is introduced at the room temperature using the second method to introduce the gaseous reagents. The liquid could be heated when the vapor pressure is too low or cooled down when the vapor pressure is too high. Ligands in the solid state are placed inside a copper oven where they are heated to the appropriate temperature by a heating cartridge. The temperature is controlled by a thermo-controller.
A copper tube filled with tap water is wrapped around the face plate surface of the piezoelectric valve to protect the valve from overheating.

The resulting metal clusters are expanded through a cluster tube into the vacuum chamber. The cluster tube is typically a straight stainless-steel tube, 2 cm in length and 2 mm in diameter. Sometimes, a specially designed S-shape cluster tube is used instead. The S-shape tube has three advantages in reducing the background. First, it blocks the scattering ablation laser light from entering the spectroscopic chamber. Second, it demolishes the plasma generated in the ablation process. Third, it provides more collisions before the expansion process. Intense collisions can relax the internal energies (In chapter 1, you include the translational energy in the internal energy, make sure you don’t confuse the readers with different definitions) and thus stabilize the clusters. In other words, they transfer the vibrational and rotational energies to translational energy along the molecular beam axis. The vibrational temperatures of the molecules are reduced to various degrees by the energy transfer process. The cooling efficiency strongly depends on the mass, the backing pressure of the carrier gas, and the property of the metal clusters. Raising the backing pressure increases the collision frequencies, and the heavier carrier gas has a larger collision cross section. Both can lead to higher cooling efficiencies. On the other hand, the effects of the seeded molecules are more complicated and not well studied yet. It might be related to the sizes, masses, and energy densities of these molecules and is beyond the scope of this dissertation.

After the supersonic expansion, the molecular beam is collimated and selected 2-5 cm downstream the cluster tube by a skimmer (inner diameter of 0.5-5 mm, typically 2 mm). The skimmer also serves as a pinhole to provide the pressure gradient between the
source and main chambers when the gate valve is open. The residual ions and electrons generated by laser vaporization are removed by a pair of deflection plates (2.5 cm spacing and ~100 V potential) located right after the skimmer. The neutral molecules travel into the main chamber for spectroscopic investigation.

The main chamber houses a two-field, space-focused, Wiley-McLaren time-of-flight (TOF) spectrometer\textsuperscript{150} with a 34 cm long flight tube and a dual microchannel plate (MCP) detector (Galileo). The clusters are photoionized by a UV laser, and the resultant ions are extracted upward into the TOF spectrometry by an electric field applied to a pair of aluminum cans. The UV laser has a pulse width of 7-10 ns. It is the frequency doubled output from a tunable dye laser (Lumonics HD-500), which is pumped by the second or third harmonic output of an Nd: YAG laser (continuum Surelite III). The key component of the frequency doubling unit is the BBO (beta-Ba\textsubscript{2}B\textsubscript{2}O\textsubscript{4}) crystal. The angle of the crystal is tuned by a motor driven system (Lumonics HyperTRAK-1000) according to the wavelength of the dye laser output and controlled by a computer interface. The TOF spectrometer is shielded by a cylindrical, double-walled, \(\mu\)-metal shield to protect the charged particles (especially electrons) from the interference of the external magnetic fields. The \(\mu\)-metal consists of 77% nickel, 16% iron, and 5% copper doped by about 2% chromium or molybdenum. This type of the alloy shows high magnetic permeability and provides a low reluctance path for the magnetic field. Thus, the \(\mu\)-metal offers an effective shield against the low-frequency magnetic fields, such as the one from the earth poles.
2.1.2 TOF mass spectrometry

The ions are extracted and accelerated upward into the TOF tube by an electric field and detected by a MCP detector. The strength of the electric field is optimized to focus the axial velocities of the ions with the same masses. The optimum value is found to be 320 V/cm generated by applying +2500 V on the outer aluminum can and +1700 V on the inner can (Figure 2.1). There are four holes with one inch diameter on the outer can. Two holes are parallel with the molecular beam and the other two are perpendicular to it. These holes allow the laser and molecular beams to enter the ionization region. To have a homogenous electric field between the two cans, the aperture at the bottom of the inner can is covered with a gold mesh of 95% transmittance. The surfaces between the two cans are coated with a layer of graphite (Sprayon, Dry graphite lube, S00204) to help remove the residual charges more efficiently.

The MCP detector consists of an array of micro-channels. These micro-channels lie with a small angle from the normal direction of surface and are isolated by a highly resistive material. In the presence of a strong electric field, each MCP can gain up to $10^4$. The signal amplification is $10^6$-$10^7$ with the two MCPs arranged in a chevron or V-like shape and applied by a total voltage of 1800 V. A voltage divider is used to supply the voltage to the detector, as illustrated in Figure 2.2 (A). The electrons are accelerated to the anode, and the charge transfer generates analog signals. The analog signals are further amplified by 25 times by a preamplifier (Stanford Research Systems SR445), averaged by a boxcar integrator (Stanford Research Systems SR250), converted to digital signals by an analog-to-digital circuit, and stored in a laboratory computer.
The TOF tube is grounded and shielded by the µ-metal to ensure a field-free flight region. It is assumed that the cations produced by UV laser photoionization are singly charged because of the following two reasons. First, the second ionization energies (the energy required to take away an electron from a +1 charged cation) of most species are far beyond the UV region. Second, the ionization laser is well defocused to minimize the two-photon ionization process. For the ions of the same charge, their total kinetic energies are about the same if they are produced at the same position. Thus, the mass-to-charge ratios of the clusters can be conveniently and uniquely determined by their flight times. Taking the uniform rectilinear motion (velocity of \( v \)) in the TOF tube as a simple model, the kinetic energy (\( E_k \)) of the molecules can be calculated by:

\[
E_k = \frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2
\]  

(2.1)

In Equation (2.1), \( m_i \) and \( v_i \) (\( i = 1, 2 \)) represent the masses and travelling velocities of different particles. The flight distance (\( L \)) can be expressed as a linear function of the flight time (\( t_i \), \( i=1, 2 \)), as shown in Equation (2.2):

\[
L = v_1t_1 = v_2t_2
\]

(2.2)

For a charged particle, its flight time and mass have a straightforward relationship:

\[
t = A\sqrt{m}
\]

(2.3)

Where \( A \) is a constant related to the structural configuration of the TOF spectrometer.

Thus, if we know the mass (\( m_{\text{ref}} \)) and flight time (\( t_{\text{ref}} \)) of a reference atom or compound, the mass of an unknown particle can be calculated with its flight time from Equation (2.4):
Typically, we use aluminum atom as a reference, for which, $t_{\text{ref}}$ is 3.66 µs and $m_{\text{ref}}$ is 27 amu. Alternately, we can use a cluster presented in the molecular beam as a reference. Because the clusters generally exhibit a stoichiometric form of $A_mB_n$ or $A_mB_nC_l$ ($A$, $B$, and $C$ are different atoms or molecules; $m$, $n$, and $l$ are integers), the identification of each peak in the mass spectrum is relatively straightforward. I will discuss the details about how to determine the masses of unknown clusters in the Appendix.

2.1.3 Photoionization efficiency (PIE) spectroscopy

The purpose of the PIE measurements is to estimate the molecular ionization threshold prior to the ZEKE or MATI experiments. A PIE spectrum records the intensity of a mass-selected ion signal as a function of the laser wavenumbers. When the photon energy exceeds the ionization threshold of the molecule, the ion signal exhibits a significant increase. The cross point of the baseline and sharp onset of the PIE spectrum indicates the ionization threshold of the molecule.

The PIE experiment can be performed in a dc or a pulsed field mode. If a PIE measurement is carried in the pulsed field mode, it is called pulsed filed PIE, or PF-PIE. In the dc mode, dc voltages are applied on the extraction cans (+2500 V and +1700 V on the outer and inner cans, respectively) to extract the ions. The ionization energy is shifted to a lower value by the Stark effect of the electric field. The energy shift can be estimated by an empirical formula:\textsuperscript{151}

\begin{equation}
m = m_{\text{ref}} \cdot \left( \frac{t}{t_{\text{ref}}} \right)^2
\end{equation}
\[ \Delta IE = 6.1 \sqrt{E_f} \quad (E_f \text{ is in V cm}^{-1} \text{ and } \Delta IE \text{ in cm}^{-1}) \]  

Where \( E_f \) is the electric field strength, which is 320 V/cm in this case. From Equation (2.5), the measured ionization energy from the dc mode PIE spectrum is corrected by adding 110 cm\(^{-1}\). In the pulsed field mode, the neutral molecules are photoionized without the presence of the electric field. The amplitude of the pulsed electric field is the same as that of the dc configuration (+1700 V/ +2500 V) and the width of the electric pulse is 5-10 µs depending on the masses of the ions. The pulsed electric field is applied about 1 µs after the ionization laser pulse to extract the photoionized molecules into the TOF tube. Although the PIE spectrum does not have enough resolution to resolve the vibrational transitions, it provides the estimated ionization energy to simplify the ZEKE/MATI measurements, which offer much higher spectral resolutions.

2.1.4 ZEKE and MATI spectroscopy

MATI and ZEKE spectroscopy have similar experimental setups. They use the same method to synthesize the clusters and have slightly different designs for electron and ion detections. Because our MATI setup is modified from the ZEKE apparatus, both techniques will be discussed in this section.

In the ZEKE measurements, UV laser is tuned to a few wavenumbers below the ionization energy of the neutral molecules to excite them to the high-lying Rydberg states. A small dc field (spoiling field, \(~0.06\) V/cm) is used to separate the electrons produced by direct photoionization (direct electrons) from the Rydberg molecules. This dc field is generated by grounding the inner can and applying \(-0.15\) V on the outer can. The dc field
correction can be estimated to be $\sim 1.49 \text{ cm}^{-1}$ from Equation (2.5), which is smaller than the typical spectral linewidths of polyatomic metal-containing molecules. Because the electron has a very small m/z value, the separation of the direct electrons from the ZEKE electrons is relatively straightforward by the dc field. With about 3 $\mu$s delay, a negative electric pulse (extraction field) is applied to the outer can. This electric pulse has an amplitude of 3 V (1.2 V/cm) and a time width of 100 ns. The pulsed field effect is measured to be $\sim 1.1 \text{ cm}^{-1}$. This field is used to ionize the high-lying Rydberg states, generate electrons with near-zero kinetic energies, and repel the electrons upwards to the MCP detector. A voltage divider circuit (Figure 2.2 (B)) is designed to apply an appropriate voltage on each MCP plate and the anode. To measure the ZEKE spectra, I start with the excitation laser at a few hundred wavenumbers below the ionization energy measured from the PIE spectrum and scan the laser to higher wavenumbers step-by-step until no further signal is observed. The stepsize of the laser scan is decided according to the width of the ZEKE peaks. Each peak has at least 16 to 20 points (8-10 for the half of the peak) to ensure the reliability of the peak shape. The laser wavelengths are calibrated by the atomic transitions of vanadium, titanium, or zirconium.

The amplitude of the electric field and the time delay of the excitation laser from the pulsed electric field in the MATI experiment are significantly different from those in ZEKE. First, because ions are much heavier than the electrons, stronger electric field is required for extraction. The amplitude of the extraction field is the same as that in the PF-PIE measurements. Second, to separate the ions produced by direct photoionization (direct ions) and electric field ionizations (MATI ions), a stronger spoiling dc field (1-15 V) and a longer delay time are required. The delay time varies with carrier gases and is typically
20 µs for He and 50 µs for Ar. The delay of the extraction electric pulse can be changed by changing the timing of either the laser firing or the electric pulse triggering. In my experiments, I fix the timing of the electric pulse and change the timing of the excitation laser. Third, because the MATI measurements use a stronger spoiling field and a longer delay time, some Rydberg states may not survive within the experimental time scale. An AC field following the falling edge of the pulsed electric field (320 V/cm, 400 ns) is used to increase the lifetime of the high-lying Rydberg states.120

2.1.5 Timing sequence and ion characterization

Pulsed delay generators (Stanford Research Systems DG535) are used to synchronize the pulses of the molecular beam, lasers and electric fields. As shown in Figure 2.3, $T_0$ is the trigger for the home-made pulsed valve driver; $T_1$ and $T_2$ are the triggers for the Q-switches of the ablation laser (Nd:YAG, GCR3) and the pump laser (Surelite III) of the dye laser; $t_1$, $t_2$, and $t_3$ are the triggers for the three electric pulses. In this type of the experiments, two sets of the events must be synchronized at the ablation and ionization zones, respectively. In the ablation zone, the pulses of the carrier gas and the ablation laser must be synchronized so that the metal vapor generated by laser ablation is seeded in the carrier gas. This is achieved by adjusting the time delay between the pulsed valve trigger ($T_0$) and the firing time of the ablation laser ($T_1$). The delay time (from $T_0$ to $T_1$) composes of the opening time of the piezoelectric valve and the traveling time of the gas pulse. Because the ablation region is only about 3 mm from the pinhole of the piezoelectric disk, the travelling time of the molecular pulse to the ablation region is small. Thus, the time delay depends largely on the opening time of the piezoelectric valve and
slightly on the traveling speed of the molecular beam. In our experiments, this time delay is 400 - 500 µs. In the ionization zone, synchronization ensures that the seeded clusters are excited by the UV laser pulse and then ionized by the extraction field. Thus, the time difference between the electric and ablation laser pulses equals the traveling time of molecular beam from the ablation region to the ionization region. It is ~300 µs when He is used as a carrier gas and ~500 µs when Ar is used. The time delay of the extraction field from the UV excitation laser is about 1 µs for the PF-PIE measurements, 3 µs for ZEKE, and 20-50 µs for MATI. The 20-50 µs delay in the MATI measurements is used for different carrier gases.

2.2 THEORETICAL CALCULATIONS

*Ab initio* calculations are carried out to help analyze the MATI spectra. The calculations are performed with GAUSSIAN03/09 and MOLPRO (v. 2010) program packages installed on the University of Kentucky Hewlett-Packard Superdome Cluster. Geometry optimization is carried out using the DFT method with Becke’s three parameter hybrid functional (B3) and the gradient-corrected correlation functionals derived by Lee, Yang, and Parr (LYP). Single-point energy calculations are performed for the optimized structures using the coupled cluster method including single, double and perturbed triple excitations (CCSD(T)). Multi-reference calculations including all the possible electronic configurations are performed for the diatomic and triatomic molecules.

The Dunning's polarized valence triple-zeta correlation consistent basis set with augmented diffuse functions (aug-cc-pVTZ) are used for carbon and oxygen and the
effective core potential (ECP) basis sets for the metal atoms (because the calculations with all-electron basis sets are prohibitively expensive). Los Alamos ECPs (LanL2\textsuperscript{156-158} and Stuttgart/Dresden ECPs (SDD)\textsuperscript{159} are available for the transition metals. They both include the relativistic effect and are of the same size for the 4th and 5th row transition elements. For lanthanides, LanL2 ECPs include a uniform potential of 28 electrons and SDD ECPs include 46 electrons. In the case of multi-reference calculations of the diatomic and triatomic molecules, the all electron atomic natural orbitals with relativistic core correlation (ANO-RCC) basis sets are used, which consider the relativistic effect in the second-order Douglas-Kroll-Hess Hamiltonian.\textsuperscript{160,161}

Frequency calculations of the neutral molecules and ions are performed to identify the minimum-energy structures and help the vibrational analysis. Multidimensional Franck-Condon (FC) factors and spectral simulations are carried out with the FCF program written by Li\textsuperscript{146}. 

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Figure 2.1 The schematic diagram of the home-built ZEKE/MATI spectrometer.
Figure 2.2 The schematic diagram of the voltage divider for ion (A) and electron (B) detections.
Figure 2.3 Time sequence of the PFI-PIE, ZEKE, and MATI experiments. $T_0$ is the trigger of piezoelectric pulsed valve; $T_1$ and $T_2$ are the Q-switch triggering times of the ablation and excitation/ionization lasers; $\Delta_1$ and $\Delta_2$ are the time delays between the laser flash lamps and Q-switches; $t_1$, $t_2$, and $t_3$ are the rising edges of various electric pulses; and $w_1$, $w_2$, and $w_3$ are the electric pulse widths.
CHAPTER 3 MASS-ANALYZED THRESHOLD IONIZATION AND EXCITED STATE OF LANTHANUM DIOXIDE

3.1 INTRODUCTION

Transition metal oxides are widely used as both catalysts and catalyst supports in chemical processes. The widespread and important applications of transition metal oxides have motivated numerous research groups to study their physical and chemical properties in the gas phase, where complicating factors such as solvents and counterions are removed. For transition metal oxide cations, extensive studies have been reported on their reactivity, UV-Vis photofragmentation, and infrared (IR) multiphoton photodissociation or single-photon vibrational predissociation. The studies of the anions were largely carried out with photoelectron spectroscopy, and additional investigations were reported about their reactivity and IR photodissociation. Neutral metal oxides are more challenging to study experimentally because they are difficult to size-select, and their formation and properties are usually determined by ionization techniques, including multiphoton IR and single-photon UV and vacuum UV laser ionization. In addition, neutral metal oxides have also been studied by matrix-isolation IR spectroscopy. In spite of the extensive studies, the current knowledge about the electronic states and molecular structures of polyatomic transition metal oxide clusters is largely derived from theoretical predictions. However, the reliable prediction of the electronic and geometric structures is often complicated by the presence of many low-energy structural isomers and a high density low-lying electronic states of each isomer. Thus, inconsistent theoretical results have often been reported on the nature of the ground electronic states and minimum energy structures of both polyatomic neutral molecules.
Therefore, a reliable identification of the molecular structures and electronic states for transition metal oxide clusters and their ions generally requires the confirmation by spectroscopic measurements, especially by high-resolution spectroscopic techniques.

Although diatomic transition metal oxides have been well studied, the spectroscopy of their polyatomic metal oxides is rather limited. As one of the simplest polyatomic transition metal oxides, LaO$_2$ has been studied previously by gas-phase guided ion beam mass spectrometry, chemielectron spectroscopy, and argon matrix-isolation IR spectroscopy. Clemmer et al. investigated the thermochemistry of LaO$_2$ and LaO$_2^+$ formed in endothermic reactions between LaO$^+$ and NO$_2$ in a guided ion beam mass spectrometer. In that study, the bond dissociation energies $D^0$ (OLa-O) and $D^0$ (OLa$^+$-O) were measured as 4.20(33) and 0.99(31) eV, respectively, and the ionization energy (IE) of LaO$_2$ was 8.11(35) eV. Cockett et al. reported chemielectron spectra obtained for the reactions of La atom with O$_2$ in the $X^3\Sigma_g^-$ and $a^1\Delta_g$ electronic states and assigned spectra to chemiionization of lanthanum dioxide formed by association reactions. In the spectrum of La + O$_2$ ($X^3\Sigma_g^-$), they observed two partially resolved vibrational progressions separated by 250 (50) cm$^{-1}$ with an averaged interval of 660 (30) cm$^{-1}$. They assigned the 250 cm$^{-1}$ separation to the symmetric O-La-O bending mode and the 660 cm$^{-1}$ interval to the symmetric La-O stretching mode of the LaO$_2^+$ cation. Andrews et al. obtained IR spectra for the reactions of laser-ablated La, La$^+$ and electrons with O$_2$ in argon matrix and observed La-O symmetric stretching frequencies of 570 cm$^{-1}$ for LaO$_2$ and 689 cm$^{-1}$ for the LaO$_2^-$ anion. It is interesting to note that the stretching frequency of the LaO$_2^+$ cation measured from the gas-phase chemielectron spectrum is similar to that of the LaO$_2^-$, but is
substantially different from that of the LaO$_2$ molecule from the argon matrix-isolation IR spectra. More recently, Todorova et al. reexamined the chemiionization reactions of La + O$_2$ using \textit{ab initio} electronic structure calculations.\textsuperscript{170} In that study, a bent C$_2v$ structure was predicted for the neutral lanthanum dioxide in the $^2B_1$ ground state and a linear structure for the cation in the $^1\Sigma_g^+$ ground state. The ionization and bond dissociation energies of LaO$_2$ were calculated to be 7.99-8.70 and 6.47-6.71 eV, respectively, depending on the level of theory. A requirement for a chemiionization reaction of a metal oxide molecule to take place is that its dissociation energy must be greater than its ionization energy. Because the dissociation energy was smaller than the ionization energy (IE), it was concluded that the chemiionization reaction La + O$_2$ $\rightarrow$ LaO$_2^+$ + e$^{-}$ was endothermic and should not have contributed to the chemielectron spectra. As an alternative, a two-step process was proposed for the formation of the chemielectrons under the La + O$_2$ ($X^3\Sigma_g^-$) reactions conditions, which included La + O$_2$ $\rightarrow$ LaO + O and La + O $\rightarrow$ LaO$^{+}$ + e$^{-}$. However, because the measured vibrational interval (660 cm$^{-1}$) in the chemielectron spectrum is too small for the La-O stretching frequency of the diatomic LaO$^{+}$ ion ($>$ 800 cm$^{-1}$),\textsuperscript{169,170} LaO may not be the carrier of the chemielectrons.

A third hypothesis may be that the chemielectrons were produced by ionization of an excited electronic state of LaO$_2$. However, nothing is known about any excited states of the molecule. The objective of this work is to search for and characterize the excited states of LaO$_2$. The LaO$_2$ molecule is produced in a pulsed laser-vaporization molecule beam source and characterized by MATI spectroscopy and electronic structure calculations.
3.2 EXPERIMENTAL AND COMPUTATIONAL METHODS

3.2.1 Experimental

The metal-cluster beam MATI spectrometer used in this work is similar to the ZEKE apparatus described in a previous publication.\textsuperscript{171} It consists of two vacuum chambers. The first houses a Smalley-type cluster source and is pumped by a 2200 l s\textsuperscript{-1} diffusion pump. The second chamber houses a time-of-flight spectrometer and is pumped by two 400 l s\textsuperscript{-1} turbo molecular pump. The time-of-flight spectrometer is composed of a two stage extraction assembly, a 34 cm long flight tube, and a dual microchannel plate detector (Burle). The entire spectrometer is housed in a cylindrical, double-walled \( \mu \)-metal shield.

Lanthanum oxides were produced by laser vaporization (Lumonics YM-800 Nd:YAG, 532 nm,) of a La rod (Alfa Aesa, 99.9\%) in the presence of a pulse of ultra-high-purity He (or Ar) carrier gas delivered by a homemade piezoelectric pulsed valve.\textsuperscript{172} The metal vapor and carrier gas passed down a clustering tube (2 mm inner diameter, 2 cm length), and the resultant clusters were supersonically expanded into the vacuum chamber. The supersonic jet was skimmed (2 mm diameter) 3 cm downstream from the exit end of the clustering tube. A pair of deflection plates (2.5 cm spacing, 220 V) located after the skimmer was used to remove residual charged species (formed during laser ablation) from the molecular beam before it entered the second chamber.

Prior to the MATI measurements, photoionization time-of-flight mass spectra were recorded to determine the chemical content of the cluster beam, and pulsed-field-ionization photoionization efficiency spectra were recorded to locate the ionization threshold of La\textsubscript{2}. With the ionization laser set above the ionization threshold, the experimental conditions (e.g., timing and power of the vaporization and ionization lasers and the backing pressure
of the carrier gas) were carefully optimized to maximize the intensity of the LaO$_2^+$ signal in the mass spectrum.

With the optimized experimental conditions, LaO$_2$ was excited to high-lying Rydberg states in a single-photon process by the frequency-doubled output of a dye laser (Lumonics HD-500) pumped by a Nd:YAG laser (Quanta Ray GCR-3, 355 nm) and then ionized by an electric pulse (DEI PVM-4140, 320 V cm$^{-1}$). The laser beam was collinear and counter propagating with the molecule beam. The time delay between the laser and electric pulses was varied to maximize the MATI signal, and it was typically 20 µs for He carrier and 50 µs for Ar. A small DC field (4.1 V cm$^{-1}$) was applied to help separate the prompt ions produced by direct photoionization from the MATI ions produced by delayed field ionization. The MATI signal was obtained by scanning the wavelength of the tunable dye laser, detected by a dual microchannel plate detector, amplified by a preamplifier (SRS SR445), averaged by a gated integrator (SRS SR250), and stored in a laboratory computer. Laser wavelengths were calibrated against vanadium atomic transitions in the spectral region.$^{153}$ The Stark shift induced by the DC field was calculated using the relation of $\Delta E = 6.1 E_f^{1/2}$, where $E_f$ is in V cm$^{-1}$ and $\Delta E$ in cm$^{-1}$.$^{151}$

3.2.2 Computational

DFT and \textit{ab initio} molecular orbital theory methods were used to calculate equilibrium geometries and vibrational frequencies of the low-lying electronic states of LaO$_2$ and LaO$_2^+$. Single-reference calculations included DFT with Becke’s three parameter hybrid functional with the correlation functional of Lee, Yang and Parr (B3LYP),$^{128,129}$ second-order Møller-Plesset (MP2) perturbation,$^{173}$ and coupled cluster
with single, double and perturbative triple excitations (CCSD(T))\textsuperscript{174,175} methods. The oxygen atomic orbitals were described by aug-cc-pVTZ basis set \textsuperscript{176} or the 6-311g(d) valence triple split basis set.\textsuperscript{177} La atomic orbitals were represented by the Stuttgart-type relativistic effective core potential basis with 28 core electrons, that is, Stuttgart RSC ANO/ECP.\textsuperscript{178} All of these single-reference calculations were carried out with Gaussian 09 program.\textsuperscript{179}

Multi-reference methods, complete active space self-consistent field (CASSCF)\textsuperscript{180,181} and CAS with second-order perturbation theory (CASPT2)\textsuperscript{182}, were used to characterize electron configurations of the electronic states of lanthanum dioxide and its cation. A level shift technique\textsuperscript{183} was employed, if necessary, to avoid intruder state problems in the CASPT2 calculations. In the CASSCF and CASPT2 calculations, the full-electron atomic natural orbital with relativistic core correlation (ANO-RCC)\textsuperscript{184} basis set and the second-order Douglas–Kroll–Hess Hamiltonian\textsuperscript{160,161} were employed to treat the scalar relativistic effect. In the ANO-RCC basis, the primitive set of (24s, 21p, 15d, 5f, 3g, 2h) was contracted to (11s, 10p, 8d, 5f, 3g, 2h) for the La atom, and the (14s, 9p, 4d, 3f, 2g) primitive set was contracted to (8s, 7p, 4d, 3f, 2g) for the O atom. Because the La atom has an outmost valence electron configuration of 5d\textsuperscript{1}6s\textsuperscript{2}, three electrons and six orbitals (6s and 5d) were included in the complete active space for the La atom. Because the O atom has a valence electron configuration of 2p\textsuperscript{4}, four electrons and three orbitals (2p) were used in the active space for each O atom. Thus, the active space for the LaO\textsubscript{2} molecule included 11 electrons and 12 orbitals, i.e., (11, 12), and that for LaO\textsubscript{2}\textsuperscript{+} was (10, 12). All of the multi-reference calculations were performed using MOLPRO 2010.1 program.\textsuperscript{185}
To compare with the experimental spectrum, Franck-Condon (FC) factors were calculated using the equilibrium geometries, harmonic frequencies, and normal mode coordinates of the neutral molecule and cation.\textsuperscript{146,147,186} In these calculations, recursion relations\textsuperscript{187} were employed and the Duschinsky effect\textsuperscript{142} was taken into consideration. Spectral simulation was obtained using the experimental linewidth and a Lorentzian line shape. Transitions from exited vibrational levels of the neutral molecule were considered by assuming thermal excitation at specific temperatures.

3.3 RESULTS AND DISCUSSION

3.3.1 MATI spectrum

Figure 3.1(a) presents the MATI spectrum of LaO$_2$ seeded in He carrier gas. LaO$_2$ was formed without addition of external oxygen gas. The presence of oxygen was due to either the impurity of the He gas or to the La rod. The spectrum displays the most intense band at 40134 (5) cm$^{-1}$ or 4.9760(8) eV and a major progression of the 656(1) cm$^{-1}$. Nested inside the major progression is a second progression with intervals of 122(1) cm$^{-1}$. In addition, the spectrum exhibits a weak band 92 (1) cm$^{-1}$ below each member of the 656 cm$^{-1}$ progression. The energy position of the origin band corresponds to the adiabatic IE of a neutral state of the molecule. The 656 and 122 cm$^{-1}$ progressions are due to transitions from the ground vibrational level of a neutral state to vibrational levels of two modes of an ion state, whereas the 92 cm$^{-1}$ weak bands are due to transitions from an excited vibrational level of a neutral mode to the ion. At first view, the 122 cm$^{-1}$ progression was thought to be vibrational sequence bands from excited vibrational levels of a neutral mode to various levels of an ion mode. However, additional measurements with Ar or He/Ar carriers show
no changes of the relative intensity (though the signal was weaker), indicating they are not vibrational hot bands. Moreover, if these transitions were sequence bands, the frequency difference between the neutral and ionic modes would be as large as 122 cm$^{-1}$. Such a large frequency difference suggests a large geometry change from the neutral molecule to the ion, inconsistent with the observed short FC profile.

The LaO$_2$ molecule and its cation may be linear or bent. A linear structure could have a D$_{xh}$ symmetry (OLaO) with one totally symmetric vibrational mode ($\sigma_g^+$) or a C$_{xv}$ symmetry (LaOO) with two symmetric modes ($\sigma^+$), whereas a bent structure could have a C$_{2v}$ symmetry (OLaO) with two symmetric modes (a$_1$) or a C$_s$ symmetry (LaOO) also with two symmetric modes (a'). Because the spectrum displays two active vibrational modes of 656 and 122 cm$^{-1}$ for the ion state, LaO$_2^+$ should be in a bent C$_{2v}$ (or C$_s$) structure or a linear C$_{xv}$ geometry from the viewpoint of the first-order selection rule. Because the spectrum exhibits a strong origin band and a short FC intensity profile, both the neutral and ion states should be in the same structural configuration, as a linear-bent conversion between the two states would produce a spectrum with a very weak origin band and a long FC intensity profile. As discussed in the Introduction, Todorova et al. reported a theoretical study of the gas-phase chemiionization reactions of La with oxygen atoms or molecules. Using DFT and ab initio molecular orbital theory methods, they predicted the ground states of LaO$_2$ and LaO$_2^+$ to be $^2$B$_1$ (C$_{2v}$) and $^1$Σ$_g^+$ (D$_{xh}$), respectively, and the IE values for the ionization process of LaO$_2^+$ ($^1$Σ$_g^+$, D$_{xh}$) $\leftarrow$ LaO$_2$ ($^2$B$_1$, C$_{2v}$) to be in the range of 7.99-8.70 eV. Obviously, this ionization process cannot be associated with the observed spectrum, as the predicted IEs are more than 3.0 eV higher than the measured value and the bent-linear structural conversion would yield a much longer FC profile than the experimental
spectrum. To help assign the electronic states and molecular structures involved in the MATI transitions, we performed an extensive theoretical search of molecular structures and electronic states, and the results are described below.

3.3.2 Low-lying electronic states of lanthanum dioxide (OLaO), lanthanum peroxide (La(O_2)), lanthanum superoxide (LaOO), and their cations

Figure 3.2 shows the possible structures of LaO_2 that were considered in our calculations. These structures include bent and linear lanthanum dioxides (OLaO), bent lanthanum peroxide (La(O_2)), and linear lanthanum superoxide (LaOO). A bent lanthanum superoxide was also considered, but it was converged to the linear structure upon geometry optimization. Table 3.1 summarizes the electronic states and energies, geometries, and vibrational frequencies from the DFT/B3LYP calculations. Among all the oxides, the OLaO dioxide is the most stable isomer, followed by the La(O_2) peroxide and the LaOO superoxide. For the OLaO dioxide, the bent structure (C_{2v}) is slightly more stable than the linear structure. The ground electronic state of the bent dioxide is predicted to be $^2B_2$. Above the $^2B_2$ state, a $^4B_2$ state is located at 3.40 eV. Ionization of the $^2B_2$ state of the bent oxide yields a linear structure (D_{xb}) in the $^1\Sigma_g^+$ ionic state; on the other hand, ionization of the $^4B_2$ state leads to a $^3B_2$ ionic state also in the bent configuration. The $^1\Sigma_g^+$ ionic state could also be formed from ionization of the $^2\Sigma_u^+$ neutral state, which is 0.05 eV above the $^2B_2$ state. The prediction of the $^2B_2$ and $^1\Sigma_g^+$ states are consistent with the previous calculations.\(^{170}\) However, the $^4B_2$ and $^2\Sigma_u^+$ neutral states and the $^3B_2$ ionic state are reported for the first time. (It is noted that the $^2B_2$ state was previously labeled as $^2B_1$ because of a different axis orientation in the Cartesian coordinate system.)
For the La(O₂) peroxide (C₃ᵥ), the ground state of the neutral molecule is \(^2\text{A}_1\), followed by an excited \(^4\text{A}_2\) state at \(\sim 2.3\) eV; the ground state of the cation is \(^1\text{A}_1\), followed by an excited \(^3\text{A}_1\) state at \(\sim 2.2\) eV. The structural differences between the dioxide and peroxide are very clear. For example, the \(\angle \text{O-La-O}\) angle and the O-O distance in the \(^2\text{B}_2\) state of the dioxide are 146.3° and 3.73 Å, whereas the corresponding angle and distance in the \(^2\text{A}_1\) state of the peroxide are 42.0° and 1.49 Å, respectively. The O-O distance in the dioxide is too far apart to have any significant interaction between the oxygen atoms, while the O-O distance in the peroxide is close to the characteristic lengths of a single O-O bond (1.48 Å). Moreover, the O-O stretching frequency of the La(O₂) \(^2\text{A}_1\) state is predicted to be 872 cm\(^{-1}\), which is very close to the O-O stretching frequencies of 878 or 866 cm\(^{-1}\) of hydrogen peroxide (H₂O₂). For the LaOO superoxide (C₄ᵥ), the ground states of the neutral molecule and cation are predicted to be \(^2\Sigma^+\) and \(^1\Sigma^+\), respectively. The O-O distance (1.37 Å) in the \(^2\Sigma^+\) neutral state is comparable to the bond length of molecular oxygen anion \((\text{O}_2^-)\) (1.35 Å) and to the characteristic bond length of a superoxide compound (1.34 Å). The O-O bond in the LaOO can be considered to have a bond order of 1.5 and an averaged bond distance of the double and single O-O bonds. The calculated O-O stretching frequency (942 cm\(^{-1}\)) in the \(^2\Sigma^+_\text{g}^+\) neutral state of LaOO is also close to that of hydrogen superoxide radical (HOO-) (929 cm\(^{-1}\)) and comparable to that of molecular oxygen anion (1090 cm\(^{-1}\)).

3.3.3 Ionization of an excited state of lanthanum dioxide (OLaO)

The electronic transition responsible for the observed MATI spectrum can be determined by comparing the measured and predicted AIEs, vibrational frequencies, and
intensity profiles. As discussed in Section IIA, the experimental AIE is 4.9760 eV, and the measured frequencies are 656 and 122 cm\(^{-1}\) for the cation and 92 cm\(^{-1}\) for the neutral molecule. From Table 3.1, the AIEs of the \(3\text{B}_2 \leftarrow 2\text{B}_2\), \(1\Sigma_g^+ \leftarrow 2\text{B}_2\), and \(1\Sigma_g^+ \leftarrow 2\Sigma_u^+\) transitions of the OLaO dioxide are predicted to be 9.03, 8.68, and 8.63 eV, respectively, and the AIE of the \(3\text{A}_2 \leftarrow 2\text{A}_1\) ionization of the La(O\(_2\)) peroxide is 7.72 eV. Because the predicted AIEs are 3.0 eV higher than the measured AIE and the difference is much larger than any expected computational errors, the above transitions can safely be excluded from the MATI spectrum. On the other hand, the predicted AIEs of the \(3\text{B}_2 \leftarrow 4\text{B}_2\) transition of the dioxide, the \(1\text{A}_1 \leftarrow 2\text{A}_1\) and \(3\text{A}_2 \leftarrow 4\text{A}_2\) transitions of the peroxide, and the \(1\Sigma^+ \leftarrow 2\Sigma^+\) transition of the superoxide are all much closer to the experimental value.

For these cases, the comparison of the experimental and theoretical AIEs alone is not sufficient for the electronic-state assignment. Therefore, vibrational frequencies are considered as well. Table 3.1 shows that none of the vibrational frequencies of the \(1\Sigma^+\) state of (LaOO)\(^+\) and the \(3\text{A}_2\) state of [La(O\(_2\))]\(^+\) matches the measured 656 or 122 cm\(^{-1}\) vibrational intervals. Although the symmetric bending frequency (\(v_2\)) of the [La(O\(_2\))]\(^+\) \(1\text{A}_1\) state (610 cm\(^{-1}\)) is in reasonable agreement with the 656 cm\(^{-1}\) interval, the singlet ionic state does not show any frequency comparable to the 122 cm\(^{-1}\) mode. In addition, none of the initial states in the \(1\text{A}_1 \leftarrow 2\text{A}_1\) and \(3\text{A}_2 \leftarrow 4\text{A}_2\) transitions of the peroxide and the \(1\Sigma^+ \leftarrow 2\Sigma^+\) transition of the superoxide exhibits a mode comparable to the measured 92 cm\(^{-1}\) mode. Thus, none of the above three transitions should be associated with the MATI spectrum. On the other hand, the symmetric O-La-O bending frequencies (\(v_2\)) of the \(4\text{B}_2\) and \(3\text{B}_2\) states of the OLaO dioxide (90 and 113 cm\(^{-1}\)) are in excellent agreement with the observed vibrational intervals of 92 and 122 cm\(^{-1}\), even though the calculated symmetric
La-O stretching frequency ($v_1$, 562 cm$^{-1}$) of the $^3\text{B}_2$ state at the B3LYP level is substantially underestimated when compared to the experimental value of 656 cm$^{-1}$. Considering both the AIE and the vibrational frequencies, $^3\text{B}_2 \leftarrow ^4\text{B}_2$ is the most likely transition probed by the MATI experiment. This conclusion is further supported by considering the spectral intensity profile. Figure 3.1(b-e) shows the simulations from transitions of $^3\text{B}_2 \leftarrow ^4\text{B}_2$ of OLaO, $^3\text{A}_2 \leftarrow ^4\text{A}_2$ and $^1\text{A}_1 \leftarrow ^2\text{A}_1$ of La(O$_2$), and $^1\Sigma^+ \leftarrow ^2\Sigma^+$ of LaOO. In these simulations, the calculated frequencies are not scaled, but the theoretical AIEs are shifted to the experimental origin band for comparison. Frequency scaling is often used for the high-frequency modes of organic molecules, but from our previous studies of numerous metal complexes, the scaling practice does not work for the low-frequency vibrational modes.$^{191}$ Low-frequency metal-ligand vibrational modes are more difficult to treat theoretically, and predicted values can be on either side of the experimental measurements. As shown in Figure 3.1, the $^3\text{A}_2 \leftarrow ^4\text{A}_2$ and $^1\text{A}_1 \leftarrow ^2\text{A}_1$ transitions of La(O$_2$) (Figure 3.1c,d) and the $^1\Sigma^+ \leftarrow ^2\Sigma^+$ transition of LaOO (Figure 3.1e) fail to reproduce the experimental 122 cm$^{-1}$ progression and the 92 cm$^{-1}$ hot bands. On the other hand, the simulation of the $^3\text{B}_2 \leftarrow ^4\text{B}_2$ transition of OLaO (Figure 3.1b) is in very good agreement with the experimental spectrum.

In an attempt to improve the theoretical AIEs and vibrational frequencies, calculations at higher levels of theory were carried out for the observed $^3\text{B}_2$ and $^4\text{B}_2$ states of OLaO. Table 3.2 summarizes the spectroscopic constants from MATI measurements and DFT/B3LYP, MP2, CCSD, CCSD(T) and CASPT2 calculations. The wave-function-based $\textit{ab initio}$ methods yield slightly better AIEs (5.37-5.39 eV) than the DFT method (5.55 eV). For the vibrational analysis of the $^3\text{B}_2$ ionic state, the MP2 method produces the
best frequency for the La-O stretching mode ($v_1$, 601 cm\(^{-1}\)), whereas the CASPT2 method gives the best frequency for the O-La-O bending mode ($v_2$, 121 cm\(^{-1}\)). For the O-La-O bending mode ($v_2$) of the $^4B_2$ neutral state, the B3LYP, MP2, CCSD, CASPT2 and CCSD(T) calculations all give bending frequencies within less than 15 cm\(^{-1}\) of experiment, the accuracy expected for such a low frequency mode. No single method produces uniform results matching the experimental values. The biggest issue is that all of the methods underestimate the value of the stretching frequency for the $^3B_2$ ionic state by 50 to 100 cm\(^{-1}\).

Figure 3.3a presents the valence electron configuration of the $^4B_2$ state of OLaO, $1a_1^21b_2^21a_2^21b_1^22a_1^12b_1^13a_1^1$, from the CASPT2 calculations. $1a_1^21b_2^21a_2^21b_1^22a_1^12b_1^1$ are oxygen 2p-based orbitals and $3a_1^1$ (highest occupied molecular orbital, HOMO) is a La 6s-based orbital. Because the ground electron configuration of La is 5d\(^4\)6s\(^2\), the formation of the $^4B_2$ state of OLaO results in two-electron transfer from the metal to oxygen atoms. Thus, the formal oxidation states of O and La in the $^4B_2$ state are -1.0 and +2.0, respectively.

Ionization of the $^4B_2$ neutral state removes the La 6s-based electron from the HOMO and gives out a $^3B_2$ ion ground state. Because the HOMO is essentially a non-bonding orbital, the ion state has a similar geometry to the neutral state and the MATI spectrum has a short FC intensity profile. In contrast to the $^4B_2$ state, the $^2B_2$ state has an electron configuration of $1b_2^21a_2^21a_1^21b_1^22a_1^22b_2^1$, where the HOMO ($2b_2^1$) is an oxygen 2p-base orbital (Figure 3.3b). The formation of the $^2B_2$ state leads to three electron loss of La to O. Thus, the formal oxidation states of La and O in this case are -1.5 and +3.0, respectively. Because the HOMO is an oxygen 2p-based orbital, the removal of this electron requires much higher
energy in the presence of the +3 lanthanide field. This explains why the predicted AIE of the $^{2}B_2$ state is much higher than that of the $^{4}B_2$ state.

Dissociation of the $^{4}B_2$ excited state of OLaO could give the La atom in an excited state $^{4}F$ and the $O_2$ molecule in an excited state of $^{1}A_g$ with spin conservation. The $^{4}F$ ($5d^26s^1$) state is 0.33 eV above the ground state $^{2}D(5d^16s^2)$.$^{153,161}$ The dissociation energies of this process are predicted to be 5.81, 5.38, and 5.25 eV by the B3LYP, MP2, and CCSD(T) calculations. The dissociation energy is slightly larger than the AIE at the B3LYP level, but slightly smaller at the MP2 and CCSD(T) levels (Table 3.2). Because the inconsistent trends of the predicted dissociation and AIEs, no conclusion could be made about if the previous chemielectron spectrum$^{165-167}$ was produced by ionization of the OLaO $^{4}B_2$ state. However, because the La-O stretching frequency of the [OLaO]$^+$ $^{3}B_2$ state (656 (1) cm$^{-1}$) measured from our MATI spectrum is consistent with the value (660 (30) cm$^{-1}$) from the chemielectron spectrum, LaO$_2$ seems to be the carrier of the chemielectrons. An accurate measurement for the dissociation energy of the OLaO $^{4}B_2$ state is required to settle this problem in a more definitive manner.

### 3.4 CONCLUSIONS

A MATI spectrum is reported for the first time for LaO$_2$ seeded in a supersonic molecular beam. The spectrum exhibits a strong origin band, La$^+$-O stretching and O-La$^+$-O bending progressions, and thermal excitation of the La-O stretching mode. Our combined experimental and computational analysis shows that the spectrum involves ionization of an excited high spin electronic state of lanthanum dioxide. This process is determined to be the $^{3}B_2 \leftarrow^{4}B_2$ transition. The $^{4}B_2$ excited neutral state is formed by
transferring two La electrons to oxygen atoms and has a valence electron configuration consisting of oxygen 2p- and lanthanum 6s-based orbitals. The $^3\text{B}_2$ state is formed by the removal of the non-bonding La 6s electron and has a molecular geometry similar to the $^4\text{B}_2$ neutral state. The ground state of the lanthanum dioxide was predicted to be a doublet, but it was not observed by the experiment, most likely because of its much higher ionization energy. In addition to possible transitions of the dioxide, ionization processes of lanthanum peroxide and superoxide were considered as well, but they were excluded after comparison with the experimental spectrum. This is the first example where a single-photon MATI spectrum is observed from an excited initial electronic state at several electronvolts above the ground electronic state.
Table 3.1 Electronic states, geometries (RLa-O for OLaO and RLa-O/RO-O for LaOO and La(O2)), A (for ∠O-La-O or ∠La-O-O), vibrational frequencies (v_i), relative energies (E_{rel}), and adiabatic ionization energies (AIE) of lanthanum dioxide (OLaO, C_{2v} or D_{∞h}), lanthanum peroxide [La(O2), C_{2v}], and lanthanum superoxide (LaOO, C_{∞v}) from the B3LYP calculations with aug-cc-pVTZ basis set for O atoms and SDD ECP and basis set for the La atom. Reprinted with permission from J. Chem. Phys., 137, 034207 (2013), Copyright 2013 AIP Publishing LLC.

<table>
<thead>
<tr>
<th>States</th>
<th>R(Å)</th>
<th>A(°)</th>
<th>v_1(cm⁻¹)</th>
<th>v_2(cm⁻¹)</th>
<th>v_3(cm⁻¹)</th>
<th>E_{rel}(eV)</th>
<th>AIE(eV)</th>
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<td></td>
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<tr>
<td>²B_2 (C_{2v})</td>
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<td>146.3</td>
<td>622</td>
<td>142</td>
<td>388</td>
<td>0</td>
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<tr>
<td>³Σ_{g}⁺ (D_{∞h})</td>
<td>1.95</td>
<td>180.0</td>
<td>609</td>
<td>56</td>
<td>457</td>
<td>0.05</td>
<td>8.68</td>
</tr>
<tr>
<td>⁴B_2 (C_{2v})</td>
<td>2.17</td>
<td>118.9</td>
<td>494</td>
<td>90</td>
<td>445</td>
<td>3.40</td>
<td>8.63</td>
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<tr>
<td>(OLaO)^+</td>
<td>1.83</td>
<td>180.0</td>
<td>631</td>
<td>194</td>
<td>750</td>
<td>8.68</td>
<td>5.63</td>
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<td>²A_1 (C_{2v})</td>
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<td>149.4</td>
<td>42.0</td>
<td>872</td>
<td>573</td>
<td>481</td>
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<td>⁴A_2 (C_{2v})</td>
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<td>32.6</td>
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<tr>
<td>²Σ⁺ (C_{∞h})</td>
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<td>504</td>
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<td>990</td>
<td>525</td>
<td>203</td>
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a For C_{2v} or D_{∞h} dioxide, v_1, v_2 and v_3 are the symmetric La-O stretch (a₁ or σ_g⁺), O-La-O bend (a₁ or π_u) and asymmetric La-O stretch (b₂ or σ_u⁺), respectively. For C_{2v} peroxide, v_1, v_2 and v_3 are the symmetric O-O stretch (a₁), symmetric La-O_2 stretch (a₁) and asymmetric La-O_2 stretch (b₂), respectively. For C_{∞v} superoxide, v_1, v_2 and v_3 are symmetric O-O stretch (σ⁺), symmetric La-O stretch (σ⁺) and degenerate La-O-O bend (π), respectively.
Table 3.2 Electronic states, geometries ($R_{\text{La-O}}$, $A$ for $\angle\text{O-La-O}$), and vibrational frequencies ($v_i$),\(^a\) of the $^4\text{B}_2$ and $^3\text{B}_2$ states and adiabatic ionization energies (AIE) of the $^4\text{B}_2$ state of bent lanthanum dioxide (OLaO, C\(_{2v}\)) from MATI spectroscopy and theoretical calculations.\(^b\) Reprinted with permission from J. Chem. Phys., 137, 034207 (2013), Copyright 2013 AIP Publishing LLC.

<table>
<thead>
<tr>
<th>Methods</th>
<th>$R$(Å)</th>
<th>$A$(°)</th>
<th>$v_1$ (cm(^{-1}))</th>
<th>$v_2$ (cm(^{-1}))</th>
<th>$v_3$ (cm(^{-1}))</th>
<th>AIE(eV)</th>
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<td>CCSD</td>
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<td>118.8</td>
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<td>$^3\text{B}_2$</td>
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<td>CCSD(T)</td>
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<td>563</td>
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</tbody>
</table>

\(^a\)The vibrational modes of $v_1$, $v_2$ and $v_3$ are the symmetric La-O stretch ($a_1$), O-La-O bend ($a_i$) and asymmetric La-O stretch ($b_2$), respectively.

\(^b\)The ANO-RCC basis set on La and O was used for the CASPT2 calculations. The Stuttgart RSC ANO/ECP basis set on La and 6-311G(d) basis set on O were used for the other calculations.

\(^c\)Vibrational frequencies calculated at the CASSCF level.
Figure 3.1 MATI spectrum of LaO$_2$ seeded in He (a) and simulations (100 K) of the $^3\text{B}_2 \leftarrow ^4\text{B}_2$ transition of lanthanum dioxide (OLaO) (b), the $^3\text{A}_2 \leftarrow ^4\text{A}_2$ (c) and $^1\text{A}_1 \leftarrow ^2\text{A}_1$ (d) transitions of lanthanum peroxide (La(O$_2$)), and the $^1\Sigma^+ \leftarrow ^2\Sigma^+$ transition of lanthanum superoxide (LaOO) (e). Reprinted with permission from J. Chem. Phys., 137, 034207 (2013), Copyright 2013 AIP Publishing LLC.
Figure 3.2 Possible structures of LaO$_2$: lanthanum dioxide (OLaO) (a, b), lanthanum peroxide [La(O$_2$)] (c) and lanthanum superoxide (LaOO) (d). A bent lanthanum superoxide was also considered, but it converged to the linear structure upon geometry optimization. Reprinted with permission from J. Chem. Phys., 137, 034207 (2013), Copyright 2013 AIP Publishing LLC.
Figure 3.3 Valence electron configurations of the $^4\text{B}_2$ (a) and $^2\text{B}_2$ (b) states of lanthanum dioxide (OLaO). The molecule is placed on the yz plane. The relative energy orderings of the valence molecular orbitals are different in the two states. Two electrons are transferred from La to two O atoms in the formation of the $^4\text{B}_2$ state, which has the HOMO of largely a La 6s character. On the other hand, three electrons are transferred from La to two O atoms to form the $^2\text{B}_2$ state, which has the HOMO of largely an O 2p character. Reprinted with permission from J. Chem. Phys., 137, 034207 (2013), Copyright 2013 AIP Publishing LLC.
CHAPTER 4 ELECTRONIC STATES AND SPIN-ORBIT SPLITTING OF LANTHANUM DIMER

4.1 INTRODUCTION

Identification of the ground electronic states of transition metal clusters challenges experimentalists and theorists because of the high-density of low-lying spin states arising from the metal d electrons. Dilanthanum may be among the simplest homonuclear diatomics, since the ground electron configuration of the metal atom (6s^2 5d^1) has only one unpaired electron. In spite of this seemingly simplicity, the ground electronic state has not yet been established for the neutral molecule, and low-lying electronic states have not been reported for the singly charged cation.

In 1992, Dolg and coworker reported the first high-level theoretical study-configuration interaction (CI) and correlation-energy DFT calculations for La_2. The ground state was predicted to be \( ^5\Sigma_u^- \) with the vibrational frequency of 130 cm\(^{-1}\) and the dissociation energy of 1.17 eV. Since the ground states of Sc_2\(^{163,193-195}\) and Y_2\(^{196-198}\) have been reported as \( ^5\Sigma_u^- \), the prediction of the quintet ground state for La_2 might be expected because the three metals have the same ground electron configuration [ns^2(n-1)d^1]. However, the predicted vibrational frequencies and dissociation energies were in disagreement with the results obtained from argon matrix-isolation Raman spectroscopy. In the Raman study, Lombardi and coworkers reported the vibrational frequency of 236.0(8) cm\(^{-1}\) and the dissociation energy of 1.8(3) eV. The bond energies from the theoretical prediction and Raman spectroscopy were both low compared to the value of 2.50 (22) eV reported by Verhaegen et al. The Verhaegen’s value was obtained by applying the third-
thermodynamic-law method to mass spectrometric measurements of dilanthanum produced in a Knudsen cell.\textsuperscript{200} However, using the third-law method to derive bond energy requires the knowledge of the electronic state and partition function, which was unknown. Moreover, Knight et al.\textsuperscript{201} failed to obtain an electron spin resonance (ESR) spectrum for La\textsubscript{2}, whereas the similar experimental conditions gave a spectrum for Sc\textsubscript{2}.\textsuperscript{193} The ESR study showed that Sc\textsubscript{2} had a \( ^5\Sigma_u^- \) ground state. These observations were interpreted as suggesting that the ground state of La\textsubscript{2} might be a singlet. In 2002, Cao and Dolg extended their 1992’s theoretical study to higher level theories.\textsuperscript{202} They performed calculations by using the coupled cluster with single, double, and perturbative triple excitation [CCSD(T)], the complete active space self-consistent field (CASSCF), and the multi-reference configuration interaction (MRCI) methods with relativistic effective core potential basis set and found that the ground state of La\textsubscript{2} was likely \( ^1\Sigma_g^+ \). The best estimates of the vibrational frequencies and bond energies were 186 (13) cm\textsuperscript{-1} and 2.31(13) eV, respectively. Although the bond energy is more close to the experimental values, the vibrational frequency is still significantly underestimated. More recently, DFT calculations were used to study lanthanum clusters,\textsuperscript{203} and several lanthanide dimers.\textsuperscript{203,204} These DFT calculations predicted that the ground states of La\textsubscript{2} were either a singlet\textsuperscript{204} or a triplet\textsuperscript{203}, with vibrational frequencies in the range of 140-163 cm\textsuperscript{-1} and bond energies of 1.1 -3.7 eV.

We report here the determination of the ground electronic states of La\textsubscript{2} and low-lying states of La\textsubscript{2}\textsuperscript{+} using a synergistic experimental and theoretical approach. The first electronic spectrum of La\textsubscript{2} was obtained with single-photon MATI spectroscopy, a sister technique of PFI-ZEKE spectroscopy. Low-lying electronic states of the neutral molecule
and cation were obtained with CASSCF, CAS with second-order perturbation theory (CASPT2), MRCI, and MRCI with Davidson’s cluster correction (MRCI+Q) multi-configuration *ab initio* methods. Single-photon ZEKE experiments have demonstrated tremendous potential to provide vibronic and structural information for metal-organic complexes. On the other hand, correlating ZEKE signals with a particular metal cluster is less straightforward. This is because the metal cluster synthesis in molecular beams is less selective than that of metal-organic complexes, and the IEs of neighboring cluster sizes are often close to each other. MATI is attractive for studying metal clusters because of the inherent mass selection. However, its potential applications to metal clusters remain to be explored. The observed MATI spectrum of La₂ is shown to be consistent with the \( \text{a}^2\Sigma_g^+ \leftarrow \text{X}^1\Sigma_g^+ \) and \( \text{b}^2\Pi_u \leftarrow \text{X}^1\Sigma_g^+ \) transitions. Both experimental measurements and theoretical calculations show that the ground electronic state of La₂ is \( \text{X}^1\Sigma_g^+ \). The ground state of La₂ is different from that of the other dimers in the same group (Sc₂ and Y₂), for which the ground state has been reported as \( \text{X}^5\Sigma_u^- \).

4.2 EXPERIMENTAL AND COMPUTATIONAL METHODS

4.2.1 Experiment

The metal-cluster beam MATI spectrometer used in this work is similar to the ZEKE apparatus described in a previous publication. It consists of two vacuum chambers. The first houses a Smalley-type cluster source and is pumped by a 2200 l s⁻¹ diffusion pump. The second chamber houses a time-of-flight spectrometer and is pumped by two 400 l s⁻¹ turbo molecular pump. The time-of-flight spectrometer is composed of a two stage extraction assembly, a 34 cm long flight tube, and a dual microchannel plate.
detector (Burle). The entire spectrometer is housed in a cylindrical, double-walled, µ-metal shield.

Lanthanum clusters were produced by laser vaporization (Lumonics YM-800 Nd:YAG, 532 nm,) of a La rod (Alfa Aesa, 99.9%) in the presence of a pulse of ultra-high-purity He (or Ar) carrier gas delivered by a homemade piezoelectric pulsed valve. The metal vapor and carrier gas passed down a clustering tube (2 mm inner diameter, 2 cm length), and the resultant clusters were supersonically expanded into the vacuum chamber. The supersonic jet was skimmed (2mm diameter) 3 cm downstream from the exit end of the clustering tube. A pair of deflection plates (2.5 cm spacing, 220V) located after the skimmer was used to remove residual charged species (formed during laser ablation) from the molecular beam before it entered the second chamber.

Prior to the MATI measurements, photoionization time-of-flight mass spectra were recorded to determine the chemical content of the cluster beam, and pulsed-field-ionization photoionization efficiency (PIE) spectra were recorded to locate the ionization threshold of La$_2$. With the ionization laser set above the PIE threshold, the experimental conditions (e.g., timing and power of the vaporization and ionization lasers and the backing pressure of the carrier gas) were carefully optimized to maximize the intensity of the La$_2^+$ signal in the mass spectrum.

With the optimized experimental conditions, La$_2$ was excited to high-lying Rydberg states in a single-photon process by the frequency-doubled output of a dye laser (Lumonics HD-500) pumped by a Nd:YAG laser (Quanta Ray GCR-3, 355 nm) and then ionized by an electric pulse (DEI PVM-4140, 320 V cm$^{-1}$). The laser beam was collinear and counter propagating with the molecule beam. The time delay between the laser and electric pulses
was varied to maximize the MATI signal, and it was typically 20 \( \mu s \) for He carrier and 50 \( \mu s \) for Ar. A small DC field (1.2 V cm\(^{-1}\)) was applied to help separate the prompt ions produced by direct photoionization from the MATI ions produced by delayed field ionization. MATI signal was obtained by scanning the wavelength of the tunable dye laser, detected by a dual microchannel plate detector, amplified by a preamplifier (SRS SR445), averaged by a gated integrator (SRS SR250), and stored in a laboratory computer. Laser wavelengths were calibrated against vanadium atomic transitions in the spectral region. The Stark shift induced by the DC field was calculated using the relation of \( \Delta E = 6.1E_f^{1/2} \), where \( E_f \) is in V cm\(^{-1}\) and \( \Delta E \) in cm\(^{-1}\).  

4.2.2 Computation

Equilibrium geometries and harmonic vibrational frequencies of the low-lying electronic states of La\(_2\) and La\(_2^+\) were calculated using CASSCF\(^{180,181}\) and CASPT2\(^{182}\) methods. A level-shift technique\(^{183}\) was employed, if necessary, to avoid the intruder state problem in the CASPT2 calculations. Single-point energies of the electronic states were refined at the MRCI and MRCI+Q levels.\(^{208}\) Spin-orbit splitting was calculated using the state interaction method,\(^{209}\) where the spin-orbit matrix elements were first obtained at the CASSCF level, and the diagonal elements of the matrix were then replaced by the CASPT2 energies. In all these calculations, the full-electron atomic natural orbital with relativistic core correlation (ANO-RCC)\(^{184}\) basis set and the second-order Douglas–Kroll–Hess Hamiltonian\(^{160,161}\) were employed to treat the scalar relativistic effect. In the ANO-RCC basis set of La atom, the primitive set of (24s,21p,15d,5f,3g,2h) was contracted to (11s,10p,8d,5f,3g,2h) basis functions. Since La atom has an electron configuration of
[Xe]6s²5d¹, three electrons and six orbitals are included in the complete active space of the La atom, i.e., CAS (3, 6); and two electrons and six orbitals are in the active space of the La⁺ ion, i.e., CAS (2, 6). Thus, the active spaces are CAS(6, 12) and CAS (5, 12) for La₂ and La₂⁺, respectively. The [Kr]4d¹⁰ core of La was frozen in electron-correlation CASPT2 and MRCI calculations. To compare with La₂, we also calculated Sc₂ and Y₂ in the same group using the same methods and same type of basis sets and active spaces. All calculations were performed using MOLPRO 2010 quantum chemistry program package.¹⁸⁵

Although for some metal dimers there is evidence that the coupling between highly excited Rydberg states has an important effect on two-photon ZEKE intensities,²¹⁰⁻²¹² for other small metal clusters, a Franck-Condon (FC) model appears to yield reasonably accurate intensities for single-photon ZEKE spectra.¹⁴⁷,¹⁹⁶,²¹³⁻²¹⁷ Thus, we calculated FC factors using the equilibrium geometries, harmonic frequencies, and normal mode coordinates of the neutral and ion molecules and simulated the MATI spectrum using experimental linewidth and Lorentzian line shape. Transitions from exited vibrational levels of the neutral complexes were considered by assuming thermal excitation at specific temperatures.

4.3 RESULTS AND DISCUSSION

4.3.1 MATI spectrum of La₂

Figure 1(a) shows the MATI spectrum of La₂ seeded in Ar carrier. It exhibits three band systems originating from the 39046, 40314, and 40864 cm⁻¹ bands, respectively. The first system originating from the 39046 cm⁻¹ band consists of at least four intervals with
the spacing of about 232 cm\(^{-1}\) at the higher energy side and a 207 cm\(^{-1}\) interval at the lower energy side. The energy of the 39046 cm\(^{-1}\) band corresponds to the adiabatic AIEs of the molecule. The 232 cm\(^{-1}\) progression arises from the excitation of the ground vibronic level of La\(_2\) to various vibrational levels of a La\(_2^+\) electronic state, and the 207 cm\(^{-1}\) spacing is the vibrational frequency of the neutral molecule. Superimposed on the origin band and several other bands are sequence transitions separated by about 25 cm\(^{-1}\). This separation is the frequency difference between the ion and neutral states. For the other two band systems, similar structures are identified and vibrational frequencies are measured for the neutral and ion states. The ion frequencies measured from these two electronic transitions are 240 cm\(^{-1}\), slightly higher than that of the first band system (232 cm\(^{-1}\)). On the other hand, the neutral frequencies are the same from all three band systems (207 cm\(^{-1}\)). These observations indicate that the three band systems originate from the same electronic state of the neutral molecule and that ion states involved in the second and third band systems have similar electron bonding characters as these two states have identical vibrational frequencies. Beside the measurements of the energies of the three ion states and the vibrational frequencies of the neutral and ion states, the spectrum shows very strong origin bands and short vibrational progression for the three transitions. This additional observation suggests that bond lengths may be rather similar in these neutral and ion states.

4.3.2 Predicted electronic states of La\(_2\) and La\(_2^+\)

Table 4.1 presents the low-energy electronic states of La\(_2\) and La\(_2^+\) obtained from the CASPT2/ANO-RCC calculations. The lowest energy state of La\(_2\) is predicted to be \(X^1\Sigma_g^+\), consistent with previous calculations by Dolg et al.\(^{13}\) and Wu et al..\(^{14}\) The \(X^1\Sigma_g^+\)
state has an electron configuration of $5d\pi_u^4 \sigma_g^2 \sigma_u^6$ in the valence space. The $\pi_u^4$ orbital is formed by the bonding interaction of two pairs of perpendicular $5d_{xz}$ and $5d_{yz}$ orbitals, and $\sigma_g$ is formed by the bonding interaction largely between the $6s$ orbitals of two La atoms. These bonding orbitals, along with the $5d\sigma_g$ and $6s\sigma_u$ empty orbitals, are presented in Figure 2. Because of the bonding nature of the $\pi_u^4$ and $\sigma_g^2$ orbitals, lanthanum dimer in the $X^1\Sigma^+_g$ state possesses a triple bond between the two metal atoms. The excitation of two electrons from the occupied $5d\pi_u$ orbital into the empty $5d\sigma_g$ and $6s\sigma_u$ orbitals produces an $a^5\Sigma_u^-$ state, with an electron configuration of $6s\sigma_g^2 5d\pi_u^2 5d\sigma_g^1 6s\sigma_u^1$. Because two electrons are placed in the higher energy orbitals, the quintet state is less stable than the singlet state. The predicted energy difference between the two states is 886 cm$^{-1}$. Because one of the electrons is in the antibonding $\sigma_u$ orbital, La$_2$ in the $a^5\Sigma_u^-$ state may be considered as having a double bond (i.e., a $\sigma$ bond plus a $\pi$ bond). The reduction of the bond order from 3 in $X^1\Sigma^+_g$ to 2 in $a^5\Sigma_u^-$ leads to an increase of the La-La bond length from 2.692 to 3.093 Å (Table 4.1). Ionization of the $X^1\Sigma^+_g$ neutral state may form two different doublet states. If a $\sigma_g$ electron is removed from the singlet state, the resulting ion will be in the $a^2\Sigma_g^+$ state with the $5d\pi_u^4 6s\sigma_g^1$ electron configuration. On the other hand, if a $\pi_u$ electron is ejected, the ion will be in the $b^2\Pi_u$ state with an electron configuration of $6s\sigma_g^2 5d\pi_u^3$. It is interesting to note from Table 4.1 that although the ejected electrons ($\sigma$ or $\pi$) have bonding character, ionization does not significantly increase the La-La bond length, and in fact, the bond length is slightly shorter in the $b^2\Pi_u$ state. This is probably due to the charge effect, which compensates the loss of a bonding electron and pulls the metal atoms closer in the cation. Ionization of the $a^5\Sigma_u^-$ state may form several quartet ion states depending
on which electron is removed. However, the lowest-energy quartet state is expected to be the one that arises from the removal of the antibonding $\sigma_u^{-1}$ electron. This quartet state is predicted to be $X^4\Sigma_g^-$ and is calculated to lie at lower energy than either $a^2\Sigma_g^+$ or $b^2\Pi_u$ state.

4.3.3 Observed electronic states of $\text{La}_2$ and $\text{La}_2^+$

On the basis of the comparison of the measurements with the theoretical calculations, three electronic transitions are assigned to the observed spectrum. These are

\[
a^2\Sigma_g^+ \leftrightarrow X^1\Sigma_g^+, \quad b^2\Pi_{3/2}, u \leftrightarrow X^1\Sigma_g^+, \quad \text{and} \quad b^2\Pi_{1/2}, u \leftrightarrow X^1\Sigma_g^+. 
\]

The $X^1\Sigma_g^+$ neutral state is the lowest-energy state, and its vibrational frequency of 194 $\text{cm}^{-1}$ is close to the measured value of 207 $\text{cm}^{-1}$. On the other hand, the $a^5\Sigma_u^-$ neutral state is an excited state, and the La-La stretching frequency (122 $\text{cm}^{-1}$) is too low compared to the measured value. Therefore, the neutral state that is responsible for the observed transitions must be $X^1\Sigma_g^+$. For the cation, three states are predicted to be in the order of $X^4\Sigma_g^- < a^2\Sigma_g^+ < b^2\Pi_u$. The $X^4\Sigma_g^-$ ion state can be excluded because the predicted stretching frequency of 120 $\text{cm}^{-1}$ in this state is too small compared to the measured frequency of 232 or 240 $\text{cm}^{-1}$. Moreover, transitions from a singlet neutral state to a quartet ion state are not allowed because of the restriction in electron spin multiplicity. Thus, the possible ion states contributing to the observed transitions should be $a^2\Sigma_g^+$ and $b^2\Pi_u$. Because of the spin-orbit coupling, the $b^2\Pi_u$ state is split into two components, $b^2\Pi_{3/2}, u$ and $b^2\Pi_{1/2}, u$. The predicted energies for the $a^2\Sigma_g^+ \leftrightarrow X^1\Sigma_g^+$, $b^2\Pi_{3/2}, u \leftrightarrow X^1\Sigma_g^+$, and $b^2\Pi_{1/2}, u \leftrightarrow X^1\Sigma_g^+$ transitions are 38976, 40114, and 40752 $\text{cm}^{-1}$, respectively; which compare nicely with the positions of 39046, 40314, and 40864 $\text{cm}^{-1}$ of the three origin bands in the MATI spectrum. The stretching frequencies for the $a^2\Sigma_g^+$, $b^2\Pi_{3/2}, u$, and $b^2\Pi_{1/2}, u$ states are calculated to be
219, 256, and 256 cm\(^{-1}\), consistent with the measured frequencies of 232, 240, and 240 cm\(^{-1}\). Thus, the observed three band systems are assigned to the \(a^2\Sigma_g^+ \leftarrow X^1\Sigma_g^+\), \(b^2\Pi_{3/2,u} \leftarrow X^1\Sigma_g^+\), and \(b^2\Pi_{1/2,u} \leftarrow X^1\Sigma_g^+\) transitions, respectively. The spin-orbit splitting between the two components of \(b^2\Pi_u\) is measured to be 550 cm\(^{-1}\). For a \(^2\Pi\) state with a \(\pi^3\) electron configuration, the spin-orbit splitting, \(\Delta E\), is given by \(\Delta E = E(\Pi_{3/2,u}) - E(\Pi_{1/2,u}) = -a_\pi\), where \(a_\pi\) is a molecular spin-orbit parameter.\(^{218}\) Because \(a_\pi\) is always a positive quantity, the \(^2\Pi\) state is inverted for the \(\pi^3\) configuration, as is well known. Since the \(\pi\) electrons are essentially pure 5d electrons, \(a_\pi\) can be set equal to the atomic spin-orbit parameter \(\xi_{5d}\). The values of \(\xi_{5d}\) for \(\text{La}(^4\text{F}, 6s^15d^2)\) and \(\text{La}^+(^3\text{D}, 6s^15d^1)\) are 499 and 619 cm\(^{-1}\), respectively, as obtained from a Hartree-Fock calculation.\(^{219}\) In computing the \(\xi_{5d}\) values, the first excited states of \(\text{La}(^4\text{F}, 6s^15d^2)\) and \(\text{La}^+(^3\text{D}, 6s^15d^1)\) are considered because the \(b^2\Pi_u\) \((6s\sigma_g^25d\pi_u^3)\) state of \(\text{La}_2^+\) is formed by removing a \(\pi_u\) electron from the \(X^1\Sigma_g^+(5d\pi_u^46s\sigma_g^2)\) ground state of \(\text{La}_2\) and the \(X^1\Sigma_g^+\) state is derived from two excited \(\text{La}(^4\text{F}, 6s^15d^2)\) atoms. Since the La atoms in the \(\text{La}_2^+\) cation can be considered to each have a charge of +1/2, the average of \(\xi_{5d}(\text{La})\) and \(\xi_{5d}(\text{La}^+)\) seems appropriate for comparison to the spin-orbit splitting of \(\text{La}_2^+\). This averaged value, \(\xi_{5d} = (449 + 619)/2\) cm\(^{-1}\) = 559 cm\(^{-1}\), is close to the measured separation of the two \(b^2\Pi_u\) levels (550 cm\(^{-1}\)).

The measured spectroscopic parameters, along with those from the CASPT2 calculations, are summarized in Table 4.2. The frequencies for the \(X^1\Sigma_g^+\) neutral state and \(b^2\Pi_{1/2,u}\) ion state are obtained directly from the spectrum. For the \(a^2\Sigma_g^+\) and \(b^2\Pi_{3/2,u}\) ion states, harmonic frequencies and anharmonicities are obtained via least-squares fitting. It is noted that the La-La stretching frequency from the current measurement (207 cm\(^{-1}\)) is
significantly lower than that measured by Ar matrix isolation Raman spectroscopy (236 cm\(^{-1}\)).\(^{199}\) This discrepancy may be due to a large Ar matrix shift. A shift of 22 cm\(^{-1}\) (\(\Delta \omega_e (ArLa_2 - La_2)\)) was estimated by \textit{ab initio} calculations.\(^{220}\) A second possibility is that the Raman frequency obtained in the Ar matrix might be for the \(La_2^+\) ion, rather than for the \(La_2\) neutral molecule, as the Raman frequency (236 cm\(^{-1}\)) is very close to the ion frequency obtained in the current work (232 or 240 cm\(^{-1}\)).

Although it does not measure the bond energies of \(La_2\) or \(La_2^+\), the MATI experiment provides the bond energy difference between the ion and neutral molecule using the thermodynamic cycle presented in Figure 3. In this figure, IEs of \(La_2\) are obtained from the MATI spectrum, and those of \(La\) atom are taken from the literature.\(^{153,189}\) From the thermodynamic cycle,

\[
D_0^+ [La_2^+ (a^2\Sigma_g^+) \rightarrow La^+ (^3F) + La (^4F)] - D_0 [La_2(X^1\Sigma_g^+) \rightarrow 2La (^4F)]
\]

\[
= IE [La^+ (^3F) \leftarrow La (^4F)] - IE [La_2^+ (a^2\Sigma_g^+) \leftarrow La_2 (X^1\Sigma_g^+)]
\]

\[
= 0.405 \text{ eV}
\]

Similarly,

\[
D_0^+ [La_2^+ (b^2\Pi_u) \rightarrow La^+ (^3D) + La (^4F)] - D_0 [La_2(X^1\Sigma_g^+) \rightarrow 2La (^4F)]
\]

\[
= IE [La^+ (^3D) \leftarrow La (^4F)] - IE [La_2^+ (b^2\Pi_u) \leftarrow La (X^1\Sigma_g^+)]
\]

\[
= 0.449 \text{ eV}
\]

The CASPT2 predicted differences for \(D_0^+ [La_2^+ (a^2\Sigma_g^+) \rightarrow La^+ (^3F) + La (^4F)] - D_0 [La_2(X^1\Sigma_g^+) \rightarrow 2La (^4F)]\) and \(D_0^+ [La_2^+ (b^2\Pi_u) \rightarrow La^+ (^3D) + La (^4F)] - D_0 [La_2(X^1\Sigma_g^+) \rightarrow 2La (^4F)]\) are 0.54 and 0.57 eV, respectively; they are slightly larger than the measured values (by 0.12-0.13 eV).
Previous studies reported that the ZEKE or MATI spectral intensities could be described by the FC principle for some metal-containing diatomic molecules,\(^{196}\) but not for others.\(^{210-212}\) To test the FC picture for La\(_2\), we calculated the MATI spectrum by using the linewidth of the experimental spectrum and the FC factors obtained from the equilibrium geometries and vibrational force fields of La\(_2\) and La\(_2^+\). The simulation is presented in Figure 2b. In this simulation, the theoretical 0-0 energy for the \(a^2 \Sigma_g^+ \leftarrow X^1 \Sigma_g^+\) transition is shifted to the experimental value, whereas vibrational frequencies for all involved states and 0-0 energies of the \(b^2 \Pi_{3/2,u} \leftarrow X^1 \Sigma_g^+\) and \(b^2 \Pi_{1/2,u} \leftarrow X^1 \Sigma_g^+\) transitions are not scaled. It can be seen that the simulation reproduces the overall features of the experimental spectrum, even though the vibrational intensity for the \(a^2 \Sigma_g^+ \leftarrow X^1 \Sigma_g^+\) transition is somewhat underestimated. This is similar to the previous observation for another metal dimer (Y\(_2\)) in the same group.\(^{196}\)

4.3.4 Comparison of group III M\(_2\) dimers (M= Sc, Y, and La)

Although they are in the same family, Sc\(_2\) and Y\(_2\) were reported to have \(5 \Sigma_u^-\) ground states previously,\(^{193-198}\) and La\(_2\) is determined to have a \(1 \Sigma_g^+\) ground state in the current study. The previous calculations on Sc\(_2\) and Y\(_2\) were carried out with different methods/basis sets from those used in the current work on La\(_2\). To ensure a fair comparison of the triad, we have also calculated \(1 \Sigma_g^+\) and \(5 \Sigma_u^-\) states of Sc\(_2\) and Y\(_2\) using the same methods as those for La\(_2\). Table 4.3 summarizes the theoretical results for the three metal dimers. It shows that the relative stability of the singlet and quintet states is indeed different between Sc\(_2\)/Y\(_2\) and La\(_2\). For the lighter species, the \(5 \Sigma_u^-\) state is more stable than the \(1 \Sigma_g^+\) state, and the energy difference decreases with higher level of theory. On the other hand,
the $^1\Sigma_g^+$ state is more stable than $^5\Sigma_u^-$ for La$_2$, and the energy difference increases with better electron-correlation treatments. In all three cases, higher-order electron configuration stabilizes the $^1\Sigma_g^+$ state relative to the $^5\Sigma_u^-$ state, supporting the previous argument obtained from the calculations on diyttrium.$^{198,221}$

A question arises about why Sc$_2$ and Y$_2$ prefer the high-spin $^5\Sigma_u^-$ state, while La$_2$ favors the low-spin $^1\Sigma_g^+$ state. The $^5\Sigma_u^-$ state of Sc$_2$ (Y$_2$) with the $4s\sigma_g^23d\pi_u^23d\sigma_g^14s\sigma_u^1$ (5s$\sigma_g^24d\pi_u^24d\sigma_g^15s\sigma_u^1$) electron configuration is derived from the $4s^23d^1 + 4s^13d^2 (5s^24d^1 + 5s^14d^2)$ atomic asymptotes, whereas the $^1\Sigma_g^+$ state of La$_2$ with the $5d\pi_u^46s\sigma_g^2$ electron configuration is derived from two excited 6s$^15d^2$ atoms. For the three metal atoms, the ground electron configuration is ns$^2$ (n-1)d$^1$ ($^2$D), and the first excited configuration is ns$^1$ (n-1)d$^2$ ($^4$F). The excitation energies are 1.428, 1.356, and 0.330 eV for Sc, Y, and La, respectively.$^{153}$ The formation of the $^1\Sigma_g^+$ dimer requires two atoms to be in the excited state, whereas the formation of the $^5\Sigma_u^-$ dimer requires one atom to be excited. Because the excitation energy for La is much smaller than that of Sc or Y, La$_2$ is expected to have a higher tendency to form the triply-bound $^1\Sigma_g^+$ state by the s$\rightarrow$d electron promotion. The stabilization of the La$_2$ $^1\Sigma_g^+$ state relative to its $^5\Sigma_u^-$ state (0.70 eV, Table 4.3) is more than sufficient to compensate for the energy cost for the s$\rightarrow$d excitation (0.330 eV). On the other hand, if Sc$_2$ (Y$_2$) were formed in the $^1\Sigma_g^+$ state by the interaction of two excited atoms, it would cost 1.428 (1.356) eV for the s$\rightarrow$d excitation of each atom.

4.4 CONCLUSIONS

A MATI spectrum is reported for La$_2$ seeded in an Ar supersonic molecular beam. Analysis shows that the spectrum involves three ionization processes originating from the
ground electronic state of the neutral molecule. In combination with multi-configuration \textit{ab initio} calculations, these processes are determined as $a^2\Sigma^+_g \leftarrow X^1\Sigma^+_g$, $b^2\Pi_{3/2,u} \leftarrow X^1\Sigma^+_g$, and $b^2\Pi_{1/2,u} \leftarrow X^1\Sigma^+_g$. $X^1\Sigma^+_g$ is the ground state of the neutral molecule, while $a^2\Sigma^+_g$ and $b^2\Pi_u$ states are low-lying excited states of the singly charged ion. The $b^2\Pi_u$ state is observed to split into two components by spin-orbit coupling. The ground state of the cation is predicted to be $X^4\Sigma^+_g$, but it is not observed by the experiment because of the electron spin restriction. Although they are in the same group in the Periodic Table, neutral dilanthanum prefers the low-spin singlet state, while its lighter analogues, discandium and diyttrium, favor the high-spin quintet states. The different electron spin multiplicities of these metal dimers are associated with the $ns \rightarrow (n-1)d$ electron excitation energies of the metal atoms.
Table 4.1 Low-lying electronic states, electron configurations, and electronic energies with vibrational zero-point corrections ($E_0$), bond length ($R$), vibrational frequencies ($\omega_e$) of La$_2$ and La$_2^+$ from CASPT2/ANO-RCC calculations. Reprinted with permission from J. Chem. Phys., 135, 034309 (2013), Copyright 2013 AIP Publishing LLC.

<table>
<thead>
<tr>
<th>State</th>
<th>Leading configuration (weight)</th>
<th>$E_0$ (cm$^{-1}$)</th>
<th>$R$ (Å)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$</td>
<td>$X^1\Sigma_g^+$ $5d\pi_u^4 6s\sigma_g^2$ (0.92)</td>
<td>0</td>
<td>2.692</td>
<td>194</td>
</tr>
<tr>
<td></td>
<td>$a^5\Sigma_u^-$ $6s\sigma_g^2 5d\pi_u^2 5d\sigma_g^1 6s\sigma_u^1$ (0.88)</td>
<td>886</td>
<td>3.093</td>
<td>122</td>
</tr>
<tr>
<td>La$_2^+$</td>
<td>$X^4\Sigma_g^-$ $6s\sigma_g^2 5d\pi_u^2 5d\sigma_g^1$ (0.92)</td>
<td>37755</td>
<td>3.015</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>$a^2\Sigma_g^+$ $5d\pi_u^4 6s\sigma_g^1$ (0.93)</td>
<td>38796</td>
<td>2.698</td>
<td>219</td>
</tr>
<tr>
<td></td>
<td>$b^2\Pi_u$ $6s\sigma_g^2 5d\pi_u^3$ (0.92)</td>
<td>40433</td>
<td>2.649</td>
<td>256</td>
</tr>
<tr>
<td></td>
<td>$b^2\Pi_{3/2, 1/2,u}$</td>
<td></td>
<td>40114/40752</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.2  Electronic energies with vibrational zero-point corrections ($E_0$), vibrational frequencies ($\omega_e$), and bond dissociation energies ($D_e$) for the observed electronic states $La_2$ and $La_2^+$. Reprinted with permission from J. Chem. Phys., 135, 034309 (2013), Copyright 2013 AIP Publishing LLC.

<table>
<thead>
<tr>
<th>State</th>
<th>$E_0$ (cm$^{-1}$)</th>
<th>$\omega_e$ (cm$^{-1}$) / $\omega_e\chi_e$ (cm$^{-1}$)</th>
<th>$D_e$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MATI</td>
<td>CASPT2</td>
<td>MATI</td>
</tr>
<tr>
<td>$La_2$</td>
<td>$X^1\Sigma_g^+$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>236.0 (8)$^b$</td>
<td>186(13)$^c$</td>
<td>219</td>
</tr>
<tr>
<td>$La_2^+$</td>
<td>$a^3\Sigma_g^+$</td>
<td>39046 (5)</td>
<td>38796</td>
</tr>
<tr>
<td></td>
<td>242.2 (8) / 0.4(1)</td>
<td></td>
<td>256</td>
</tr>
<tr>
<td>$b^2\Pi_{3/2,u}$</td>
<td>40314 (5)</td>
<td>40114</td>
<td>240(1)$^a$</td>
</tr>
<tr>
<td>$b^2\Pi_{1/2,u}$</td>
<td>40864 (5)</td>
<td>40752</td>
<td>240(1)$^a$</td>
</tr>
</tbody>
</table>

$a$ From direct spectral measurements, this work.

$b$ From Ar-matrix isolation Raman spectrum, reference$^{199}$. 

$c$ From MRCI+Q and CCSD(T) calculations, reference$^{202}$. 

d,e From thermodynamical absolute-entropy method, references$^{200,222}$. 
Table 4.3 Comparison of group III M₂ (M = Sc, Y, and La). Reprinted with permission from J. Chem. Phys., 135, 034309 (2013), Copyright 2013 AIP Publishing LLC.

<table>
<thead>
<tr>
<th></th>
<th>Bond length (Å)</th>
<th>ΔE (1^{\Sigma_{g}^{+}} - 3^{\Sigma_{u}^{-}}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{5}\Sigma_{u}^{-}$</td>
<td>$^{1}\Sigma_{g}^{+}$</td>
</tr>
<tr>
<td>Sc₂</td>
<td>2.745</td>
<td>2.430</td>
</tr>
<tr>
<td></td>
<td>2.704</td>
<td>2.360</td>
</tr>
<tr>
<td>Y₂</td>
<td>3.011</td>
<td>2.755</td>
</tr>
<tr>
<td></td>
<td>3.03</td>
<td>2.76</td>
</tr>
<tr>
<td>La₂</td>
<td>3.093</td>
<td>2.692</td>
</tr>
</tbody>
</table>

$^a$ The MRCI and MRCI+Q energies are obtained at CASPT2/ANO-RCC geometries, this work.

$^b$ From multi-reference single and double CI + Q calculations, reference$^{223}$.

$^c$ From CASSCF/SOCI+Q calculations, reference$^{198}$. 
Figure 4.1 MATI spectrum (a) of La$_2$ seeded in Ar gas and simulations (b) of the $a^2\Sigma_g^+ \leftarrow X^1\Sigma_g^+$, $b^2\Pi_{3/2,u} \leftarrow X^1\Sigma_g^+$, and $b^2\Pi_{1/2,u} \leftarrow X^1\Sigma_g^+$ transitions at 300 K. Reprinted with permission from J. Chem. Phys., 135, 034309 (2013), Copyright 2013 AIP Publishing LLC.
Figure 4.2 Valence-space molecular orbitals that are involved in the $X^1\Sigma_g^+$ and $a^5\Sigma_u^-$ states of La$_2$ and the $X^4\Sigma_g^-$, $a^2\Sigma_g^+$, and $b^2\Pi_u$ states of La$_2^+$ presented in Table 4.1. Reprinted with permission from J. Chem. Phys., 135, 034309 (2013), Copyright 2013 AIP Publishing LLC.
Figure 4.3 Schematic diagram for the thermodynamic cycles used to calculate the bond energy differences between La$_2^+$ and La$_2$ from ionization energies of the metal dimer and atom: IE (La) – IE (La$_2$) = $D_0^+$ (La$_2^+$) – $D_0$ (La$_2$). See text for details. Reprinted with permission from J. Chem. Phys., 135, 034309 (2013), Copyright 2013 AIP Publishing LLC.
5.1 INTRODUCTION

Because small metal oxide clusters serve as the building blocks of nanostructural materials and exhibit size-dependent properties, investigation of their structures has attracted considerable interests in spectroscopy and theory.\textsuperscript{87,224} Figure 5.1 shows possible structural isomers reported for \( \text{M}_2\text{O}_2 \) clusters, where \( \text{M} \) is a transition metal atom.\textsuperscript{87} They are three cycles and three open structures. The cyclic structures include a \( \text{D}_{2h} \) MOMO rhombus (Figure 5.1a), a \( \text{C}_{2v} \) MOMO nonplanar cycle (Figure 5.1b), and a \( \text{C}_{2v} \) MMOO planar metal peroxide (Figure 5.1c). The open structures consist of a "S"-shaped \( \text{C}_{2h} \) OMMO (Figure 5.1d), a curved \( \text{C}_5 \) MOMO (Figure 5.1e), and a triangular \( \text{C}_{2v} \) OOMM (Figure 5.1f). For group 3 \( \text{M}_2\text{O}_2 \) (\( \text{M} = \text{Sc}, \text{Y}, \text{and La} \)), several experimental and computational studies have been reported about their structures and electronic states. Andrews and coworkers reported in 1997 the infrared spectrum of \( \text{Sc}_2\text{O}_2 \) in a study of reactions of the laser-ablated Sc atom with \( \text{O}_2 \) in the Ar matrix and proposed the formation of two \( \text{Sc}_2\text{O}_2 \) isomers.\textsuperscript{225} One was an open ScOScO and the other a ring (ScO)_2. Two years later, Johnson and Panas reported a DFT study of a series of scandium oxide molecules, including the anionic, neutral and cationic \( \text{Sc}_2\text{O}_2 \) species.\textsuperscript{226} The DFT calculations with the B3LYP functional predicted that the neutral molecule was in a planar cyclic structure, with the ground state of \( ^3\text{B}_{1u} \) in \( \text{D}_{2h} \) point group (Figure 5.1a), and the molecular structure undertook only minor changes upon adding or removing an electron. In contrast to the DFT/B3LYP calculations, Yang \textit{et al.} predicted using the DFT/PBE
calculations that the cyclic Sc$_2$O$_2$ molecule preferred a singlet state.\textsuperscript{227} Besides the D$_{2h}$ ring structure, the authors located an open ScOScO isomer (Figure 5.1d) at about 2.0 eV higher in energy. For Y$_2$O$_2$, Nakajima, Kaya, and coworkers reported the photoelectron spectrum of the anion and proposed the most likely structures for the neutral molecule and anion to be rhombus.\textsuperscript{67} On the other hand, Yang and Xiong predicted using the DFT/B3LYP method that the most stable Y$_2$O$_2$ molecule was in a cyclic C$_{2v}$ peroxide structure (Figure 5.1c) with the $^3A_2$ ground state, and considerable structural changes occurred upon adding an electron to the molecule.\textsuperscript{228} The preferred structures of Y$_2$O$_2$ and Y$_2$O$_2^-$ from these calculations were different from those proposed by the photoelectron measurements\textsuperscript{67} and also from those of the Sc analogs predicted by the DFT/B3LYP or DFT/PBE methods.\textsuperscript{226,227} To our knowledge, there has been no spectroscopic or computational report about La$_2$O$_2$, the heaviest species among the triad. However, Willson and Andrews studied a series of (LnO)$_2$ (Ln = Ce, Pr, Nd, Sm, Eu, Tb, Dy, Tm, Yb, Lu) by using Ar matrix-isolation infrared spectroscopy.\textsuperscript{229,230} They observed D$_{2h}$ or C$_{2v}$ ring structures formed by dimerization of LnO or addition of a second Ln atom to LnO$_2$. Burow \textit{et al.} reported a CeOCeO ring structure of Ce$_2$O$_2^+$ in the study of a series of cerium oxide clusters using free electron laser infrared vibrational predissociation spectroscopy.\textsuperscript{231}

In spite of the continuous efforts reported in the literature, the preferred structures and electronic states of the group 3 M$_2$O$_2$ cluster remain in debate. In a recent study of the group 3 M$_3$O$_4$ clusters, we proposed that the M$_3$O$_4$ clusters were formed by fusing three cyclic MOMO fragments together, each sharing two O-M bonds with others.\textsuperscript{232} The objectives of this work is to investigate the structures and electronic states of M$_2$O$_2$.
through a synergetic spectroscopic and computational approach. The spectroscopic method is MATI, and the computational effort includes electronic structure calculations and spectral simulations. This synergetic approach has been shown to be powerful for studying small metal clusters and oxides.\cite{149,171,232}

5.2 EXPERIMENTAL AND COMPUTATIONAL METHODS

The metal-cluster beam MATI spectrometer has been described in a previous publication.\cite{14,171} The group 3 metal cluster oxides were produced by laser vaporization (Lumonics YM-800 Nd:YAG, 532 nm,) of a metal rod in the presence of ultra-high-purity He or Ar carrier gas (delivered by a homemade piezoelectric pulsed valve)\cite{172} and a small amount of ultra-high purity oxygen (supplied with a metering valve). The metal vapor and gas mixture passed down a clustering tube (2 mm inner diameter, 2 cm length), and the resultant clusters were supersonically expanded into the vacuum chamber. The supersonic jet was skimmed by a cone-shape skimmer (2 mm artifice diameter) at 3 cm downstream from the exit end of the clustering tube. A pair of deflection plates (2.5 cm spacing, 220 V) located after the skimmer was used to remove residual charged species formed during laser ablation from the molecular beam before it entered the spectroscopic chamber. Prior to the MATI measurements, photoionization time-of-flight mass spectra were recorded to determine the chemical content of the cluster beam, and photoionization efficiency spectra were recorded to locate approximate ionization thresholds of the M$_2$O$_2$ clusters. With the energy of the ionization laser being set above the ionization threshold, the experimental conditions (e.g., timing and power of the vaporization and ionization lasers, the backing pressure of the carrier gas, and the concentration of oxygen) were carefully optimized to
maximize the intensity of the $\text{M}_2\text{O}_2^+$ signal in the mass spectra. Under the optimized conditions, $\text{M}_2\text{O}_2$ was excited to high-lying Rydberg states in a single-photon process by the frequency-doubled output of a dye laser (Lumonics HD-500) pumped by a Nd:YAG laser (Quanta Ray GCR-3, 355 or 532 nm) and then ionized by an electric pulse (DEI PVM-4140, 320 V cm$^{-1}$). The laser beam was collinear and counter propagating with the molecule beam. The time delay between the laser and electric pulses was varied to maximize the MATI signal and was typically 20 $\mu$s for He carrier and 50 $\mu$s for Ar. A small DC field (0.7, 1.2, and 1.2 V cm$^{-1}$ for Sc$_2$O$_2$, Y$_2$O$_2$, and La$_2$O$_2$, respectively) was applied to separate the prompt ions produced by direct photoionization from the MATI ions produced by delayed field ionization. The MATI signal was obtained by scanning the wavelength of the tunable dye laser, detected by a dual microchannel plate detector, amplified by a preamplifier (SRS SR445), averaged by a gated integrator (SRS SR250), and stored in a laboratory computer. Laser wavelengths were calibrated against vanadium atomic transitions in the spectral region.$^{153}$ The Stark shift induced by the DC separation field was calculated using the relation of $\Delta E = 6.1E_f^{1/2}$, where $E_f$ is in V cm$^{-1}$ and $\Delta E$ in cm$^{-1}$.$^{151}$

DFT/B3LYP$^{128,129}$ method was used to calculate the equilibrium geometries and vibrational frequencies of $\text{M}_2\text{O}_2$ and $\text{M}_2\text{O}_2^+$. Coupled cluster with single, double and perturbative triple excitations (CCSD(T)) method$^{174,175}$ was employed to calculate the single point energies at the DFT/B3LYP geometries. These calculations were carried out with Gaussian 09 program$^{179}$. In addition, the CCSD(T) method was also used to calculate the equilibrium geometries with MOLPRO 2010.1 program.$^{185}$ In all these calculations, oxygen and scandium atomic orbitals were described by the aug-cc-pVTZ basis
set, and yttrium and lanthanum atomic orbitals were represented by the segmented basis set with Stuttgart-type small core (28 electrons) relativistic effective core potential (Stuttgart RSC segmented/ECP).

To compare with the experimental spectra, Franck-Condon (FC) factors were calculated using the equilibrium geometries, harmonic frequencies, and normal mode coordinates of the neutral cluster and cation. In these calculations, recursion relations from Doktorov et al. were employed, and the Duschinsky effect was taken into consideration. Spectral simulations were obtained using the experimental linewidth and a Lorentzian line shape. Transitions from exited vibrational levels of the neutral molecule were considered by assuming thermal excitation at specific temperatures.

5.3 RESULTS AND DISCUSSION

5.3.1 MATI spectra

Figure 5.2 shows the MATI spectra of M$_2$O$_2$ (M=Sc, Y, La) seeded in He or Ar carrier gas. The spectra of the three clusters exhibit a similar profile, and each shows a predominant original band (0-0) and several weaker ones. The bands from possibly common-type transitions of the three molecules are linked with dotted lines, and additional vertical lines in the spectrum of La$_2$O$_2$ are used to indicate the transitions that are specific for the molecule. For Sc$_2$O$_2$, the origin band is at 44967(5) cm$^{-1}$ with several multiples 17-21 cm$^{-1}$ apart. Relative to the origin band, two doubles are at 415/431 and 713/728 cm$^{-1}$ and an additional pair at -267/-245 cm$^{-1}$. The multiples around the 0-0 band are sequence transitions with the vibrational frequencies of the ion modes being larger than those of the neutral modes. Similarly, the higher energy satellite band in each pair (i.e., -245, 431, and
728 cm\(^{-1}\)) arises from the sequence transition as well. The spectrum of Y\(_2\)O\(_2\) shows the 0-0 band at 42456 (5) cm\(^{-1}\), four weaker bands at 142, 285, 655, and 970 cm\(^{-1}\), and two additional ones at -279 and -142 cm\(^{-1}\). There is also a shoulder at \(~ 30\) cm\(^{-1}\) above the origin band. For La\(_2\)O\(_2\), the strong 0-0 band is at 36936 (5) cm\(^{-1}\) surrounded by three satellite bands at -51, -19, and 16 cm\(^{-1}\). Besides, five bands with weak or medium intensities are located at 107, 245, 421, 591, and 857 cm\(^{-1}\) and three more at -569, -254, and -140 cm\(^{-1}\). The transitions at energies below the 0-0 bands are all likely from excited vibrational levels of the neutral clusters. Table 5.1 lists the energy position of each band, relative to that of the origin band. The observed spectral profiles indicate that the three clusters probably exist in similar geometries and the structure of each cluster is not significantly affected by ionization. The small ionization effect on the molecular structures implies that the ejected electron is likely weakly bound (or anti-bound) in the highest occupied molecular orbital (HOMO). The HOMO should be a metal-based orbital, as the adiabatic AIEs of these metal atoms is much lower than that of the oxygen atom.\(^{189}\) Compared to those of the metal atoms, the AIEs (i.e., energy positions of the origin bands) of the clusters are red shifted by 7955 cm\(^{-1}\) for Sc, 7690 cm\(^{-1}\) for Y, 8044 cm\(^{-1}\) for La.\(^{189}\) Since the AIE shifts are comparable, the metal-oxygen bonding is expected to be similar in the three clusters.

5.3.2 Theoretical structural isomers and electronic states

In searching for preferred structures of the M\(_2\)O\(_2\) clusters, we included all six possible isomers showed in Figure 5.1 in our theoretical calculations and located three minimum energy structures with alternative M-O bonds (Figure 5.1(a, b, and e)). The other
three isomers were not converged in the geometry optimization. Because group 3 metal atoms have an \((n-1)d^{1}ns^2\) ground electron configuration and the electron spin multiplicities of the \(\text{M}_2\text{O}_2\) clusters are determined by the orientation of the metal-based electrons, we considered the singlet and triplet states for the neutral species and doublet and quartet states for the singly charged cations. The singlet state is formed if all metal-based electrons are in pairs, whereas the triplet state is formed if two of which are unpaired and with the same spin orientation. Ionization of the singlet state is expected to yield a doublet state, while ionization of the triplet state produces a doublet or a quartet state. Table 5.2 summarizes the electronic states and energies of each isomer of the \(\text{M}_2\text{O}_2\) clusters. Among the three converged structures, the rhombus \(\text{D}_{2h}\) isomer is predicted to be the most stable one, followed by the \(\text{C}_5\) open chain (1-2 eV) and the non-planar \(\text{C}_{2v}\) cyclic structure (\(\geq 6\) eV). For the \(\text{D}_{2h}\) structure, the triplet states of \(\text{Sc}_2\text{O}_2\) and \(\text{Y}_2\text{O}_2\) have slightly lower energies than the singlet states, while the opposite is predicted for \(\text{La}_2\text{O}_2\). The prediction of the \(^3\text{B}_{1u}\) ground state of \(\text{Sc}_2\text{O}_2\) is consistent with the previous DFT/B3LYP calculation.\(^{226}\) On the other hand, the prediction of the rhombus \(\text{Y}_2\text{O}_2\) is not in agreement with the previous calculation, where a cyclic peroxide structure was calculated to be more stable.\(^{228}\) There has been no previous report on the structures and electronic states of \(\text{La}_2\text{O}_2\). Upon ionization, the resultant doublet is more stable than the quartet state, and the energy differences between the two ion states are much larger (\(\geq 2\) eV) than those between the two neutral states (\(\leq 0.15\) eV).

Because the DFT/B3LYP predicted energy differences between the \(^1\text{A}_g\) and \(^3\text{B}_{1u}\) neutral states are within the computational errors of the theoretical method, further calculations at higher levels of theory have also been performed on these two states. Table 5.3 lists the relative energies of the \(^1\text{A}_g\) and \(^3\text{B}_{1u}\) states from the CCSD(T) single point
calculations at the B3LYP optimized geometries and the CCSD(T) geometry optimizations. In contrast to DFT/B3LYP, the CCSD(T) calculations give the $^1A_g$ ground state for all three clusters, with $^3B_{1u}$ at 0.15-0.20 eV above the singlet state. The inconsistent results among the three methods and the small energy differences between the two states suggest that a reliable identification of the ground states of the $M_2O_2$ clusters is not trivial and requires confirmation by experimental measurements.

5.3.3 Observed structural isomers and electronic states

5.3.3.1 Sc$_2$O$_2$

Although three isomers ($D_{2h}$, $C_{2v}$, and $C_s$ in Table 5.2) are predicted to be stable, the non-planar $C_{2v}$ ring and the $C_s$ chain have much higher energies and are expected to be quenched by the supersonic cooling if they are formed in the molecular beams. Moreover, because ionization of the $C_{2v}$ and $C_s$ isomers yields a $^2A_g$ ion state in the $D_{2h}$ structure, the resultant spectrum would exhibit a very weak origin band and a long FC profile, incompatible with the measured spectrum. Although a $^4A'$ ion state is found for the $C_s$ isomer, formation of this ion state (from ionization of the $^3A'$ neutral state) requires 7.9 eV energy, 2.3 eV higher than the experimental AIE. Therefore, both $C_{2v}$ and $C_s$ isomers are unlikely the carriers of the observed spectrum, and the following discussion will be focused on the ionization of the $D_{2h}$ isomer.

Three ionization processes are possible for the $D_{2h}$ isomer. They are $^2A_g \leftarrow ^1A_g$, $^2A_g \leftarrow ^3B_{1u}$, and $^4B_{3g} \leftarrow ^3B_{1u}$ (Table 5.2), with the predicted transition energies of 5.27, 5.42, and 8.96 eV, respectively. Among the three processes, the $^4B_{3g} \leftarrow ^3B_{1u}$ transition can be excluded from the observed spectrum. This is because its transition energy (8.96 eV) is
much higher than the measured AIE (5.5752 eV) and the geometry of the \( ^4\text{B}_{3g} \) ion state 
\( \text{R(M-M) = 3.168 Å, R(M-O) = 1.946 Å, and } \angle\text{O-M-O = 71°} \) is considerably different from that of the \( ^3\text{B}_{1u} \) neutral state 
\( \text{R(M-M) = 2.782 Å, R(M-O) = 1.886 Å, and } \angle\text{O-M-O = 85°} \) (Table 5.6). The large differences in the M-M bond distance and the O-M-O angle would lead to a weak origin band and a long spectral profile, which are inconsistent with the observation. For the remaining \( ^2\text{A}_g \leftarrow ^1\text{A}_g \) and \( ^2\text{A}_g \leftarrow ^3\text{B}_{1u} \) processes, their transition energies (5.27 and 5.42 eV) are comparable to each other and to the measured AIE (5.5752 eV). The geometries of \( ^1\text{A}_g \) (R(M-M) = 2.728 Å, R(M-O) = 1.873 Å, and \( \angle\text{O-M-O = 86°} \)) and \( ^3\text{B}_{1u} \) (R(M-M) = 2.782 Å, R(M-O) = 1.886 Å, and \( \angle\text{O-M-O = 85°} \)) are also similar to each other and undergo small changes upon ionization (i.e., R(M-M) = 2.743 Å, R(M-O) = 1.863 Å, and \( \angle\text{O-M-O = 85°} \) for the \( ^2\text{A}_g \) ion state). Therefore, the two transitions should yield comparable spectra with a strong origin band and a short FC profile originated from the vibronic ground state, as the experimental spectrum shows. The B3LYP calculations predict the \( ^3\text{B}_{1u} \) neutral state to be 1202 cm\(^{-1}\) more stable than the \( ^1\text{A}_g \) state, whereas the CCSD(T)//B3LYP and CCSD(T) methods yield a more stable \( ^1\text{A}_g \) state than \( ^3\text{B}_{1u} \) by 1270 and 1812 cm\(^{-1}\), respectively. Thus, a definitive assignment of the ground state of \( \text{Sc}_2\text{O}_2 \) is not straightforward from the energy viewpoint.

However, despite the similarities in energies and geometries of the two neutral states, the vibrational frequencies of several modes are considerably different, especially for \( \nu_4 \) and \( \nu_6 \) (Table 5.4). These differences are expected to be evident in the spectrum because vibrational hot bands are observed (Table 5.1 and Figure 5.3). Therefore, the distinction of the \( ^2\text{A}_g \leftarrow ^1\text{A}_g \) and \( ^2\text{A}_g \leftarrow ^3\text{B}_{1u} \) transitions may be possible by considering the transitions from thermally excited vibrational levels. For small molecules seeded in
supersonic molecular beams, they are generally not in the thermal equilibrium. Different vibrational modes are expected to cool with different efficiencies and thus have different temperatures. Lower frequency modes tend to have lower temperatures than the higher frequency modes. This non-thermal equilibrium behavior was previously observed for small molecules. To estimate the vibrational temperature of each mode, we first used the intensity ratio of the hot band at \(-267 \text{ cm}^{-1}\) to the origin band to calculate the temperature of the vibrational mode corresponding to this transition. From Table 5.4, this band likely originates from the sequence transition of \(v_4\) (4) as the frequency difference \((-291 \text{ cm}^{-1})\) of this mode between the \(2A_g\) ion and \(1A_g\) neutral states are mostly close to the observed value \((-267 \text{ cm}^{-1})\). After the \(v_4\) temperature is determined, the temperatures of all other neutral modes of the \(1A_g\) state and those of the \(3B_{1u}\) are calculated, which are listed in Table 5.7. Using these estimated vibrational temperatures, we calculated the spectra of the \(2A_g \leftarrow 1A_g\) and \(2A_g \leftarrow 3B_{1u}\) transitions, which are shown in Figure 5.3(b, c). In these simulations, the theoretical transition energies are shifted to the experimental AIE, but the vibrational frequencies are not scaled. There are two major differences between the two simulations. First, the \(2A_g \leftarrow 1A_g\) transition exhibits the sequence bands at the higher energy side of the 0-0 transition as the experimental spectrum, while \(2A_g \leftarrow 3B_{1u}\) shows these bands at both sides of the origin band. Second, the 4\(_1^1\) band of \(2A_g \leftarrow 1A_g\) is predicted at \(-291 \text{ cm}^{-1}\) from the 0-0 transition, which is fairly close to the \(-267 \text{ cm}^{-1}\) band in the measured spectrum; on the other hand, the 4\(_1^1\) band of \(2A_g \leftarrow 3B_{1u}\) is \(-395 \text{ cm}^{-1}\) away from the 0-0 transition, more than 100 \text{ cm}^{-1}\) larger than the experimental measurement. These comparisons suggest that the \(2A_g \leftarrow 1A_g\) transition is responsible for the observed spectrum and \(2A_g \leftarrow 3B_{1u}\) can be excluded. The good agreement of the \(2A_g \leftarrow 1A_g\) simulation and the
measured spectrum helps to assign the observed bands. The 21, 38, 58, and 75 cm\(^{-1}\) sequence bands above the origin band are assigned to \(2^1_1\), \(6^1_1\), \(2^1_{61}\), and \(6^1_2\); the 415 and 713 cm\(^{-1}\) bands to \(2^1_0\) and \(1^1_y\), the 431 and 728 cm\(^{-1}\) bands to \(2^2_2\) and \(1^2_{01}^2_1\); and the -267 and -245 cm\(^{-1}\) bands to \(4^1_1\) and \(2^1_4^1_1\), respectively. \(v_1\) (a\(_g\)) and \(v_2\) (a\(_g\)) are the symmetric O-Sc and Sc-Sc stretching modes, and \(v_4\) (b\(_{1u}\)) and \(v_6\) (b\(_{3u}\)) are the asymmetric O-Sc stretch and O atom out-of-plane rock, respectively. Table 5.1 summarizes these spectral assignments.

In a previous Ar-matrix-isolation IR study, Andrews and coworkers reported three weak bands at 866.0, 699.1, and 647.8 cm\(^{-1}\) and assigned the 866.0 cm\(^{-1}\) band to an open ScOScO dimer and the other two bands to a ring (ScO)\(_2\) dimer. The 699.1 cm\(^{-1}\) IR transition is slightly lower in vibrational frequency than the 713 cm\(^{-1}\) band measured in our MATI spectrum. The small frequency shift could be due to the Ar-matrix effect that reduces the O-Sc bond strength or the charge effect from the neutral molecule to the cation. However, because the symmetric O-Sc stretch is an a\(_g\) species in D\(_{2h}\) point group, this mode is not expected to be IR active. Thus, the ring (ScO)\(_2\) dimer formed in the Ar matrix should have a lower molecular symmetry than D\(_{2h}\).

5.3.3.2 \(\text{Y}_2\text{O}_2\) and \(\text{La}_2\text{O}_2\)

Because Y and La are in the same group as Sc in the periodical table, \(\text{Y}_2\text{O}_2\) and \(\text{La}_2\text{O}_2\) are assumed to adopt the D\(_{2h}\) structure as Sc\(_2\)O\(_2\). This assumption is confirmed by the predicted energies, where the C\(_{2v}\) and C\(_g\) isomers are much less stable than D\(_{2h}\) (Table 5.2). Among the three possible transitions of the D\(_{2h}\) structure (i.e., \(2^1\text{Ag} \leftrightarrow 1^1\text{Ag}\), \(2^1\text{Ag} \leftrightarrow 3^1\text{B}_{1u}\), \(4^1\text{B}_{3g} \leftrightarrow 3^1\text{B}_{1u}\)), the \(4^1\text{B}_{3g} \leftrightarrow 3^1\text{B}_{1u}\) process would yield a very different spectrum from
the observed one because the energy of this transition is much higher than the measured AIE (Table 5.2) and the geometries of the two states are very different (Supporting Material, S1). Therefore, the \( ^4B_{3g} \rightarrow ^3B_{1u} \) transition can be ruled out, and \( ^2A_g \rightarrow ^1A_g \) and \( ^2A_g \rightarrow ^3B_{1u} \) will be discussed below.

In contrast to Sc\(^2\)O\(^2\), the \( ^2A_g \rightarrow ^3B_{1u} \) transition, rather than \( ^2A_g \rightarrow ^1A_g \), is responsible for the observed spectra of the two heavier species, as shown in Figures 5.4 and 5.5. For Y\(^2\)O\(^2\), the \( ^2A_g \rightarrow ^3B_{1u} \) simulation reproduces all of the observed bands, while the \( ^2A_g \rightarrow ^1A_g \) simulation fails to produce the transitions at \(-279(2^0_1), -142(4^1_1), 142 (2^1_0,2^1_1), \) and 970 \((1^1_0,2^1_0,2^3_1) \) cm\(^{-1}\). For La\(^2\)O\(^2\), the \( ^2A_g \rightarrow ^3B_{1u} \) simulation also has better agreement with the experimental spectrum than \( ^2A_g \rightarrow ^1B_g \) because several bands \((1^0_0,2^0_1,4^1_1,1^1_0,3^1_1,6^3_1) \) are missing in the latter simulation. The assignment for each of the observed bands is listed in Table 5.1. The O-M stretching frequencies \((v_1^+)\) in the \( ^2A_g \) ion states are measured to be 655 cm\(^{-1}\) for Y\(^2\)O\(^2\) and 591 cm\(^{-1}\) for La\(^2\)O\(^2\). For La\(^2\)O\(^2\), the O-La stretching frequency \( v_1 \) in the \( ^3B_{1u} \) neutral state is also observed, which is 569 cm\(^{-1}\). The different O-La stretching frequencies in the ion and neutral states are the result of the different degree of the charge effect in the two states. For Y\(^2\)O\(^2\), the O-Y stretching frequency in the neutral state is not observed, but it is predicted to be 614 cm\(^{-1}\), which is also slightly lower than the predicted value of 643 cm\(^{-1}\) for the ion state. The M-M stretching frequencies in the ion/neutral states \((v_2^+/v_2)\) are measured as 285/279 and 245/254 cm\(^{-1}\) for Y\(^2\)O\(^2\) and La\(^2\)O\(^2\), respectively. It is noted that the M-Mstretching frequencies in the ion and neutral states of either species are very similar, suggesting that the highest occupied molecular orbital (HOMO) in the neutral cluster should have a weak bonding or antibonding character. The reduced O-M and M-M
frequencies from Y$_2$O$_2$ to La$_2$O$_2$ are associated with the mass increase from Y to La. In addition to the O-M and M-M stretching modes, the frequency differences between the ion and neutral states are measured for two O-M asymmetric stretching modes of the two species and for an O atom out-of-plane rocking mode of La$_2$O$_2$.

The experimental and theoretical AIEs and vibrational frequencies of the three clusters are summarized in Table 5.5. The theoretical AIEs of Sc$_2$O$_2$ and Y$_2$O$_2$ are from the CCSD(T) calculations and that of La$_2$O$_2$ is from the CCSD(T)//B3LYP calculations. All theoretical frequencies are obtained by the B3LYP calculations. The table shows excellent agreements between the measured and calculated values.

5.3.3.3 Singlet versus triplet states of M$_2$O$_2$ (M = Sc, Y, and La)

The M$_2$O$_2$ clusters in the rhombus D$_{2h}$ structure can be expressed as [M$^{2+}$]$_2$[O$^2$]$_2$ in the neutral state. In this structure, two electrons are transferred out from each M atom, one to each O to form four O-M bonds. Because the group 3 metal atoms have three electrons in the valence shell ($(n-1)d^1ns^2$), the formation of the D$_{2h}$ structure leaves only one $ns$ electron on each of the M atoms. Therefore, each M atom in M$_2$O$_2$ has an alkali-like electron configuration, and the interaction of the two M atoms may be described by a simple two-level, two-electron diagram, as shown in Figure 5.6. The separation of the two energy levels ($\Delta$) depends on the strength of the interaction, and the electron spin multiplicity of a M$_2$O$_2$ cluster is determined by the energy separation and the Coulomb repulsion of the two $ns$ electrons. If the energy separation of the two levels is larger than the repulsion energy, the two $ns$ electrons will prefer stay in the same molecular orbital ($a_g$) and a singlet state ($^{1}A_g$) will be formed. On the other hand, if the energy separation is smaller than the
Coulomb energy, the two electrons will prefer to be in the two orbitals \( (a_g \text{ and } b_{1u}) \) and a triplet state \( (\text{^3B}_{1u}) \) will be formed. In either cases, one of the \( ns \) electrons is removed upon ionization, and the resultant ions have the same \( ^2A_g \) state with the \( ns \) electron in the lower \( a_g \) orbital. For all three ions, the \textit{ab initio} calculations show that the highest occupied molecular orbital (HOMO) is \( a_g \) and the lowest unoccupied molecular orbital (LUMO) is \( b_{1u} \). Because the \( ns \) electrons on the two \( M \) atoms are weakly interacted, the removal of an \( ns \) electron from either \( a_g \) or \( b_{1u} \) orbital has a small effect on the \( M-M \) bond length, which is consistent with the strong 0-0 band in the spectra of the three clusters. However, the direction of the \( M-M \) bond-length change is different between \( \text{Sc}_2\text{O}_2 \) and \( \text{Y}_2\text{O}_2/\text{La}_2\text{O}_2 \). For \( \text{Sc}_2\text{O}_2 \), the \( \text{Sc-Sc} \) bond length is 2.728 Å in the \( ^1A_g \) neutral state and increased to 2.743 Å in the \( ^2A_g \) ion state due to the removal of the weakly-bound \( 4s \) electron in the \( a_g \) orbital. For \( \text{Y}_2\text{O}_2/\text{La}_2\text{O}_2 \), the \( M-M \) bond lengths are 3.088/3.324 Å in the \( ^3B_{1u} \) neutral state and decreased to 3.048/3.289 Å in the \( ^2A_g \) ion state due to the ionization of the weak antibonding \( b_{1u} \) orbital. Because the \( M-M \) bond lengths are longer in \( \text{Y}_2\text{O}_2/\text{La}_2\text{O}_2 \) than that in \( \text{Sc}_2\text{O}_2 \), the interactions between the two \( 5s/6s \) electrons are expected to be weaker than that between the two \( 4s \) electrons. The weaker interaction leads to a smaller energy separation between the \( a_g \) and \( b_{1u} \) orbital and makes the higher spin state \( (\text{^3B}_{1u}) \) preferable for the two heavier species.

5.4 CONCLUSIONS

\textit{MATI} spectra are reported for the first time for the three \( M_2\text{O}_2 \) (\( M = \text{Sc}, \text{Y}, \text{and La} \)) clusters seeded in supersonic molecular beams. The spectra display a strong origin band and several weak bands associated with the excitation of the vibrational modes in the
neutral and ion states. The AIEs of the clusters are measured from the origin bands and the symmetric O-M and M-M stretching frequencies from the weak transitions. The M$_2$O$_2$ clusters are determined to be in the most stable D$_{2h}$ rhombus structure by comparing the spectroscopic measurements with the theoretical predictions. The rhombus structure is formed by fusing two MO$_2$ fragments together through sharing two oxygen atoms. In addition to the rhombus structure, five other structures are considered, but they are at higher energies or not converged and not observed by the experiment. The ionization processes are determined to be $^2$A$_g \leftarrow 1$A$_g$ for Sc$_2$O$_2$ and $^2$A$_g \leftarrow 3$B$_{1u}$ for Y$_2$O$_2$ and La$_2$O$_2$. In both $^1$A$_g$ and $^3$B$_{1u}$ neutral states, each metal atom loses two electrons in forming the cluster, and the resultant cluster can be described as [M$^{2+}$]$_2$[O$^2$]$_2$. The $^1$A$_g$ and $^3$B$_{1u}$ states are very close in energy, and the small energy difference is determined by the two-level, two electron interaction and Coulomb repulsion of the ns electrons on the metal atoms. Ionization of either $^1$A$_g$ or $^3$B$_{1u}$ states gives the $^2$A$_g$ ion state with a similar geometry.
Table 5.1 Band positions (cm$^{-1}$) and assignments for the MATI spectra of M$_2$O$_2$ (M = Sc, Y, La). The band positions are relative to those of the origin bands, and the absolute energies of the origin bands are listed inside square brackets. The relative intensities of the MATI bands are indicated by "s" (strong), "m" (medium) and "w" (weak).

<table>
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<th>Y$_2$O$_2$</th>
<th>La$_2$O$_2$</th>
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<td></td>
<td>-51, w</td>
<td>$6^1_1$</td>
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</tr>
<tr>
<td>58, m</td>
<td></td>
<td></td>
<td>$2^1_1; 6^1_2$</td>
<td></td>
</tr>
<tr>
<td>75, w</td>
<td>30, m</td>
<td>16, m</td>
<td>$3^1_1$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>142, w</td>
<td>107, w</td>
<td>$2^1_1; 4^1_2$</td>
<td></td>
</tr>
<tr>
<td>415, m</td>
<td>285, m</td>
<td>245, w</td>
<td>$2^0_2$</td>
<td></td>
</tr>
<tr>
<td>431, m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>421, m</td>
<td>$1^0_1; 3^1_1; 4^1_2; 6^1_2$</td>
<td></td>
</tr>
<tr>
<td>713, m</td>
<td>655, m</td>
<td>591, m</td>
<td>$1^0_0$</td>
<td></td>
</tr>
<tr>
<td>728, m</td>
<td></td>
<td></td>
<td>$1^0_1; 2^1_1$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>970, m</td>
<td>857, m</td>
<td>$1^0_1; 2^1_0; 3^1_1$</td>
<td></td>
</tr>
</tbody>
</table>

95
Table 5.2 Point groups, electronic states, relative energies (E_{rel}), and transition energies (\Delta E) of M_2O_2 (M=Sc, Y, La) from the B3LYP calculations, with the aug-cc-pVTZ basis for the Sc and O atoms and the Stuttgart RSC segmented/ECP basis for the Y and La atoms.

<table>
<thead>
<tr>
<th>Point Group^a</th>
<th>Neutral State</th>
<th>E_{rel} (eV)</th>
<th>Ion State</th>
<th>E_{rel} (eV)</th>
<th>\Delta E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_{2h} Sc_2O_2</td>
<td>^1A_g</td>
<td>0.15</td>
<td>^2A_g</td>
<td>5.42</td>
<td>5.27 (^2A_g \leftrightarrow ^1A_g)</td>
</tr>
<tr>
<td>^3B_{1u}</td>
<td>0</td>
<td>^4B_{3g}</td>
<td>8.96</td>
<td></td>
<td>5.42/8.96 (^2A_g / ^4B_{3g} \leftrightarrow ^3B_{1u})</td>
</tr>
<tr>
<td>C_{2v}</td>
<td>^1A_1</td>
<td>6.71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>^3B_2</td>
<td>6.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_s</td>
<td>^1A'</td>
<td>1.69</td>
<td>^4A'</td>
<td>9.96</td>
<td></td>
</tr>
<tr>
<td>^3A'</td>
<td>2.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y_2O_2</td>
<td>^1A_g</td>
<td>0.04</td>
<td>^2A_g</td>
<td>5.14</td>
<td>5.10 (^2A_g \leftrightarrow ^1A_g)</td>
</tr>
<tr>
<td>^3B_{1u}</td>
<td>0</td>
<td>^4B_{3g}</td>
<td>8.60</td>
<td></td>
<td>5.14/8.60 (^2A_g / ^4B_{3g} \leftrightarrow ^3B_{1u})</td>
</tr>
<tr>
<td>C_{2v}</td>
<td>^1A_1</td>
<td>5.85</td>
<td>^2B_2</td>
<td>11.23</td>
<td></td>
</tr>
<tr>
<td>^3B_2</td>
<td>6.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_s</td>
<td>^1A'</td>
<td>1.84</td>
<td>^4A'</td>
<td>9.69</td>
<td></td>
</tr>
<tr>
<td>^3A'</td>
<td>2.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La_2O_2</td>
<td>^1A_g</td>
<td>0</td>
<td>^2A_g</td>
<td>4.43</td>
<td>4.43 (^2A_g \leftrightarrow ^1A_g)</td>
</tr>
<tr>
<td>^3B_{1u}</td>
<td>0.06</td>
<td>^4B_{3g}</td>
<td>9.47</td>
<td></td>
<td>4.37 (^2A_g \leftrightarrow ^3B_{1u})</td>
</tr>
<tr>
<td>C_{2v}</td>
<td>^1A_1</td>
<td>6.89</td>
<td>^2A_1(TS)^b</td>
<td>11.25</td>
<td></td>
</tr>
<tr>
<td>^3A_2</td>
<td>6.87</td>
<td>^4B_1</td>
<td>11.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_s</td>
<td>^1A'</td>
<td>1.25</td>
<td>^2A'</td>
<td>6.03</td>
<td>4.78 (^2A' \leftrightarrow ^1A')</td>
</tr>
<tr>
<td>^3A'</td>
<td>1.89</td>
<td></td>
<td></td>
<td></td>
<td>4.14 (^2A' \leftrightarrow ^3A')</td>
</tr>
</tbody>
</table>

^a D_{2h}, C_{2v}, and C_s correspond to the three isomers shown in Figure 5.1 (a, b, and e), and other isomers in Figure 5.1 are not converged. For Sc_2O_2, the doublet states of the C_{2v} and C_s structures are converged to the ^2A_g state of D_{2h}, and the quartet state of C_{2v} is not converged. For Y_2O_2, the doublet and triplet states of C_s are converged to the ^2A_g and ^3B_{1u} states of D_{2h}, respectively, and the quartet state of C_{2v} is not converged. For La_2O_2, the quartet state of D_{2h} and the doublet of C_{2v} are transition states and the quartet state of C_s is not converged. ^b TS is the transition state.
Table 5.3 Relative electronic energies \((E_{\text{rel}}, \text{cm}^{-1})\) of the \(^1\text{A}_g\) and \(^3\text{B}_{1u}\) neutral states of \(\text{M}_2\text{O}_2\) (\(\text{M} = \text{Sc}, \text{Y}, \text{La}\)) from the B3LYP, CCSD(T)//B3LYP, and CCSD(T) calculations, with the aug-cc-pVTZ basis for the Sc and O atoms and the Stuttgart RSC segmented/ECP basis for the Y and La atoms. For the CCSD(T)//B3LYP calculations, single point energies are calculated at the B3LYP optimized geometries.

<table>
<thead>
<tr>
<th>Methods</th>
<th>(^1\text{A}_g) ((\text{cm}^{-1}))</th>
<th>(^3\text{B}_{1u}) ((\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Sc}_2\text{O}_2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3LYP</td>
<td>1202</td>
<td>0</td>
</tr>
<tr>
<td>CCSD(T)//B3LYP</td>
<td>0</td>
<td>1270</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>0</td>
<td>1812</td>
</tr>
<tr>
<td>(\text{Y}_2\text{O}_2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3LYP</td>
<td>0</td>
<td>522</td>
</tr>
<tr>
<td>CCSD(T)//B3LYP</td>
<td>0</td>
<td>1712</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>0</td>
<td>1562</td>
</tr>
<tr>
<td>(\text{La}_2\text{O}_2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3LYP</td>
<td>293</td>
<td>0</td>
</tr>
<tr>
<td>CCSD(T)//B3LYP</td>
<td>0</td>
<td>1727</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>0</td>
<td>1618</td>
</tr>
</tbody>
</table>
Table 5.4 Vibrational modes and frequencies of the $^1A_g$ and $^3B_{1u}$ neutral states and $^2A_g$ ion state of $\text{M}_2\text{O}_2$ ($\text{M} = \text{Sc}, \text{Y}, \text{La}$) from the B3LYP calculations, with the aug-cc-pVTZ basis for the Sc and O atoms and the Stuttgart RSC segmented/ECP basis for the Y and La atoms.$^a$

<table>
<thead>
<tr>
<th>Electronic States</th>
<th>$v_1$ (a$_g$)</th>
<th>$v_2$ (a$_g$)</th>
<th>$v_3$ (b$_{3g}$)</th>
<th>$v_4$ (b$_{1u}$)</th>
<th>$v_5$ (b$_{2u}$)</th>
<th>$v_6$ (b$_{3u}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sc}_2\text{O}_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^1A_g$</td>
<td>713</td>
<td>397</td>
<td>469</td>
<td>613</td>
<td>659</td>
<td>110</td>
</tr>
<tr>
<td>$^2A_g$</td>
<td>733</td>
<td>421</td>
<td>472</td>
<td>322</td>
<td>676</td>
<td>163</td>
</tr>
<tr>
<td>$^3B_{1u}$</td>
<td>697</td>
<td>407</td>
<td>449</td>
<td>717</td>
<td>638</td>
<td>217</td>
</tr>
<tr>
<td>$\text{Y}_2\text{O}_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^1A_g$</td>
<td>629</td>
<td>275</td>
<td>446</td>
<td>558</td>
<td>568</td>
<td>118</td>
</tr>
<tr>
<td>$^2A_g$</td>
<td>643</td>
<td>290</td>
<td>455</td>
<td>501</td>
<td>574</td>
<td>152</td>
</tr>
<tr>
<td>$^3B_{1u}$</td>
<td>614</td>
<td>282</td>
<td>433</td>
<td>647</td>
<td>542</td>
<td>194</td>
</tr>
<tr>
<td>$\text{La}_2\text{O}_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^1A_g$</td>
<td>573</td>
<td>233</td>
<td>355</td>
<td>534</td>
<td>491</td>
<td>93</td>
</tr>
<tr>
<td>$^2A_g$</td>
<td>597</td>
<td>242</td>
<td>344</td>
<td>461</td>
<td>510</td>
<td>115</td>
</tr>
<tr>
<td>$^3B_{1u}$</td>
<td>573</td>
<td>235</td>
<td>330</td>
<td>619</td>
<td>485</td>
<td>171</td>
</tr>
</tbody>
</table>

$^a$The approximate descriptions of the vibrational modes are symmetric O-M stretch with O atoms moving in the opposite directions ($v_1$), symmetric M-M stretch ($v_2$), O-M asymmetric stretch with two O atoms moving in opposite directions ($v_3$), O-M asymmetric stretch with two O atoms moving in the same direction ($v_4$), O-M symmetric stretch with two O atoms moving in the same direction ($v_5$), and O atoms out-of-plane rock ($v_6$).
Table 5.5 Measured adiabatic ionization energies (AIE, eV) of M$_2$O$_2$ (M = Sc, Y, and La) and vibrational frequencies of the ion ($\nu^+_i$, cm$^{-1}$) and neutral states ($\nu_i$, cm$^{-1}$), along with those in parentheses from the theoretical calculations.$^a$ The AIEs correspond to the ionization processes of Sc$_2$O$_2^+$ ($^2\text{A}_g$, D$_{2h}$) $\leftrightarrow$ Sc$_2$O$_2$ ($^1\text{A}_g$, D$_{2h}$) and M$_2$O$_2^+$ ($^2\text{A}_g$, D$_{2h}$) $\leftrightarrow$ M$_2$O$_2$ ($^3\text{B}_{1u}$, D$_{2h}$) for M=Y and La.$^b$

<table>
<thead>
<tr>
<th></th>
<th>Sc$_2$O$_2$</th>
<th>Y$_2$O$_2$</th>
<th>La$_2$O$_2$</th>
<th>Approx. description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIE</td>
<td>5.5752±0.0006 (5.62)</td>
<td>5.2639±0.0006 (5.27)</td>
<td>4.5795±0.0006 (4.54)</td>
<td></td>
</tr>
<tr>
<td>$\nu^+_1$</td>
<td>713 (733)</td>
<td>655 (643)</td>
<td>591 (597)</td>
<td>O-M symmetric stretch</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td></td>
<td></td>
<td>569 (573)</td>
<td></td>
</tr>
<tr>
<td>$\nu^+_2$</td>
<td>415 (421)</td>
<td>285 (290)</td>
<td>245 (242)</td>
<td>M-M symmetric stretch</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>395 (397)</td>
<td>279 (282)</td>
<td>254 (235)</td>
<td></td>
</tr>
<tr>
<td>$\nu^+_3$ $\sim$ $\nu_3$</td>
<td>30 (22)</td>
<td></td>
<td>16 (14)</td>
<td>O-M asymmetric stretch atoms moving in the</td>
</tr>
<tr>
<td>$\nu^+_4$ $\sim$ $\nu_4$</td>
<td>-267 (-291)</td>
<td>-142 (-146)</td>
<td>-140 (-158)</td>
<td>O-M asymmetric stretch atoms moving in the</td>
</tr>
<tr>
<td>$\nu^+_6$ $\sim$ $\nu_6$</td>
<td></td>
<td></td>
<td>-51 (-56)</td>
<td>O atoms out-of-plane rock</td>
</tr>
</tbody>
</table>

$^a$ The theoretical AIEs of Sc$_2$O$_2$ and Y$_2$O$_2$ are from the CCSD (T) calculations and that of La$_2$O$_2$ from the CCSD(T)//B3LYP calculations. The CCSD(T) geometry optimization was not converged for the La$_2$O$_2$ ion. The theoretical vibrational frequencies are from the B3LYP calculations. Basis sets in all calculations are aug-cc-pVTZ for the Sc and O atoms and Stuttgart RSC segmented/ECP for the Y and La atoms.
Table 5.6 Calculated metal-metal (M-M) and metal-oxygen (M-O) bond lengths and oxygen-metal-oxygen (O-M-O) bond angles of the D\textsubscript{2h} M\textsubscript{2}O\textsubscript{2} (M = Sc, Y, La) clusters from the DFT/B3LYP calculations. The aug-cc-pVTZ basis sets are used for the Sc and O atoms and Stuttgart RSC segmented/ECP for the Y and La atoms.

<table>
<thead>
<tr>
<th></th>
<th>M-M (Å)</th>
<th>M-O (Å)</th>
<th>O-M-O (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc\textsubscript{2}O\textsubscript{2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^1\text{A}g)</td>
<td>2.728</td>
<td>1.873</td>
<td>86</td>
</tr>
<tr>
<td>(^2\text{A}g)</td>
<td>2.743</td>
<td>1.863</td>
<td>85</td>
</tr>
<tr>
<td>(^3\text{B}_{1u})</td>
<td>2.782</td>
<td>1.886</td>
<td>85</td>
</tr>
<tr>
<td>(^4\text{B}_{3g})</td>
<td>3.168</td>
<td>1.946</td>
<td>71</td>
</tr>
<tr>
<td>Y\textsubscript{2}O\textsubscript{2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^1\text{A}g)</td>
<td>3.042</td>
<td>2.032</td>
<td>83</td>
</tr>
<tr>
<td>(^2\text{A}g)</td>
<td>3.048</td>
<td>2.019</td>
<td>82</td>
</tr>
<tr>
<td>(^3\text{B}_{1u})</td>
<td>3.088</td>
<td>2.043</td>
<td>82</td>
</tr>
<tr>
<td>(^4\text{B}_{3g})</td>
<td>3.497</td>
<td>2.093</td>
<td>67</td>
</tr>
<tr>
<td>La\textsubscript{2}O\textsubscript{2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^1\text{A}g)</td>
<td>3.271</td>
<td>2.111</td>
<td>78</td>
</tr>
<tr>
<td>(^2\text{A}g)</td>
<td>3.289</td>
<td>2.103</td>
<td>77</td>
</tr>
<tr>
<td>(^3\text{B}_{1u})</td>
<td>3.324</td>
<td>2.124</td>
<td>77</td>
</tr>
<tr>
<td>(^4\text{B}_{3g})</td>
<td>3.846</td>
<td>2.257</td>
<td>63</td>
</tr>
</tbody>
</table>
Table 5.7 Vibrational temperatures (K) used in spectral simulations. The temperatures are determined by using the $^4_1$ sequence transition intensities. See text for the estimation of the vibrational temperatures.

<table>
<thead>
<tr>
<th></th>
<th>$^2A_g \leftrightarrow ^1A_g$</th>
<th>$^2A_g \leftrightarrow ^3B_{1u}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v_1$</td>
<td>$v_2$</td>
</tr>
<tr>
<td>Sc$_2$O$_2$</td>
<td>872</td>
<td>486</td>
</tr>
<tr>
<td>Y$_2$O$_2$</td>
<td>335</td>
<td>149</td>
</tr>
<tr>
<td>La$_2$O$_2$</td>
<td>370</td>
<td>151</td>
</tr>
</tbody>
</table>
Figure 5.1 Possible structural isomers of $M_2O_2$ ($M = \text{Sc, Y, La}$) (O: red, M: cyan).
Figure 5.2 MATI spectra of Sc$_2$O$_2$ (a) and Y$_2$O$_2$ (b) seeded in He carrier gas and La$_2$O$_2$ seeded in Ar carrier gas (c).
Figure 5.3 MATI Spectrum of Sc$_2$O$_2$ seeded in He carrier gas (a) and simulations of the $^{2}A_{g} \leftarrow ^{1}A_{g}$ (b) and $^{2}A_{g} \leftarrow ^{3}B_{1u}$ (c) transitions from B3LYP calculations.
Figure 5.4 MATI Spectrum of Y$_2$O$_2$ seeded in He carrier gas (a) and simulations of the $^2$A$_g$ $\leftarrow$ $^3$B$_{1u}$ (b) and $^2$A$_g$ $\leftarrow$ $^1$A$_g$ (c) transitions from B3LYP calculations.
Figure 5.5 MATI Spectrum of L\textsubscript{2}O\textsubscript{2} seeded in Ar carrier gas (a) and simulations of the \( \text{^2A_g} \leftarrow \text{^3B_{1u}} \) (b) and \( \text{^2A_g} \leftarrow \text{^1A_g} \) (c) transitions from B3LYP calculations.
Figure 5.6 Interaction diagram of two $ns$ orbitals of the $M_2$ fragment (a) and HOMO and LUMO of $M_2O_2$ ($M = Sc, Y, La$) (b).
CHAPTER 6 MASS-ANALYZED THRESHOLD IONIZATION AND ELECTRONIC STATES OF M₃O₄ (M = SC, Y, AND LA)

6.1 INTRODUCTION

Transition metal oxide clusters serve as building blocks of nanostructural materials and exhibit size-dependent physical and chemical properties. Their important applications and interesting properties have motivated numerous research groups to study these clusters in the gas phase, where complicating factors such as solvents and counterions are removed. For transition metal oxide cluster cations, extensive studies have been reported on their reactivity,\textsuperscript{40-43} UV-Vis photodissociation,\textsuperscript{44-46} and infrared (IR) multiphoton photodissociation or single-photon vibrational predissociation.\textsuperscript{47-55,224} The studies of cluster anions were largely carried out with photoelectron spectroscopy,\textsuperscript{56-71} and additional investigations were reported about their reactivity\textsuperscript{40,42,72-75} and IR photodissociation.\textsuperscript{51,76-78} Neutral cluster oxides are more challenging to study experimentally because they are difficult to size-select, and their formation and properties are usually determined by ionization techniques, including multiphoton IR\textsuperscript{79} and single-photon UV\textsuperscript{80-82} and vacuum UV laser ionization.\textsuperscript{83-86} In addition, neutral metal oxides have also been studied by matrix-isolation IR spectroscopy.\textsuperscript{87} In spite of the extensive studies, the current knowledge about the electronic states and molecular structures of transition metal oxide clusters is largely derived from theoretical predictions. However, the reliable prediction of the electronic states and geometric structures is often complicated by the presence of many low energy structural isomers and high density low-lying electronic states of each isomer. Thus, inconsistent theoretical results have often been reported on
the nature of the ground electronic states and minimum energy structures of both neutral\textsuperscript{88,89} and ionic clusters.\textsuperscript{51,90,91} Therefore, a reliable identification of the molecular structures and electronic states for transition metal oxide clusters and their ions generally requires the confirmation by spectroscopic measurements, especially by high resolution spectroscopic techniques.

For group 3 multinuclear metal oxide clusters, there have been several reports on photoionization, photoelectron, and mass spectrometric measurements. Zhao et. al reported anion photoelectron spectra of Sc\textsubscript{3}O\textsubscript{6}\textsuperscript{-} and proposed the ground state of the cluster was an oxygen-centered biradical.\textsuperscript{236} Nakajima, Kaya, and coworkers measured photoelectron spectra of yttrium oxide clusters Y\textsubscript{n}O\textsubscript{m}\textsuperscript{-} (n = 2-10, m = 1-3) and observed an increase of the EAs for the monoxide clusters with increasing cluster size.\textsuperscript{67} On the other hand, Yang and Knickelbein observed from photoionization efficiency spectra the reduction of the IEs of the Sc\textsubscript{n}O (n = 5-36) and Y\textsubscript{n}O (n = 2-31) monoxide clusters with increasing cluster size.\textsuperscript{81,82} Aubriet and Muller studied the formation of scandium and yttrium cluster oxide ions using laser ablation mass spectrometry.\textsuperscript{237} Reed and Duncan studied the stoichiometry and photodissociation of yttrium and lanthanum oxide cluster cations produced by laser vaporization of metal targets in a He/O\textsubscript{2} expansion.\textsuperscript{46} The mass spectra exhibited a strong preference for the odd-numbered metal clusters, with the intense peaks in the MO(M\textsubscript{2}O\textsubscript{3})\textsubscript{n}\textsuperscript{+} (M = Y and La) stoichiometry. The preference of the MO(M\textsubscript{2}O\textsubscript{3})\textsubscript{n}\textsuperscript{+} stoichiometry was also reported by Schweikert and coworkers in the study of the metastable decay of lanthanum oxides produced from the high energy atom bombardment,\textsuperscript{238} by Gibson in laser ablation synthesis of lanthanide oxide cluster ions incorporating a heterovalent metal,\textsuperscript{239,240} and by Kahwa and Selbin in the study of stability
trends and fragmentation patterns of yttrium oxide clusters by fast atom bombardment tandem mass spectrometry. The smallest cluster with the MO(M$_2$O$_3$)$_n$+ stoichiometry, M$_3$O$_4$, was predicted to prefer a C$_{3v}$ cage-like structure (Figure 6.1a), but no experimental confirmation was reported. Similar cage structures were identified for Al$_3$O$_4^+$ and Ce$_3$O$_4^+$ by free electron IR laser spectroscopy. On the other hand, a C$_s$ ring structure (Figure 6.1c) was reported for Ta$_3$O$_4^-$ and a D$_{2d}$ double ring structure (Figure 6.1e) for Si$_3$O$_4^{-1/0}$ from anion photoelectron spectroscopic studies. These studies suggest that the preferred structure of a M$_3$O$_4$ cluster depend on the identity of the metal elements.

In this chapter, we report MATI spectroscopy of group 3 metal trimer tetroxides produced by laser ablation. From the MATI spectra, we measured AIEs of the neutral clusters and vibrational frequencies of the singly charged cations. By combining the spectroscopic measurements with DFT calculations, we determined the preferred structures and ground electronic states of these clusters.

6.2 EXPERIMENTAL AND COMPUTATIONAL METHODS

The metal-cluster beam MATI spectrometer has been described in a previous publication. Metal cluster oxides were produced by laser vaporization (Lumonics YM-800 Nd:YAG, 532 nm,) of a metal rod in the presence of a pulse of ultra-high-purity He or Ar carrier gas, delivered by a homemade piezoelectric pulsed valve, and a small amount of oxygen, supplied with a metering valve. The metal vapor and gas mixture passed down a clustering tube (2 mm inner diameter, 2 cm length), and the resultant clusters were supersonically expanded into the vacuum chamber. The supersonic jet was skimmed (2mm
diameter) 3 cm downstream from the exit end of the clustering tube. A pair of deflection plates (2.5 cm spacing, 220V) located after the skimmer was used to remove residual charged species (formed during laser ablation) from the molecular beam before it entered the spectroscopic chamber. Prior to the MATI measurements, photoionization time-of-flight mass spectra were recorded to determine the chemical content of the cluster beam, and pulsed-field-ionization photoionization efficiency spectra were recorded to locate the ionization threshold of the M₃O₄ clusters. With the ionization laser set above the ionization threshold, the experimental conditions (e.g., timing and power of the vaporization and ionization lasers, the backing pressure of the carrier gas, and the concentration of oxygen) were carefully optimized to maximize the intensity of the M₃O₄⁺ signal in the mass spectra. With the optimized experimental conditions, M₃O₄ was excited to high-lying Rydberg states in a single-photon process by the frequency-doubled output of a dye laser (Lumonics HD-500) pumped by a Nd:YAG laser (Quanta Ray GCR-3, 355 nm) and then ionized by an electric pulse (DEI PVM-4140, 320 V cm⁻¹). The laser beam was collinear and counter propagating with the molecule beam. The time delay between the laser and electric pulses was varied to maximize the MATI signal and was typically 20 µs for He carrier and 50 µs for Ar. A small DC field (1.2, 1.7, and 1.0 V cm⁻¹ for Sc₃O₄, Y₃O₄, and La₃O₄, respectively) was applied to help separate the prompt ions produced by direct photoionization from the MATI ions produced by delayed field ionization. The MATI signal was obtained by scanning the wavelength of the tunable dye laser, detected by a dual microchannel plate detector, amplified by a preamplifier (SRS SR445), averaged by a gated integrator (SRS SR250), and stored in a laboratory computer. Laser wavelengths were calibrated against vanadium atomic transitions in the spectral region. The Stark shift induced by the DC
field was calculated using the relation of \( \Delta IE = 6.1 \varepsilon f^{1/2} \), where \( \varepsilon f \) is in \( V \ cm^{-1} \) and \( \Delta E \) in \( cm^{-1} \).

Calculation of molecular geometries and vibrational frequencies were carried with Gaussian 09 program. In these calculations, DFT was employed with Becke’s three parameter hybrid functional with the correlation functional of Lee, Yang and Parr (B3LYP). Oxygen and scandium atomic orbitals were described by the aug-cc-pVTZ basis set or the 6-311+g(d) valence triple split basis set. Yttrium and lanthanum atomic orbitals were represented by the Stuttgart-type relativistic effective core potential basis with 28 core electrons (Stuttgart RSC segmented/ECP). To compare with the experimental spectra, Franck-Condron (FC) factors were calculated using the equilibrium geometries, harmonic frequencies, and normal mode coordinates of the neutral cluster and cation. In these calculations, recursion relations were employed and the Duschinsky effect was taken into consideration. Spectral simulations were obtained using the experimental linewidth and a Lorentzian line shape. Transitions from exited vibrational levels of the neutral molecule were considered by assuming thermal excitation at specific temperatures.

6.3 RESULTS AND DISCUSSION

6.3.1 MATI spectra

Figure 6.2 presents the MATI spectra of the \( M_3O_4 \) (\( M = Sc, Y, \) and \( La \)) clusters seeded in argon carrier gas. Each spectrum displays a predominant origin band (0-0) and many weak bands. The band positions are listed in Table 6.1. The observed spectral profile suggests that the three clusters have similar structures and that the structure of each cluster does not change significantly.
upon ionization. The small ionization effect on the molecular structure implies that the ejected electron from the highest occupied molecular orbital (HOMO) is weakly bound. The energy of the origin band corresponds to the AIE of each cluster, and the AIEs of three clusters decrease considerably from Sc to Y to La. The large AIE differences among the three clusters indicate the ejected electron originates from a metal-based, rather than an oxygen-based orbital. Compared to those of free metal atoms,\textsuperscript{189} the AIEs of the clusters are red shifted by 17985 cm\textsuperscript{-1} for Sc, 17441 cm\textsuperscript{-1} for Y, and 16952 cm\textsuperscript{-1} for La. Because the AIE shifts are comparable, the metal-oxygen bonding is expected to be similar in these clusters.

6.3.2 Possible structural isomers

Because a cage-like structure was previously predicted for Sc\textsubscript{3}O\textsubscript{4}, Y\textsubscript{3}O\textsubscript{4}\textsuperscript{+}, and La\textsubscript{3}O\textsubscript{4}\textsuperscript{+},\textsuperscript{46,227} we considered this structure a starting point in our computational search for possible isomers of the M\textsubscript{3}O\textsubscript{4}\textsuperscript{0/+1} clusters, which are shown in Figure 6.2. The search for a preferred isomer is performed on Sc\textsubscript{3}O\textsubscript{4} only, as the other two clusters are expected to have similar structures. The C\textsubscript{2v} isomer (Figure 6.2b) is derived from the C\textsubscript{3v} cage (Figure 6.2a) by breaking an O\textsubscript{t}-M bond, the C\textsubscript{1} ring (Figure 6.2c) from the C\textsubscript{2v} structure by breaking another O\textsubscript{t}-M bond, and the C\textsubscript{1} isomer from the C\textsubscript{3v} cage by cleaving an O\textsubscript{d}-M bond. O\textsubscript{t} and O\textsubscript{d} are referred to triply and doubly coordinated oxygen atoms, respectively. The D\textsubscript{2d} isomer (Figure 6.2d) is formed by fusing two M\textsubscript{2}O\textsubscript{2} four-member rings together through a M atom, and the two rings are perpendicular to each other. The C\textsubscript{s} isomer was previously identified for Ta\textsubscript{3}O\textsubscript{4}\textsuperscript{-1/0} and the D\textsubscript{2d} isomer for Si\textsubscript{3}O\textsubscript{4}\textsuperscript{-1/0}, both by anion photoelectron spectroscopy.\textsuperscript{244-246}

Table 6.2 summarizes the electronic states and energies of various Sc\textsubscript{3}O\textsubscript{4} isomers from the DFT/B3LYP calculations. Among these isomers, the C\textsubscript{3v} cage structure is the most stable one. For each isomer, the doublet state is the ground state of the neutral cluster and the singlet is the ground state of the cation. The geometry optimization of the initial C\textsubscript{s} and C\textsubscript{1} isomers in the singlet ion
states leads to the $^1A_1$ state of the $C_{3v}$ cage structure, indicating the cluster ion with a terminal oxygen atom is not stable. On the other hand, the geometry optimization of the initial $C_{3v}$ and $D_{2d}$ isomers are not converged in their high spin quartet neutral states and triplet ion states. Instead, the re-optimization without symmetry restriction leads to the quartet and triplet states in distorted $C_1$ structures.

6.3.3 Observed structural isomer and electronic transition

We first focus on the Sc$_3$O$_4$ cluster for which extensive computations are performed for various electronic states of five isomers (Table 6.2) and use the results from the Sc cluster as guide for the structural and spectral assignments of the two heavier analogues. Because the quartet state of each isomer has much higher energy than the doublet ground state, we will consider ionization of the doublet neutral state in the discussion of the spectral and structural assignments. Ionization of a doublet spin state would yield a triplet or a singlet ion state, but the triplet $\rightarrow$ doublet transition of each isomer requires $AIE > 8.0$ eV, which is more than 3.0 eV than the measured value. Thus, the triplet $\rightarrow$ double ionization is not likely responsible for the observed MATI spectrum. Moreover, because ionization of the $^2A'$ state of the $C_s$ isomer or the $^2A$ state of the $C_1$ isomer yields the $^1A_1$ ion state in $C_{3v}$ geometry, the $^1A_1 (C_{3v}) \rightarrow ^2A' (C_s)$ or $^2A (C_1)$ transition would give a MATI spectrum with a very long FC profile, inconsistent with the observation. Therefore, the $^1A_1 (C_{3v}) \rightarrow ^2A' (C_s)$ or $^2A (C_1)$ transition can be excluded from the spectral assignment. From the energy viewpoint, the $^1A_1 \rightarrow ^2A_1$ transitions of the $C_{3v}$, $C_{2v}$, or $D_{2d}$ isomers are possible candidates for the observed MAIT spectrum. These are the lowest-energy isomers, with the predicted AIEs within 0.4 eV of the experimental measurement. However, the MATI spectrum does not seem to involve multiple electronic transitions because it displays only a single origin band. The most likely transition for the observed spectrum is the $^1A_1 \rightarrow ^2A_1$ process of the $C_{3v}$ isomer because of the following evidences. First, the $C_{3v}$ isomer is the most stable one among the three isomers, with the
C$_{2v}$ and D$_{2d}$ structures lying 0.35 and 1.27 eV, respectively. Second, the predicted AIE of the $^1A_1 \leftrightarrow ^2A_1$ process of the C$_{3v}$ isomer (4.58 eV) is in excellent agreement with the experimental value (4.5939 ±0.0006 eV), while those of the C$_{2v}$ and D$_{2d}$ are 0.4 eV higher. Third, the spectral simulation of the $^1A_1 \leftrightarrow ^2A_1$ transition of the C$_{3v}$ structure reproduces nicely the overall features of the experimental spectrum, while those of the C$_{2v}$ and D$_{2d}$ isomer are not, as shown by Figure 6.3. In these simulations, the calculated vibrational frequencies (Table 6.3) are not scaled, but the theoretical AIEs are shifted to the experimental origin band for comparison. Similarly, the simulations of the $^1A_1 \leftrightarrow ^2A_1$ transitions of the C$_{3v}$ isomers of the Y$_3$O$_4$ and La$_3$O$_4$ reproduce the overall features of the experimental spectra (Figure 6.4 and 6.5), suggesting that the singlet $\leftrightarrow$ doublet transition is also responsible for the two heavier clusters.

With the identification of the electronic transition, the vibrational assignments of the MATI spectra are straightforward. Figures 6.3-6.5 show the assignments for the MATI bands from single mode excitations, and Table 6.1 lists the assignments for all observed bands. In the table, the band positions are relative to that of the origin band, the predicted band wavenumbers are listed inside parentheses, and the vibrational modes are labeled in the Herzberg order. The Herzberg order for the C$_{3v}$ point group proceeds as follows: symmetry species $a_1$ is before $a_2$ before $e$; for a given symmetry type, normal mode frequencies are arranged in descending order. It can be seen from Table 6.1 that $1^l_0$, $2^l_0$, $3^l_0$, $4^l_1$, and $6^l_0$ transitions are observed in the spectra of all three clusters and additional $9^l_0$ and $10^l_1$ are obtained in the spectrum of Sc$_3$O$_4$. Because $v_1^+$, $v_2^+$, $v_3^+$, and $v_4^+$ are totally symmetric modes (Table 6.3), the observation of their excitations is expected on the basis of the general electronic selection rule. On the other hand, $v_6^+$, $v_9^+$ and $v_{10}^+$ are doubly degenerate modes and their activity arises from the vibronic coupling. Because the direct product of the vibronic species of the neutral and ion states ($a_1\otimes e$) is the same as the species of the $(x,y)$ component of the electric dipole moment (e), the vibronic coupling makes these modes active. However, vibronic coupling is not included in the spectral simulations, the $10^l_0$, $9^l_0$, and $6^l_0$
transitions are not reproduced by the $^1A_1 \leftarrow ^2A_1$ simulation of the Sc$_3$O$_4$ cluster (Figure 6.3b) and the $6_0^0$ transition is missing in the $^1A_1 \leftarrow ^2A_1$ simulations of the Y$_3$O$_4$ and La$_3$O$_4$ clusters (Figures 6.4b and 6.5b).

Table 6.4 summarizes the AIEs and vibrational frequencies from the MATI measurements and DFT calculations. The predicted AIEs and vibrational frequencies are within 0.2 eV and 10 cm$^{-1}$ of the measured values, respectively. The AIEs of the clusters decrease down the triad, similar to those of the free atoms.\textsuperscript{189} The observed vibrational modes include metal-oxygen stretching ($v_1^+$, $v_2^+$, and $v_5^+$), metal triangle breathing ($v_3^+$ and $v_9^+$), oxygen-metal-oxygen rocking ($v_4^+$ and $v_{10}^+$). Because there are two types of oxygen atoms in C$_{3v}$ M$_3$O$_4$ clusters (Figure 6.1a), two different symmetric metal-oxygen stretching frequencies are observed: one ($v_1^+$) corresponds to the stretching motion associated with three doubly-coordinated oxygen atoms (O$_d$) and the other ($v_2^+$) with triply-coordinated oxygen (O$_t$). It is noted that the frequencies of the symmetric La-O$_d$ (531 cm$^{-1}$, $v_1^+$) and La-O$_t$ (421 cm$^{-1}$, $v_2^+$) stretching and antisymmetric La-O$_d$ stretching (627 cm$^{-1}$, $v_9^+$) are comparable to those of the corresponding Ce-O stretching motions (536, 413, and 633 cm$^{-1}$, respectively) in the Ce$_3$O$_4$–Ne cluster measured by IR vibrational predissociation spectroscopy.\textsuperscript{231} This is not surprising as La and Ce metals have similar atomic masses and comparable bonding to oxygen.

Figure 6.6 present frontier molecular orbitals of M$_3$O$_4$ using M = Sc as an example. The HOMO is consists of essentially a Sc 4s character, contributed equally by each of the three metal atoms. No other valence occupied orbitals consist of significant M nd or (n+1)s characters (Lu, please check this statement by looking more occupied MOs). HOMO-1 is doubly degenerate, largely with an O 2p character. The lowest unoccupied molecular orbital (LUMO) is also doubly degenerate, but mainly with a M (n+1)s character. The orbital analysis suggests that each M atom in M$_3$O$_4$ has only $\frac{1}{3}$ (n+1)s electron on average. Because each free M atom has three valence
electrons (with the ground electron configuration of nd\(^1\)(n+1)s\(^2\)), three M atom lose a total of eight electrons in forming the M\(_3\)O\(_4\) cluster, and each M atom may be consider having a formal oxidation state of \(\frac{+2}{3}\).

6.4 CONCLUSIONS

MATI spectra are reported for the first time for the M\(_3\)O\(_4\) (M = Sc, Y, and La) clusters seeded in supersonic molecular beams. The spectra exhibit a strong origin band and many weak bands associated with excitations of vibrational modes of the cationic clusters. Our joint experimental and computational analysis shows that each spectrum involves the \(^1\!A_1 \leftarrow ^2\!A_1\) transition of the most stable cage-like structure. The cage-like structure contains alternative M-O-M-O bonds and is formed by joining three M\(_2\)O\(_2\) fragments together, each sharing two O-M bonds with others. One of the four oxygen atoms is bonded to three metal atoms and the other three are bonded to two metals, whereas each metal atom forms at least three bonds with oxygen atoms. Molecular orbital analysis shows that the three metal atoms in the \(^2\!A_1\) neutral ground state of M\(_3\)O\(_4\) lose a total of eight electrons in forming the cluster and each metal atom may be considered having \(\frac{+2}{3}\) oxidation state. Ionization of the \(^2\!A_1\) state yields the \(^1\!A_1\) ion by removing a metal-based s electron. For the \(^1\!A_1\) state, four vibrational modes are measured for all three clusters, and additional two modes are observed for Sc\(_3\)O\(_4\). In addition to the cage-like structure, four other structural isomers are considered, but they have higher energies and are not probed by the MATI experiment.

This is the first high-resolution ion spectroscopic measurement on the transition metal clusters of the MO(M\(_2\)O\(_3\))\(_n\) stoichiometry, and further measurements on larger clusters would be valuable in understanding the formation of this class of metal clusters.

Table 6.1 Spectral band positions (cm\(^{-1}\)) and assignments of M\(_3\)O\(_4\) (M = Sc, Y and La) from MATI measurements and DFT/B3LYP calculations.\(^a\) The band positions are relative
to that of the origin band, and the calculated values are given inside parentheses. The energy of the origin band for each molecule is listed inside square brackets. Reprinted with permission from J. Chem. Phys., 137, 084312 (2014), Copyright 2013 AIP Publishing LLC.

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\textsuperscript{a}Basis sets are aug-cc-pVTZ for Sc and O atoms and Stuttgart RSC Segmented/ECP for Y and La atoms.

\textsuperscript{b}The relative intensities of the MATI bands are indicated by “s” (strong), “m” (medium), “w” (weak), and “vw” (very weak).
Table 6.2 Point groups, electronic states and relative energies ($E_{rel}$), and transition energies ($\Delta E$) of Sc$_3$O$_4$ isomers from DFT/B3LYP calculations.\textsuperscript{a} Reprinted with permission from J. Chem. Phys., 137, 084312 (2014), Copyright 2013 AIP Publishing LLC.

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<th>Ion State</th>
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\textsuperscript{a} 6-311+G(d,p) basis set are used for the Sc and O atoms.

\textsuperscript{b} The structure of each point group is shown in Figure 6.1. The singlet states of the C\textsubscript{s} and C\textsubscript{1} isomers are converged to the \textsuperscript{1}A\textsubscript{1} state of the C\textsubscript{3v} structure. The quartet and triplet states with initial C\textsubscript{3v} and D\textsubscript{2d} structures are not converged, but reoptimization without symmetry restriction leads to distorted C\textsubscript{1} structures.
Table 6.3 Vibrational modes and frequencies of $\text{M}_3\text{O}_4$ ($C_{3v}$) and $\text{M}_3\text{O}_4^+$($C_{3v}$) ($\text{M} = \text{Sc}, \text{Y},$ and $\text{La}$) from DFT/B3LYP calculations.\textsuperscript{a} Reprinted with permission from J. Chem. Phys., 137, 084312 (2014), Copyright 2013 AIP Publishing LLC.

<table>
<thead>
<tr>
<th></th>
<th>$v_1$ ($a_1$)</th>
<th>$v_2$ ($a_1$)</th>
<th>$v_3$ ($a_1$)</th>
<th>$v_4$ ($a_1$)</th>
<th>$v_5$ ($a_2$)</th>
<th>$v_6$ ($e$)</th>
<th>$v_7$ ($e$)</th>
<th>$v_8$ ($e$)</th>
<th>$v_9$ ($e$)</th>
<th>$v_{10}$ ($e$)</th>
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<tr>
<td>$\text{Sc}_3\text{O}_4^+$ ($^1A_1$)</td>
<td>671</td>
<td>549</td>
<td>439</td>
<td>275</td>
<td>465</td>
<td>746</td>
<td>672</td>
<td>433</td>
<td>293</td>
<td>202</td>
</tr>
<tr>
<td>$\text{Sc}_3\text{O}_4$ ($^2A_1$)</td>
<td>643</td>
<td>532</td>
<td>390</td>
<td>252</td>
<td>457</td>
<td>650</td>
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<td>424</td>
<td>288</td>
<td>185</td>
</tr>
<tr>
<td>$\text{Y}_3\text{O}_4^+$ ($^1A_1$)</td>
<td>589</td>
<td>470</td>
<td>311</td>
<td>242</td>
<td>456</td>
<td>676</td>
<td>567</td>
<td>402</td>
<td>212</td>
<td>169</td>
</tr>
<tr>
<td>$\text{Y}_3\text{O}_4$ ($^2A_1$)</td>
<td>571</td>
<td>453</td>
<td>294</td>
<td>232</td>
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<td>562</td>
<td>518</td>
<td>390</td>
<td>204</td>
<td>160</td>
</tr>
<tr>
<td>$\text{La}_3\text{O}_4^+$ ($^1A_1$)</td>
<td>526</td>
<td>416</td>
<td>250</td>
<td>202</td>
<td>335</td>
<td>633</td>
<td>494</td>
<td>329</td>
<td>152</td>
<td>140</td>
</tr>
<tr>
<td>$\text{La}_3\text{O}_4$ ($^2A_1$)</td>
<td>508</td>
<td>396</td>
<td>234</td>
<td>184</td>
<td>329</td>
<td>507</td>
<td>435</td>
<td>319</td>
<td>149</td>
<td>128</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Basis sets are aug-cc-pVTZ for Sc and O atoms and Stuttgart RSC Segmented/ECP for Y and La atoms.
Table 6.4 Measured adiabatic ionization energies (AIE, eV) and ionic vibrational frequencies (ν_i^+, cm^{-1}) of M_3O_4 (M = Sc, Y, and La), along with those in parentheses from DFT/B3LYP calculations.\textsuperscript{a} The AIE corresponds to the ionization process of M_3O_4\textsuperscript{+} (\textsuperscript{1}A\textsubscript{1}, C\textsubscript{3v}) ← M_3O_4 (\textsuperscript{2}A\textsubscript{1}, C\textsubscript{3v}). Reprinted with permission from J. Chem. Phys., 137, 084312 (2014). Copyright 2013 AIP Publishing LLC.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Sc\textsubscript{2}O\textsubscript{4}</th>
<th>Y\textsubscript{3}O\textsubscript{4}</th>
<th>La\textsubscript{3}O\textsubscript{4}</th>
<th>Approx. description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIE</td>
<td>4.4556±0.0006</td>
<td>4.0586±0.0006</td>
<td>3.4750±0.0006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(4.59)</td>
<td>(4.25)</td>
<td>(3.53)</td>
<td></td>
</tr>
<tr>
<td>ν\textsubscript{i}^+, a\textsubscript{i}</td>
<td>667 (671)</td>
<td>591 (589)</td>
<td>531 (526)</td>
<td>Symmetric O\textsubscript{d}-M stretch</td>
</tr>
<tr>
<td>ν\textsubscript{2}^+, a\textsubscript{i}</td>
<td>545 (549)</td>
<td>475 (470)</td>
<td>421 (416)</td>
<td>Symmetric O\textsubscript{t}-M stretch</td>
</tr>
<tr>
<td>ν\textsubscript{3}^+, a\textsubscript{i}</td>
<td>437 (439)</td>
<td>314 (311)</td>
<td>251 (250)</td>
<td>Symmetric M\textsubscript{3} ring breath</td>
</tr>
<tr>
<td>ν\textsubscript{4}^+, a\textsubscript{i}</td>
<td>273 (275)</td>
<td>238 (242)</td>
<td>204 (202)</td>
<td>Symmetric O\textsubscript{d}-M-O\textsubscript{d} rock</td>
</tr>
<tr>
<td>ν\textsubscript{6}^+, e</td>
<td>751 (746)</td>
<td>678 (676)</td>
<td>627 (633)</td>
<td>Antisymmetric O\textsubscript{d}-M stretch</td>
</tr>
<tr>
<td>ν\textsubscript{9}^+, e</td>
<td>300 (293)</td>
<td>(212)</td>
<td>(152)</td>
<td>Antisymmetric M\textsubscript{3} breath</td>
</tr>
<tr>
<td>ν\textsubscript{10}^+, e</td>
<td>204 (202)</td>
<td>(169)</td>
<td>(140)</td>
<td>Antisymmetric O\textsubscript{d}-M-O\textsubscript{d} rock</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Basis sets are aug-cc-pVTZ for Sc and O atoms and Stuttgart RSC Segmented/ECP for Y and La atoms.

\textsuperscript{b} “O\textsubscript{d}” and “O\textsubscript{t}” are doubly- and triply-bound oxygen atoms, respectively.
Figure 6.1 Possible structural isomers of $\text{M}_3\text{O}_4$ ($\text{M} = \text{Sc}$, $\text{Y}$, and $\text{La}$). Reprinted with permission from J. Chem. Phys., 137, 084312 (2014), Copyright 2013 AIP Publishing LLC.
Figure 6.2 MATI spectra of $M_3O_4$ ($M = \text{Sc, Y, and La}$) seeded in argon carrier. Reprinted with permission from J. Chem. Phys., 137, 084312 (2014), Copyright 2013 AIP Publishing LLC.
Figure 6.3 MATI spectrum of Sc$_3$O$_4$ seeded in argon carrier gas (a) and simulations (50 K) of the $^1A_1 \leftarrow ^2A_1$ transitions of the C$_{3v}$ (b), C$_{2v}$ (c), and D$_{2d}$ isomers. Spectral bands associated with single vibrational mode are labeled in the figure. Others are either overtone or combination bands. Reprinted with permission from J. Chem. Phys., 137, 084312 (2014), Copyright 2013 AIP Publishing LLC.
Figure 6.4 MATI spectrum of Y\(_3\)O\(_4\) seeded in argon carrier gas (a) and simulation (50 K) of the \(^1\)A\(_1\) ← \(^2\)A\(_1\) transition of the C\(_{3v}\) isomer (b). Spectral bands associated with single vibrational mode are labeled in the figure. Others are either overtone or combination bands. Reprinted with permission from J. Chem. Phys., 137, 084312 (2014), Copyright 2013 American Institute of Physics.
Figure 6.5 MATI spectrum of La$_3$O$_4$ seeded in argon carrier gas (a) and simulation (50 K) of the $^1$A$_1 \leftarrow ^2$A$_1$ transition of the C$_{3v}$ isomer (b). Spectral bands associated with single vibrational mode are labeled in the figure. Others are either overtone or combination bands. Reprinted with permission from J. Chem. Phys., 137, 084312 (2014), Copyright 2013 American Institute of Physics.
Figure 6.6 LUMO (a), HOMO (b), and HOMO-1 (c) of the $^2A_1$ ground state of the $C_{3v}$ isomer of $\text{Sc}_3\text{O}_4$. The LUMO and HOMO are mainly Sc 4s character, and HOMO-1 is largely O 2p. Y$_3$O$_4$ and La$_3$O$_4$ have similar characters in these frontier orbitals.

CHAPTER 7 MASS-ANALYZED THRESHOLD IONIZATION OF METAL TRIMER CARBIDES AND CARBOXIDES

7.1 INTRODUCTION

Probing the structures and electronic states of transition metal cluster carbides are challenging because of the existence of many possible isomers and the high density of low-lying electronic states of each isomer. Nevertheless, several experimental techniques have been used to study these clusters. Mass spectrometry has been used to investigate their stoichiometry and stability, especially for the ‘met-car’ clusters and nanocrystals. 250 Photoionization efficiency (PIE) spectroscopy has been used to estimate the ionization thresholds of the neutral clusters251-253 and PES to measure the EAs of the anions. Multiphoton IR ionization spectroscopy has been applied to measure the vibrational frequencies of the neutral molecules, especially the ‘met-car’ clusters and the nanocrystals. 254-256 Typically, the met-cars and nanocrystals have lower ionization energies than dissociation energies. Moreover, PFI-ZEKE spectroscopy has been used to measure the accurate AIEs of the neutral molecules and the vibrational frequencies of the cations. 214,216,257 Closely related to this work was the PFI-ZEKE study of Y₃C₂ by Yang and co-workers. 214 In that study, they determined a trigonal bipyramidal structure of Y₃C₂ with the neutral state in C₂ᵥ point group and ion state in D₃h. The precise ionization energy of Y₃C₂ was reported to be 34065 (5) cm⁻¹ [4.334(8) eV]. The Y₃ ring-breathing frequency was observed to be 228 cm⁻¹ for Y₃C₂⁺. The two deformation modes have frequencies of 82 and 24 cm⁻¹ in the neutral state and a degenerate frequency of 86 cm⁻¹ in the ion.

In this work, we extend the previous work by Yang and co-workers to include Sc₃C₂ and La₃C₂ using MATI spectroscopy. As discussed in the section of Introduction of this
dissertation, the MATI technique provides similar spectroscopic information as ZEKE does, but has the advantage of easy mass selection. We consider both C\textsubscript{2v} and D\textsubscript{3h} trigonal bipyramid geometries for the neutral clusters (and D\textsubscript{3h} for the ions) and find the C\textsubscript{2v} structure to be more stable and responsible for the observed MATI spectra. In the process of studying La\textsubscript{3}C\textsubscript{2}, I observe unexpectedly a strong mass peak corresponding to La\textsubscript{3}C\textsubscript{2}O. Therefore, MATI measurements are also carried out for this species. In La\textsubscript{3}C\textsubscript{2}O, the oxygen atom is located in the La\textsubscript{3} plane and bound to two of the lanthanum atoms of the trigonal bipyramidal La\textsubscript{3}C\textsubscript{2}. La\textsubscript{3}C\textsubscript{2}O has a C\textsubscript{2v} structure in both neutral and ion states.

7.2 EXPERIMENTAL AND COMPUTATIONAL METHODS

7.2.1 Experiment

The cluster beam apparatus has been described in detail in a previous publication.\textsuperscript{147} The apparatus consists of two vacuums chambers. The first houses a Smalley-type cluster source and is pumped by a 2200 l s\textsuperscript{-1} diffusion pump. The second chamber houses the MATI spectrometer and is pumped by a 400 l s\textsuperscript{-1} turbo-molecular pump. The MATI spectrometer is composed of a two stage extraction assembly, a 34 cm long flight tube, and a dual microchannel plate detector (Galileo). The entire spectrometer is housed in a cylindrical, double-walled, μ-metal shield. The spectrometer could also be operated as a two-field, space-focused, Wiley-McLaren time-of-flight mass spectrometer by supplying the appropriate voltages.

Lanthanum carbides were produced by laser vaporization (Spectra Physics, 355 nm, 12 mJ, focused by a 30 cm focal length lens) of a lanthanum rod (99.9%, Alfa Aesar) in the presence of inert carrier gases (He or Ar, UHP, Scott-Gross, 50 psi backing pressure,
doped with 2 \times 10^{-6} \text{ ethylene, Scott-Grass, and traces of O}_2 \text{ gas, Scott-Gross), delivered by a home-built pulsed valve. The clusters passed down a clustering tube (2 mm inner diameter, 2 cm length) and were supersonically expanded into the vacuum chamber. The supersonic jet was skimmed 2.5 cm downstream from the exit end of the clustering tube. A pair of deflection plates (2 cm spacing, 300 V) located after the skimmer removed residual charged species from the molecular beam before it entered the second chamber.

Before the MATI experiments, pulse field ionization photoionization efficiency (PFI-PIE) experiments were performed. PFI-PIE measurements were taken to locate the approximate ionization potentials. With the ionization energy set to the PIE threshold, the experiment conditions, such as the firing time and fluence of the vaporization and ionization laser, the ethylene concentration, and the backing pressure of the carrier gases, were carefully optimized in order to maximize the intensity of the cluster (i.e., Sc$_3$C$_2$, La$_3$C$_2$, or La$_3$C$_2$O) of interest in the time-of-flight mass spectrum relative to those of all other mass peaks.

To perform the MATI experiment, the clusters were exited to high-lying Rydberg states in a single photon process. The tunable UV beam (1 mJ/pulse) was obtained from a frequency-doubled dye laser (Lumonics HD-5000) pumped by a Nd:YAG laser (Quanta-Ray GCR 3), which was then expanded and collimated by a simple telescope to give a 5 mm-diameter circular beam. The excitation laser is counterpropagated on the axis of the molecular beam. The high-lying Rydberg states were then ionized by a delayed pulsed field of 320 V/cm applied to the repeller plate. The time delay of the pulsed field from the laser is controlled by a digital delay generator (Standfor DG 535) and optimized to separate the prompt ion (generated by direct ionization) from the long-lived Rydberg states. A
typical delay time of 20 µs and 50 µs were used for He and Ar carrier gases, respectively. During the time-delay, the prompt ions generated by UV photon ionization were separated from the high-Rydberg states by a spoiling dc field (4 to 9V/cm for Ar and He carrier gases, respectively) before the pulsed field ionization. A small ac field was used to lengthen the life time of the Rydberg states. The MATI ion signals were capacitively coupled from the MCP anode and were amplified by a preamplifier (standfor SR 445), averaged by a gated integrator (standfor SR 250), and collected in a micro-computer. Laser wavelength was calibrated against appropriate atomic transitions in the wavelength range. The Stark shift induced by the DC field was calculated using the relation of $\Delta E = 6.1E_f^{1/2}$, where $E_f$ is in V cm$^{-1}$ and $\Delta E$ in cm$^{-1}$.151

7.2.2 Computation

Equilibrium geometries, harmonic vibrational frequencies, and normal coordinates of the low-lying electronic states of the clusters were calculated with GAUSSIAN03 program package.259 In these calculations, we used Becke’s three-parameter hybrid functional with the correlation functional of Lee, Yang, and Parr (B3LYP) and LanL2DZ basis set for the metal atoms (Sc and La) and aug-cc-pVTZ basis set for the non-metal atoms (C and O).

Multidimensional Franck–Condon (FC) factors were calculated from the equilibrium geometries, harmonic vibrational frequencies, and normal coordinates of the neutral and ionized complexes. The Duschinsky effect was considered to account for normal mode differences between the neutral and ionic complexes in the FC calculations. More details of the FC calculations were described previously.
A Lorentzian line shape with the experimental linewidth was used to simulate spectral broadening. Transitions from the excited vibrational levels of the neutral clusters were simulated by assuming thermal excitations at specific temperatures.

7.3 RESULTS AND DISCUSSION

7.3.1 Spectroscopic measurements

Figure 7.1 shows the time-of-flight mass spectra of Sc and La carbide molecular beams. Both spectra exhibit similar features, with $M_nC_2$ ($M = \text{Sc and La}$) as the dominant peaks. Zooming into the region of the trimetal clusters, the two spectra show the same mass sequences: $M_3C_2$, $M_3C_2H_4$, $M_3O_2$, $M_3C_3$, and $M_3C_2O$. These similar features indicate that similar laser vaporization processes and reactions with $C_2H_4$ and $O_2$ occurred for Sc and La. This is understandable both metals are in the same group in the periodic table. However, the intensity ratios of the $M_3C_2O$ to $M_3C_2$ peaks are different between the two metal elements, which are 0.28 for Sc and 0.76 for La. The difference may be due to the different contents of the oxygen impurity in the Sc/La rods or the different reactivity of Sc/La carbides with $O_2$.

Figures 7.2 and 7.3 present the MATI spectra of $\text{Sc}_3C_2$ and $\text{La}_3C_2$ seeded in different carrier gases. The spectrum of each cluster with He as the carrier gas exhibits similar intensity profiles to those with Ar or He/Ar mixture as the carrier gases. The MATI spectra of $\text{Sc}_3C_2$ and $\text{La}_3C_2$ show three and four major progressions, respectively. The band positions of the spectra are summarized in Table 7.1. These progressions have the same energy spacing: 95 cm$^{-1}$ for $\text{Sc}_3C_2$ and 66 cm$^{-1}$ for $\text{La}_3C_2$. Comparing the peak intensities of the MATI spectra with different carrier gases (i.e., He, Ar, or 2:1 He/Ar), the progression with intense peaks are attributed to the cold transitions. The energy separations in these progressions are the vibrational frequencies of the cations. The
observations are consistent with the PFI-ZEKE spectrum of Y$_3$C$_2$, which exhibits four progressions with the same spacing of 86 cm$^{-1}$. These observations indicate that all three clusters should have similar structures and the observed transitions should involve the same M$_3$ deformation mode of the ionic cluster. The long progression profiles can be explained by significant geometry changes upon ionization. The significant decreases of the energy spacing from Sc$_3$C$_2$ to La$_3$C$_2$ are due to the mass effect. The AIEs can be determined by the first peak in the cold transitions, which are 4.512(8) eV for Sc$_3$C$_2$ and 3.742(8) eV for La$_3$C$_2$. Compared to the ionization energies of the free metal atoms, the AIEs of the clusters are red shifted by 2.049 eV for Sc, 1.993 eV for Y, and 1.835 eV for La. Because the AIE shifts are comparable, the metal-carbon bonding is expected to be similar in these clusters.

Figure 7.4 presents the MATI spectra of La$_3$C$_2$O seeded in He and Ar gases. The peak positions are summarized in Table 7.2. Unlike the MATI spectra of La$_3$C$_2$, the La$_3$C$_2$O spectra show the most intense peak at the 0-0 position and have much shorter FC profiles. These are strong evidences that the neutral molecule and cation have similar structures. The AIE of La$_3$C$_2$O is measured to be 3.830 eV, and several cold transition progressions are located at 160, 235, 530, and 665 cm$^{-1}$ from the 0-0 transition toward the high energies. These peaks are related to the vibrational modes of the ions. Superimposed on the high-energy side of each cold transition are satellite peaks separated by about 38 cm$^{-1}$ from the main peak. In addition, the MATI spectrum with He exhibits a weak transition of 115 cm$^{-1}$ at the lower energy side of the 0-0 transition. The intensities of these peaks decrease significantly from He to Ar carrier (Figure 7.4a), indicating that these weak transitions originate from the excited vibrational levels of the neutral state.
7.3.2 Possible isomers and electronic states

7.3.2.1 $M_3C_2$ ($M = \text{Sc, La}$)

Similar spectral profiles indicate that $\text{Sc}_3C_2$ and $\text{La}_3C_2$ may have the similar structures to that of $\text{Y}_3C_2$ suggested by the previous work.\textsuperscript{214} Moreover, the geometric optimizations of $\text{Sc}_3C_2$ and $\text{La}_3C_2$ from different starting geometries all converge to the trigonal bipyramid structures. The molecular symmetries are either $C_{2v}$ or $D_{3h}$, depending on the electronic states and are summarized in Table 7.3. In all these structures, three metal atoms form a triangle and two carbon atoms are on the opposite side of the metal plane. In the $C_{2v}$ structures, two of the metal atoms are equivalent, labeled as $M_d$, and the third metal atom is labeled as $M_s$. In the $D_{3h}$ structures, these $M_d$ and $M_s$ atoms are equivalent, but labeled in the same way for the convenience and consistency.

Two sets of isomers are located for the $M_3C_2$ molecules, and their geometries as listed in Table 7.3. Type I isomers have shorter C-C distances (1.6~1.8 Å) than the type II isomers (~2.4 Å for $\text{Sc}_3C_2^{0/+}$, and ~2.7 Å for $\text{La}_3C_2O^{0/+}$). The transitions between the two types of structures can be excluded for the following reasons. The geometry from type I to type II structures is changed by increasing the C-C distances and shrinking the $M_3$ ring (indicated by the decrease of the M-M distances in Table 7.1). This change is related to a total-symmetry vibration mode with the frequencies greater than 300 cm$^{-1}$ for $\text{Sc}_3C_2^{+}$ and 160 cm$^{-1}$ for $\text{La}_3C_2^{+}$. According to Franck-Condon principle, this vibration mode is expected to be active in the MATI spectrum, and the transitions are expected to form a long progression. However, there is no long progression observed with frequencies greater than 300 or 160 cm$^{-1}$. 

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For both isomers, we considered the local minima of the doublet and quartet states in the neutral molecules and the singlet and triplet states in the cations. Type I isomer is close to what observed for Y$_3$C$_2$. It is not obvious which isomer is responsible for the observed spectra by considering the calculated energies only. First, the predicted energies of the low-lying excited neutral states are not too far from that of the ground state. Second, six transitions are possible (i.e. those with the multiplicity change by 1). The predicted energies of these transitions vary from 4.407 to 5.124 eV for Sc$_3$C$_2$ and 3.733 to 4.566 eV for La$_3$C$_2$, which are not too far from the measured values. Thus, it is necessary to consider the geometric parameters and spectral profiles to determine which isomer is responsible to the observed spectra. Because the MATI spectra have long progressions, the predicted neutral and ionic states should have significant structural changes. The transitions from the doublet to the singlet and triplet states of isomer II can be excluded because the simulations show only very short progressions. There are four possible transitions with significant geometry changes, which are $^1$A$_1'\leftrightarrow^2$B$_2$, $^3$B$_2\leftrightarrow^2$B$_2$ and $^3$B$_2\leftrightarrow^4$A$_2$ transitions of isomer I and $^3$A$_2''\leftrightarrow^4$A$_2$ transition of isomer II. The simulations of these transitions (with the 0-0 transition energies being shifted to the experimental values) are shown in Figure 7.5 for Sc$_3$C$_2$ and Figure 7.6 for La$_3$C$_2$ and compared with the experimental spectra. From the comparison, the $^1$A$_1'\leftrightarrow^2$B$_2$ transition of isomer I matches the MATI spectra best. The $^3$B$_2\leftrightarrow^2$B$_2$ and $^3$B$_2\leftrightarrow^4$A$_2$ transitions of isomer I show much longer progressions than the experimental spectra, as shown in Figure 7.5(c,d) for Sc$_3$C$_2$ and Figure 7.6(c,d) for La$_3$C$_2$. The $^3$A$_2''\leftrightarrow^4$A$_2$ transition of isomer II shows similar spectral profile to the measured spectrum. But the predicted cationic frequencies are much higher than the measured values (Figures 7.5(g) and 7.6(g) for Sc$_3$C$_2$ and La$_3$C$_2$, respectively)
From the comparison of the simulations with the measurements, the $^{1}A_{1}′\rightarrow{}^{2}B_{2}$ transition of isomer I is assigned to the MATI spectra, which is consistent with the previous study of Y$_{3}$C$_{2}$\textsuperscript{214}. As summarized in Table 7.1, the four observed progressions are $4_0^{n\rightarrow{}p}q_0^0$ and its combinations with $4_1^1, 9_2^0$ and $3_0^1$. The spacing of all these progressions are related to the degenerate mode $\nu_4^+$ of the cation, with the measured frequencies of 95 and 66 cm\textsuperscript{-1} for Sc$_3$C$_2$ and La$_3$C$_2$, respectively. This vibrational mode corresponds to $\nu_4$ and $\nu_9$ of the neutral molecule because the Jahn-Teller distortion lowers the molecular symmetry from D$_{3h}$ to C$_{2v}$. Besides, the $3_0^1$ mode is the M$_3$ ring breathing mode, which has the frequencies of 338 and 154 cm\textsuperscript{-1} for Sc$_3$C$_2$ and La$_3$C$_2$, respectively. These values differ from the vibration modes of Y$_3$C$_2$ ($\nu_3^+ = 228, \nu_4^+ = 86$, and $\nu_4 = 86$ cm\textsuperscript{-1}) mainly because of the mass effect.

### 7.3.2.2 La$_3$C$_2$O

To our knowledge, there is no previous study on this type of the metal clusters. We started the calculations by substituting La for Nb and Ta in the previously reported clusters of M$_3$C$_3$, M$_4$C$_2$ and M$_5$C (M = Nb and Ta).\textsuperscript{251,253,260,261} Figure 7.7 shows eight optimized isomers. Isomers (A) and (B) have the same shape and are derived from one of the M$_4$C$_2$ or M$_5$C isomers. They have the carbon and oxygen atoms substituted at different positions. Similarly, isomers (C), (D), and (E) take the structures of the other isomers of M$_4$C$_2$ or M$_5$C clusters. Isomer (G) and (H) are based on the M$_3$C$_3$ isomers. Isomer (F) is obtained by rotating the direction of C-C bond in isomer (C). The relative energies of the low-lying electronic states of each isomer are summarized in Table 7.4. Because the molecules with
high energies will unlikely survive after the supersonic expansion, isomer (B), (D), (E), (G) and (H) will not be included in the spectral analysis. Five transitions are considered because their energies (3.895-4.440 eV) are comparable to the measured value. These transitions include $^1A_1 \leftrightarrow ^2A_1$ of isomer (A), $^1A' \leftrightarrow ^2A'$, $^3A'' \leftrightarrow ^2A'$ and $^3A'' \leftrightarrow ^4A'$ of isomer (C), and $^3A' \leftrightarrow ^2A''$ of isomer (F). The simulations of these transitions are compared with the MATI spectra in Figure 7.8. The neutral states of isomer (C) have lower energies than those of the other isomers. However, the $^1A' \leftrightarrow ^2A'$, $^3A'' \leftrightarrow ^2A'$ and $^3A'' \leftrightarrow ^4A'$ transitions of this isomer can be excluded because they have much weaker 0-0 transitions and longer progressions than the MATI spectrum. The other two transitions, $^1A_1 \leftrightarrow ^2A_1$ of isomer (A) and $^3A' \leftrightarrow ^2A''$ of isomer (F), have intense 0-0 bands and short progressions. However, the $^3A' \leftrightarrow ^2A''$ transition of isomer (F) is not likely responsible for the observed MATI spectrum. First, the predicted AIE is 0.61 eV above the measured value, which is 0.5 eV higher than that of the other transition. Second, it does not reproduce the two peaks at 530 and 665 cm$^{-1}$.

Thus, the most likely transition for the observed spectrum is $^1A_1 \leftrightarrow ^2A_1$ of isomer (A). Isomer (A) has a C$_{2v}$ symmetry, formed by binding an oxygen atom to two metal atoms of La$_3$C$_2$ (isomer I). It has five total symmetric vibrational modes, and four of them are observed in the MATI spectrum. They are $v_1^+$ (665 cm$^{-1}$), $v_3^+$ (530 cm$^{-1}$), $v_4^+$ (235 cm$^{-1}$) and $v_5^+$ (160 cm$^{-1}$) of La$_3$C$_2$O$^+$ and $v_5$ (155 cm$^{-1}$) of La$_3$C$_2$O. These vibrational modes are associated mainly to the C-La$_d$ stretching ($v_1^+$), O-La$_d$ stretching ($v_3^+$), La$_d$-La$_d$ stretching ($v_4^+$), and La$_d$C$_2$-La$_d$OLa$_d$ stretching ($v_5^+$). The predicted $v_2^+$ is 596 cm$^{-1}$ and associate with C-C stretching mode. The predicted Franck-Condon intensity of this mode is negligible, which is consistent with the observed MATI spectrum. Besides, a sequence
band \((9\frac{1}{2})\) is observed at 38 cm\(^{-1}\) from the 0-0 band. \(v_9\) has \(b_1\) symmetry in both neutral and ion states, but the sequence transition is allowed. This mode is associated to the deformation of the cluster.

7.3.2.3 Chemical bonding effects

Because they are in the same group in the periodic table, the scandium and lanthanum clusters are expected to have similar bonding features as the corresponding yttrium clusters. The \(\text{M}_3\text{C}_2\) (\(\text{M} = \text{Sc, La}\)) clusters are identified to be in the doublet ground state of isomers I, which is the same as \(\text{Y}_3\text{C}_2\).\(^{214}\) The AIEs of the \(\text{M}_3\text{C}_2\) (\(\text{M} = \text{Sc, Y, La}\)) clusters (4.512/4.291/3.742 eV for \(\text{Sc/Y/La}\)) decrease from Sc to Y to La as that of the free metal atoms. The frequencies of the \(\text{M}_3\) ring-breath mode (338/228/154 cm\(^{-1}\) for \(\text{Sc/Y/La}\)) and \(\text{Md-C-Md}\) deformation mode (95/84/67 cm\(^{-1}\) for \(\text{Sc/Y/La}\)) in the cations also decrease as the increase of the metal atomic masses.

The metal carbides have the ionic bonding character of \([\text{M}^{2+}]_3[\text{C}^{3-}]_2\) (\(\text{M} = \text{Sc, La}\)), and a total of two more electrons are transferred from the metal atoms to oxygen when forming the \([\text{M}^{8/3+}]_3[\text{C}^{4-}]_2\text{O}^2^-\) cluster. The unsaturated electron configurations on the carbon atoms are because of the small C-C distances. The C-C distances in isomers I are predicted to be in the range of 1.6-1.8 Å, which are slightly longer than the \(\text{C}(sp^3) - \text{C}(sp^3)\) bonds.\(^{262}\) The \(\sigma\)-type anti-bonding molecular orbital formed by the carbon p orbitals in this cluster has the high energy and remains empty upon the electron transfer. Thus, the C-C bond order is 1. In contrast, the C-C distances of the type II isomer are predicted to be much longer (> 2.4 Å), and the doublet ground state of isomer II has \(D_{3h}\) symmetry and the \([\text{M}^{8/3+}]_3[\text{C}^{4-}]_2\) form. The C-C bond order is 0 in this case.

Because each free M atom has three valence electrons (with the ground electron configuration of \(nd^l(n+1)s^2\)), the total number of the metal-based valence electrons is 3 in the ground states of Type I isomers of \(\text{M}_3\text{C}_2\) and 1 for Type II isomers of \(\text{M}_3\text{C}_2\) and the ground state of

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The remaining metal-based electrons have \((n+1)s\) characters, similar to the group 3 metal oxides. Three molecular orbitals \((2a_1 + b_2)\) are generated from the linear combination of the valence \((n+1)s\) orbitals in \(C_{2v}\) point group. Figure 7.9 represents the molecular orbital diagrams of the trimetal clusters by using the lanthanum clusters as examples. The highest occupied molecular orbital (HOMO) of \(\text{La}_3\text{C}_2\) isomer I is an anti-bonding orbital localizing on the two \(\text{La}_d\) atoms. The repulsion force caused by the anti-bonding electron pushes the two atoms apart and causes a \(C_{2v}\) structure with a large \(\text{La}_d\)-C-C-La\(_d\) dihedral angle (134°). After removing the anti-bonding electron, \(\text{La}_3\text{C}_2^+\) exhibits a \(D_{3h}\) structure and has two electrons evenly distributed among the three La atoms. The average La-La bond order is 1/3. As a comparison, \(\text{La}_3\text{C}_2\) isomer II has a \(D_{3h}\) structure with one electron being shared by the three La atoms, which is similar to the case of \(\text{La}_3\text{O}_4\). Its cation has an average La-La bond order of 0.

The observed \(\text{La}_3\text{C}_2\text{O}\) is not the most stable isomer, which indicates that it is likely generated by a kinetic-driven mechanism. Because it has a similar structure with \(\text{La}_3\text{C}_2\), it is probably formed by the reaction of \(\text{La}_3\text{C}_2\) with O atoms or \(\text{O}_2\). For \(\text{La}_3\text{C}_2\text{O}\), its HOMO is largely the 6s orbital of the \(\text{La}_s\) atom. Thus, removing the HOMO electron will increase the bonding of \(\text{La}_3\text{C}_2\) with O because of the increasing static electronic attractions. The AIE of \(\text{La}_3\text{C}_2\text{O}\) is measured as 3.830 eV from the MATI spectrum, which is 0.088 eV higher than that of \(\text{La}_3\text{C}_2\). The thermodynamic cycle \(D_0(\text{La}_3\text{C}_2^+ - \text{O}) - D_0(\text{La}_3\text{C}_2 - \text{O}) = \text{AIE}(\text{La}_3\text{C}_2) - \text{AIE}(\text{La}_3\text{C}_2\text{O})\) shows that \(\text{La}_3\text{C}_2\text{O}^+\) has a lower dissociation energy than \(\text{La}_3\text{C}_2\text{O}\). It is noted that the change of the \(\text{La}_d\)-C-C-\(\text{La}_d\) dihedral angle upon oxygen dissociation is much larger in the neutral state (134° - 96° = 38°) than in the ion (120° - 94° = 26°). The \(\text{La}_d\text{C}_2\text{-La}_d\text{OLa}_d\) stretching mode (160 cm\(^{-1}\)) of \(\text{La}_3\text{C}_2\text{O}^+\) is comparable to the M\(_3\) ring breathing mode of \(\text{La}_3\text{C}_2^+\) (154 cm\(^{-1}\)), both are smaller than the ring-breathing mode of \(\text{La}_3\text{O}_4\) (251 cm\(^{-1}\)). On the other hand, the \(\text{La}_d\)-\(\text{La}_d\) stretching frequency (235 cm\(^{-1}\)) of \(\text{La}_3\text{C}_2\text{O}^+\) is much larger than that of \(\text{La}_3\text{C}_2^+\) (67 cm\(^{-1}\).
This can be explained by the increasing tensions between metal atoms caused by the lanthanum-oxygen bonds.

7.4 CONCLUSIONS

We have obtained the vibrationally resolved MATI spectra of M₃C₂ (M = Sc and La) and La₃C₂O. Their AIEs have been measured as 36391 (5), 30181 (5) and 30891 (5) cm⁻¹. The M₃C₂ clusters exhibit similar spectral features as Y₃C₂ does. Two sets of the isomers are explored for M₃C₂. They are differentiated by the C-C distance, which causes the different number of electrons being transferred to form the ionic M-C bonds ([M⁺²]₃[C⁻³])₂ for isomer I and [M⁺⁸/₃]₃[C⁻⁴]₂ for isomer II) and different C-C bond orders. Isomer I with shorter C-C distance is responsible for the observed MATI spectrum. The spectrum of La₃C₂O shows short progressions of different vibrational modes of the cluster in its neutral and ionic ground states. They were identified as the C-La₈, O-La₈, La₈-La₈, and La₈C₂-La₈O-La₈ stretching modes. La₃C₂O is likely formed by the reaction of La₃C₂ with an oxygen atom or molecule. The oxygen atom in the cluster is in the La₈ plane and binds to the La₈ atoms.
Table 7.1 Peak positions (cm⁻¹) and assignments for the MATI spectra of Sc₃C₂ and La₃C₂.

The values in parentheses are relative to the positions of the origin bands.

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Table 7.2 Peak positions (cm$^{-1}$) and assignments for the MATI spectrum of La$_3$C$_2$O.

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Table 7.3 Calculated electronic states, geometric parameters, and relative energies (eV) of M$_3$C$_2^{0/+1}$ (M=Sc, La) and La$_3$C$_2$O$^{0/+1}$. Five bond distances (Å) are M$_d$-M$_d$ (R$_1$), M$_s$-M$_s$ (R$_2$), M$_d$-C (R$_s$), M$_d$-C (R$_d$) and M$_d$-O (R$_d'$), four angles (degree) are the dihedral angle of M$_d$-C-C-M$_d$ (D) and the bond angles of M$_d$-C-M$_d$ (A$_1$), M$_s$-C-M$_d$ (A$_2$), and M$_d$-O-M$_d$ (A$_1'$).

The calculations are carried out at DFT/B3LYP level with lanL2DZ basis sets for metals and aug-cc-pVTZ basis set for carbon and oxygen.

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Table 7.4 Point groups, electronic states and relative energies ($E_{rel}$), and transition energies ($\Delta E$) of the La$_3$C$_2$O isomers from DFT/B3LYP calculations.\textsuperscript{a}

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<td>2.069</td>
<td>$^1$A'</td>
</tr>
<tr>
<td></td>
<td>$^4$A''</td>
<td>2.594</td>
<td>3A'</td>
</tr>
<tr>
<td>(E) C$_s$</td>
<td>$^2$A'</td>
<td>2.904</td>
<td>$^1$A'</td>
</tr>
<tr>
<td></td>
<td>$^4$A''</td>
<td>3.413</td>
<td>3A'</td>
</tr>
<tr>
<td>(F) C$_s$</td>
<td>$^2$A''</td>
<td>0.066</td>
<td>$^1$A'</td>
</tr>
<tr>
<td></td>
<td>$^4$A'</td>
<td>0.641</td>
<td>$^3$A'</td>
</tr>
<tr>
<td>(G) C$_s$</td>
<td>$^2$A''</td>
<td>3.419</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^4$A''</td>
<td>3.434</td>
<td>$^3$A''</td>
</tr>
<tr>
<td>(H) C$_1$</td>
<td>$^2$A</td>
<td>2.445</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$^4$A</td>
<td>2.444</td>
<td>$^3$A</td>
</tr>
</tbody>
</table>

\textsuperscript{a} LanL2DZ basis set is used for La atom, aug-cc-pVTZ basis sets are used for C and O atoms.

\textsuperscript{b} The triplet state of structure (A), singlet and triplet states of structure (B), and singlet and quartet states of structure (F) are transition states.
Table 7.5 Calculated vibrational frequencies (cm\(^{-1}\)) and their symmetries in comparison with the experimental measurements for \(M_3C_2\) (\(M=\text{Sc and La}\)) and their cations.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Symmetry</th>
<th>Frequencies (^{a})</th>
<th>Vibrational Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_3)</td>
<td>(a_1)</td>
<td>338(314) 154(178)</td>
<td>(M_3) ring breathing</td>
</tr>
<tr>
<td>(v_4)</td>
<td>(a_1)</td>
<td>95(96) 67(58)</td>
<td>(M_d)-C-(M_d) bending</td>
</tr>
<tr>
<td>(v_9)</td>
<td>(a_1)</td>
<td>95(96) 67(58)</td>
<td>(M_s) deformation</td>
</tr>
<tr>
<td>(v_4)</td>
<td>(a_1)</td>
<td>116(109) 77(66)</td>
<td>(M_d)-C-(M_d) bending</td>
</tr>
<tr>
<td>(v_9)</td>
<td>(b_1)</td>
<td>28(33) (21)</td>
<td>(M_s) deformation</td>
</tr>
</tbody>
</table>

\(^{a}\) the calculated values are in the brackets.
Table 7.6 Calculated vibrational frequencies (cm$^{-1}$) and their symmetries in comparison with the experimental measurements for La$_3$C$_2$O in its neutral and ion states at C$_{2v}$ symmetry.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Symmetry</th>
<th>Frequencies$^a$</th>
<th>Vibrational Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v^+_1$</td>
<td>$a_i$</td>
<td>665 (669)</td>
<td>C-La$_s$ stretch</td>
</tr>
<tr>
<td>$v^+_2$</td>
<td>$a_i$</td>
<td>(596)</td>
<td>C-C stretch</td>
</tr>
<tr>
<td>$v^+_3$</td>
<td>$a_i$</td>
<td>530 (519)</td>
<td>O-La$_d$ stretch</td>
</tr>
<tr>
<td>$v^+_4$</td>
<td>$a_i$</td>
<td>235 (212)</td>
<td>La$_d$-La$_d$ stretch</td>
</tr>
<tr>
<td>$v^+_5$</td>
<td>$a_i$</td>
<td>160 (143)</td>
<td>La$_s$C$_2$-La$_d$OLa$_d$ stretch</td>
</tr>
<tr>
<td>$v^-_5$</td>
<td>$a_i$</td>
<td>155 (157)</td>
<td>La$_s$C$_2$-La$_d$OLa$_d$ stretch</td>
</tr>
<tr>
<td>$v^+_9 - v^-_9$</td>
<td>$b_i$</td>
<td>38 (29)</td>
<td>La$_s$ deformation</td>
</tr>
</tbody>
</table>

$^a$ the calculated values are in the brackets.
Figure 7.1 MS-TOF spectra of Sc +C2H4 (a) and La + C2H4 (b) recorded with 240 nm UV laser, the five peaks shown in the zoomed region from left to right are: M3C2, M3C2H4, M3O2, M3C3, and M3C2O (M = Sc and La).
Figure 7.2 MATI spectra of Sc$_3$C$_2$ with He (a) and He/Ar (2:1) mixture (b) carrier gas.
Figure 7.3 MATI spectra of La$_3$C$_2$ with He (a) and Ar (b) carrier gas.
Figure 7.4 MATI spectra of La₃C₂O with He (a) and Ar (b) carrier gas.
Figure 7.5 MATI spectra of Sc$_3$C$_2$ in He/Ar (2:1) mixture as carrier gas (a) and simulations (30 K) of isomer I (b-d) and isomer II (e-g) from B3LYP calculations with the lanL2DZ basis for Sc and the aug-cc-pVTZ basis for O.
Figure 7.6 MATI spectra of La$_3$C$_2$ in Ar as carrier gas (a) and simulations (10K) of isomer I (b-d) and isomer II (e-g) from B3LYP calculations with the lanL2DZ basis for La and the aug-cc-pVTZ basis for O.
Figure 7.7 Possible isomers of La$_3$C$_2$O.
Figure 7.8 MATI spectra of La$_3$C$_2$O in He (a) and simulations (100 K) of possible transitions (b-f) from B3LYP calculations with the lanL2DZ basis for La and the aug-cc-pVTZ basis for O.
Figure 7.9 Molecular orbital diagrams for the ground states of isomer I (a) and II (b) of La$_3$C$_2$, and the ground state of La$_3$C$_2$O (c).
CHAPTER 8 SUMMARY OF DISSERTATION

In this dissertation, the MATI spectra have been reported for eleven group 3 small metal clusters, including six lanthanum, two yttrium and three scandium clusters. These spectra are summarized in Figure 8.1 with the measured AIEs. The AIEs, bonding, structures, electronic states, and some of the vibrational frequencies of the metal clusters are determined by combining the spectroscopic analysis with the quantum mechanical calculations. These spectroscopic properties are compared by different cluster sizes with the same metal element and also same size clusters with different metal substitutes.

The AIEs of the metal clusters exhibit a red shift comparing to that of the free atoms, as summarized in Table 8.1. For the same metal, the AIEs show decrease trend when the size of cluster increases. Lanthanum clusters, for example, show an increase trend in AIEs following the sequence of La₂, La₂O₂, and La₃O₄. One the other hand, La₃O₄, La₃C₂ and La₃C₂O clusters with the similar sizes have comparable AIEs. For different metal clusters with the same size, the AIEs have comparable red shifts from the free atoms. The AIEs are about 1 eV lower than the respective free atoms for the M₂O₂ clusters and about 2 eV for the M₃O₄ and M₃C₂ clusters.

Strong ionic characters exist between the metal and oxygen or carbon atoms and can be described for different metal clusters as [O⁰][La²⁺][O⁰], [M²⁺]₂[O²⁻]₂, [M⁸⁺⁺]₃[O²⁻]₄, [M²⁺]₃[C³⁻]₂, and [La⁸⁺⁺]₃[C³⁻]₂[O²⁻]. The interactions between the metal atoms form covalent bonds, which can be described by a triple bond in La₂, a two-center two electron bond in M₂O₂, a three-center one electron bond in M₃O₄, and a three-center three electron
bond in M$_3$C$_2$. Besides, the electrons in the non-bonding HOMO is localized in La 6s orbital in LaO$_2$ and La$_3$C$_2$O.

The ground states of these molecules are all in low electron-spin states, and are generally responsible for the MATI spectra. M$_2$O$_2$ and M$_3$O$_4$ have planar rhombic and cage-like three dimensional structures, respectively; whereas M$_3$C$_2$ has a trigonal bipyramid structure. Low-lying electronic states are observed instead for LaO$_2$ and La$_3$C$_2$O. Although the ground electronic state of LaO$_2$ is in a linear structure, the excited state of the molecule is determined to be in a bent structure. La$_3$C$_2$O is formed by oxygen binding with two La atoms of La$_3$C$_2$, but its ground state is the trigonal bipyramid structure with C$_2$ and O on each side of the La$_3$ plane. Ionization removes a metal-based (n+1)s electron in all neutral molecules, and the resultant ions have similar geometries to those of the corresponding neutral states. In the case of La$_2$, additional ionization of a La 5d electron is also observed.

The vibrational motions are complicated in the polyatomic clusters. However, some of the modes are distinguishable in different clusters. The metal-metal stretch mode, La-La for example, are observed as 236/242, 245, and 235 cm$^{-1}$ in La$_2^+$, La$_2$O$_2^+$ and La$_3$C$_2$O$^+$, respectively. These frequencies varies within a small range and are also close to the M$_3$ breath mode of La$_3$O$_4$. However, the M$_3$-breathing frequency is much smaller in La$_3$C$_2$, probably because of its more deformative structure compared to the fused four-member ring structures in La$_3$O$_4$. The metal-ligand stretch frequencies have larger derivatives, but they are overall larger than the metal-metal stretch frequencies. All these metal-metal, metal-ligand (oxygen or carbon) stretch and bending frequencies are summarized in Table 8.2.
Table 8.1 Summary of ionization energies (eV) for $\text{M}_2\text{O}_2$, $\text{M}_3\text{O}_4$ and $\text{M}_3\text{C}_2$ ($\text{M} = \text{Sc, Y, and La}$). The relative ionization energies (eV), comparing to the free atoms, are included in the brackets.

<table>
<thead>
<tr>
<th></th>
<th>Sc</th>
<th>Y</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{M}^a$</td>
<td>6.561 (0)</td>
<td>6.217 (0)</td>
<td>5.577 (0)</td>
</tr>
<tr>
<td>$\text{MO}_2$</td>
<td></td>
<td>4.976 (-0.601)</td>
<td></td>
</tr>
<tr>
<td>$\text{M}_2$</td>
<td></td>
<td>4.841 $^b$ (-0.736)</td>
<td></td>
</tr>
<tr>
<td>$\text{M}_2\text{O}_2$</td>
<td>5.575 (-0.986)</td>
<td>5.264 (-0.953)</td>
<td>4.580 (-0.997)</td>
</tr>
<tr>
<td>$\text{M}_3\text{O}_4$</td>
<td>4.456 (-2.105)</td>
<td>4.059 (-2.158)</td>
<td>3.475 (-2.102)</td>
</tr>
<tr>
<td>$\text{M}_3\text{C}_2$</td>
<td>4.512 (-2.049)</td>
<td>4.224$^c$ (-1.993)</td>
<td>3.742 (-1.835)</td>
</tr>
<tr>
<td>$\text{M}_3\text{C}_2\text{O}$</td>
<td></td>
<td>3.829 (-1.748)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ From ref. $^{194}$

$^b$ The ionization energy when removing a metal based 6s electrons.

$^c$ From ref. $^{214}$
Table 8.2 Summary of the observed metal-metal (M-M) stretch, and metal-ligand (M-L) stretch or bending frequencies (in cm$^{-1}$). The stretch and bending modes are noted as $v$ and $\delta$; superscript ‘+' indicates the frequencies of the ions; asymmetric modes are noted in the superscript ‘as’.

<table>
<thead>
<tr>
<th></th>
<th>M-M$^a$</th>
<th>M-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaO$^b$</td>
<td>$v / v^+ = 207 / 236( \Sigma^+_g, 242( \Pi)$</td>
<td>$v^+ = 808 / 878$</td>
</tr>
<tr>
<td>La$_2$</td>
<td>$v / v^+ = 254 / 245$</td>
<td>$v^+ = 569 / 591$</td>
</tr>
<tr>
<td>La$_2$O$_2$</td>
<td>$v / v^+ = 279 / 285$</td>
<td>$v^+ = 655$</td>
</tr>
<tr>
<td>Y$_2$O$_2$</td>
<td>$v / v^+ = 395 / 415$</td>
<td>$v^+ = 713$</td>
</tr>
<tr>
<td>Sc$_2$O$_2$</td>
<td>$v / v^+ = 251$</td>
<td>$v^+ = 531,421$</td>
</tr>
<tr>
<td>La$_3$O$_4$</td>
<td>$v^{+} = 627, \delta^{+} = 204$</td>
<td>$v^{+} = 627,475$</td>
</tr>
<tr>
<td>Y$_3$O$_4$</td>
<td>$v^{+} = 314$</td>
<td>$v^{+} = 678,238$</td>
</tr>
<tr>
<td>Sc$_3$O$_4$</td>
<td>$v^{+} = 437, v^{\pm,as} = 300$</td>
<td>$v^{+} = 667,545$</td>
</tr>
<tr>
<td>La$_3$C$_2$</td>
<td>$v^{+} = 154$</td>
<td>$v^{+} = 751,273, \delta^{+,as} = 204$</td>
</tr>
<tr>
<td>Y$_3$C$_2$</td>
<td>$v^{+} = 228$</td>
<td>$\delta^{+} = 77 / 67$</td>
</tr>
<tr>
<td>Sc$_3$C$_2$</td>
<td>$v^{+} = 338$</td>
<td>$\delta^{+} = 82 / 86$</td>
</tr>
<tr>
<td>La$_3$C$_2$O</td>
<td>$v^{+} = 235 (La-La stretch)$</td>
<td>$v^{+} = 665(C-La stretch)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$v^{+} = 530(O-La stretch)$</td>
</tr>
</tbody>
</table>

$^a$ Frequencies in this column mean M-M stretch for the La$_2$, M$_2$O$_2$ and La$_3$C$_2$O, and M$_3$ ring breath for M$_3$O$_4$ and M$_3$C$_2$

$^b$ Unpublished results

$^c$ From Ref. 214
Figure 8.1 Summary of the MATI spectra of metal clusters and their AIEs (eV).
In the following, we will show that Equation (2.4) is correct when the additional acceleration times of the particles are considered. For the convenience of the discussion, the TOF spectrometer can be divided into four travelling zones of the charged particles, as illustrated in Figure-A. The particles travel with constant velocities in zone III, which is a field-free TOF tube. They are speeded up with constant accelerations in zone I, II and IV, which have uniform electric fields. In the ith flight zone, the strength and potential of the electric field, the flight distance, flight time, and exiting velocity of the particle are $E_i$, $U_i$, $d_i$, $t_i$ and $v_i$ ($i = 1, 2, 3, 4$), respectively.

For a particle with the initial velocity, mass, and charge of $v_0$, $m$ and $q$, its exiting velocity in each flight zone can be calculated by the energy conservation rule from Equation (A-1):

$$\frac{1}{2}mv_i^2 - \frac{1}{2}mv_0^2 = \sum_j E_jd_jq$$

(A-1)

Where $v_0$ is zero for a TOF spectrometer with perpendicular configuration. $E_i$ and $d_i$ ($i= 1, 2, 3, 4$) are constants related to the setup of the TOF spectrometer.

Thus, Equation (A-1) can be simplified as:

$$v_i = \sqrt{\frac{2q}{m}} \cdot \sqrt{\sum_j E_jd_j}$$

(A-2)

The travelling time can be calculated from the following equations:
Where $A_i$ ($i = 1, 2, 3, 4$) are constants related to the parameters of the TOF spectrometer.

The total travelling time can be calculated with Equation (2.4), and the coefficient $A$ is the summation of the $A_i$s ($i = 1, 2, 3, 4$). By considering aluminum ($m = 27$ amu, $t = 3.66 \mu s$) atom as the reference, the constant $A$ in Equation (2.3) is calculated to be $0.7044 (\mu s \cdot amu^{-1/2})$.

Besides the travelling time, the total flight time of the charged particles also includes the response time of the MCP detector ($< 1$ ns), the travelling time of the electrons emitted from the MCP detector to the anode, and the travelling time of the signal from anode to the computer. The time consumed in these processes is small and constants and thus generally ignored in the measurements. If we include all these factors, the total flight time can be calculated more precisely by adding a small constant $B$:

$$t = A\sqrt{m} + B$$  \hspace{1cm} (A-4)

For the current experimental setup, by considering helium ($m = 4$ amu, $t = 1.44 \mu s$) and aluminum ($m = 27$ amu, $t = 3.66 \mu s$) atoms as references, $A$ and $B$ are calculated to be: $A = 0.6946 (\mu s \cdot amu^{-1/2}), B = 0.0508 (\mu s)$. Thus, the bias of the total flight time from Equation (2.3) is expressed as:
\[ \Delta t / (\mu s) = 0.0098 \sqrt{m/(amu.)} - 0.0508 \]  
(A-5)

\( \Delta t \) is small at a lower mass range and will increase with the masses of the particles, as shown in Equation (A-5). In Chapter 2, two methods are mentioned to predict the flight time and help assign the mass spectra. In the mass spectra of the metal oxides, the adjacent peaks generally have a mass difference of 16 (amu.) or larger. The first method is sufficiently accurate to distinguish different mass peaks when the masses of the metal oxides are small. For example, the travelling time of ScO (m = 71 amu.) is calculated to be 5.9354 \( \mu s \) from Equation (2.3). In the mass spectrum of scandium oxides, three adjacent peaks appear at 5.20, 5.90 and 6.53 \( \mu s \). Thus, the middle peak can be assigned to ScO straightforwardly. However, this method fails when the masses of the particles are very different from that of the reference element (aluminum). For example, the flight time of La_3O_4 (m = 481 amu.) is calculated to be 15.45 \( \mu s \) by Equation (2.4), but the mass spectrum of lanthanum oxides exhibits two peaks with the flight times of 15.29 and 15.54 \( \mu s \), both are close to the calculated value of 15.45 \( \mu s \). Therefore, the second method must be used to assign this mass spectrum. To do so, we use La_2O_2 (t = 12.28 \( \mu s \), m = 310 amu.) or La_3O_3 (t = 15.18 \( \mu s \), m = 465 amu.) as a reference and calculate the flight time of La_3O_4 using Equation (2.4). The flight times of La_3O_4 are predicted to be 15.29 and 15.30 \( \mu s \) with La_2O_2 and La_3O_3 as the references, respectively. Both values match nicely with the measured flight time of 15.29 \( \mu s \), but are quite different from 15.54 \( \mu s \). Thus, the peak at 15.29 \( \mu s \) can easily be assigned to La_3O_4.
Figure Appendix Illustration of the acceleration zones in the time-of-flight spectrometer, \( d \) is the distance between the two metal cans; \( d_1 \) is the distance between the molecular beam and the upper can; \( d_2 \) is the distance from the upper can to the bottom of the TOF tube; \( d_3 \) is the length of the TOF tube; \( d_4 \) is the distance from the top of TOF tube to the MCP detector.
REFERENCES:


K.-F. Hu, Phys. Rev., 11, 505 (1918)
121 M. Born and J. P. Oppenheimer, Ann. Phys., 84, 457 (1927)
122 M. Head-Gordon, R. J. Rico, M. Oumi and T. J. Lee, Chem. Phys. Lett., 219, 21
123 (1994)
125 C. Møller and M. S. Plesset, Phys. Rev., 46, 618 (1934)
134 K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, Chem. Phys. Lett.,
135 157, 479 (1989)
141 288, 299 (1998)
149 S. Li, Threshold Photoionization and ZEKE Photoelectron Spectroscopy of Metal
150 Complexes, (University of Kentucky, 2004)
151 D.-S. Yang, M. Z. Zgierski, D. M. Rayner, P. A. Hackett, A. Martinez, D. R.
153 A. Berces, M. Z. Zgierski and D. S. Yang, Computational Molecular Spectroscopy,
154 (Weley, New York City, 2000).
156 034307 (2012)
161 of Standards.
VITA

B. Sc., Chemical Physics
University of Science and Technology of China 2003-2007

Publications:


5. Lu Wu, Changhua Zhang, Serge A. Krasnokutski, and Dong-Sheng Yang, "Mass-analyzed threshold ionization and structural isomers of M$_2$O$_2$ (M = Sc, Y, and La)" submitted
Conference Presentations:

1. **Lu Wu**, Roudjane Mourad, Yang Liu, and Dong-Sheng Yang, "Mass-Analyzed threshold ionization of lutetium dimer" (oral), June 18-22, 2013, 68th International Symposium on Molecular Spectroscopy, Columbus, Ohio.

2. **Lu Wu**, Beni Dangi, Roudjane Mourad, and Dong-Sheng Yang, "Mass-Analyzed threshold ionization of $M_2O_2$ ($M =$ Ce and Pr)" (oral), June 17-21, 2012, 67th International Symposium on Molecular Spectroscopy, Columbus, Ohio.

3. **Lu Wu** and Dong-Sheng Yang, 7th Kentucky Innovation and Entrepreneurship Conference (poster), June 1, 2011, Louisville, Kentucky.


5. **Lu Wu** and Dong-Sheng Yang, 7th Kentucky Innovation and Entrepreneurship Conference (poster), June, 2011, May 26, Louisville, Kentucky.

6. **Lu Wu**, Changhua Zhang, Sergiy Krasnokutski, and Dong-Sheng Yang, "Mass-Analyzed threshold ionization of La$_2$O$_2$" (oral), June 21-25, 2010, 65th International Symposium on Molecular Spectroscopy, Columbus, Ohio.

7. **Lu Wu** and Dong-Sheng Yang, 6th Kentucky Innovation and Entrepreneurship Conference (poster), April 6, 2010, Lexington, Kentucky.

8. **Lu Wu**, Changhua Zhang, Sergiy Krasnokutski, and Dong-Sheng Yang, "Mass-Analyzed threshold ionization of Lanthanum oxide clusters", June 22-26, 2009, 64th International Symposium on Molecular Spectroscopy, Columbus, Ohio.