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Optical-optical double resonance, laser induced fluorescence, and revision of the signs of the spin-spin constants of the boron carbide (BC) free radical

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The cold boron carbide free radical ($\text{BC } X^4\Sigma^-$) has been produced in a pulsed discharge free jet expansion using a precursor mixture of trimethylborane in high pressure argon. High resolution laser induced fluorescence spectra have been obtained for the $B^4\Sigma^- - X^4\Sigma^-$ and $E^4\Pi - X^4\Sigma^-$ band systems of both ^{11}BC and ^{10}BC . An optical-optical double resonance (OODR) scheme was implemented to study the finer details of both band systems. This involved pumping a single rotational level of the B state with one laser and then recording the various allowed transitions from the intermediate B state to the final E state with a second laser by monitoring the subsequent $E-X$ ultraviolet fluorescence. In this fashion, we were able to prove unambiguously that, contrary to previous studies, the spin-spin constant λ is negative in the ground state and positive in the $B^4\Sigma^-$ excited state. It has been shown that $\lambda'' < 0$ is in fact expected based on a semiempirical second order perturbation theory calculation of the magnitude of the spin-spin constant. The OODR spectra have also been used to validate our assignments of the complex and badly overlapped $E^4\Pi - X^4\Sigma^-$ 0-0 and 1-0 bands of ^{11}BC . The $E-X$ 0-0 band of ^{10}BC was found to be severely perturbed. The ground state main electron configuration is $\dots 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^2 2\pi^0$ and the derived bond lengths show that there is a $0.03 \text{ \AA}$ contraction in the B state, due to the promotion of an electron from the 4σ antibonding orbital to the 5σ bonding orbital. In contrast, the bond length elongates by $0.15 \text{ \AA}$ in the E state, a result of promoting an electron from the 5σ bonding orbital to the 2π antibonding orbitals. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4936255>]

I. INTRODUCTION

Solid boron carbide (BC) is a dark gray or black ceramic material with approximate molecular formula B_4C . It has numerous industrial applications because of its extreme hardness (9.497 on the Mohs scale), high melting point (2763°C), and chemical inertness. It is used in scratch and wear resistant coatings, cutting tools and dies, brake linings, bulletproof vests and abrasives to name just a few. Boron carbide films and structures are usually produced by chemical vapor deposition (CVD) processes, often involving precursor mixtures of methane, hydrogen, and a suitable boron compound such as BCl_3 , BBr_3 , or B_2H_6 , or a boron-carbon species such as trimethylborane $[\text{B}(\text{CH}_3)_3]$.¹ Despite considerable interest and inquiry both experimentally and theoretically, much remains to be understood about the detailed mechanism of boron carbide CVD.

The simple diatomic molecule, gas phase BC, is in many ways the antithesis of solid boron carbide. It is a highly reactive free radical with very limited chemical stability and no known industrial applications. Yet, it may be an important intermediate in boron carbide CVD processes. To date, it has not been studied under CVD conditions, at least in part

because the necessary spectroscopic data for remote sensing or *in situ* detection are lacking.

BC was first generated in the gas phase using high temperature boron-carbon reactions in a Knudsen cell and detected by electron impact mass spectrometry.² In 1988, Knight *et al.*³ reported generating BC by laser vaporization of a boron-carbon mixture, trapping the molecules in rare gas matrices at 4 K, and measuring the ESR spectrum, confirming prior theoretical predictions that BC has a $^4\Sigma^-$ ground state. In 1990, Fernando, O'Brien, and Bernath⁴ published the first electronic spectrum of BC, the $B^4\Sigma^- - X^4\Sigma^-$ transition, observed in emission near 559 nm. The authors determined a ground state equilibrium bond length of $1.49116 \text{ \AA}$, which elongated to $1.46023 \text{ \AA}$ in the excited state. The spin-spin parameter for the ground state was evaluated to be $\lambda = +0.0282 \text{ cm}^{-1}$, whereas the excited state had an anomalous negative value of -0.046 cm^{-1} . In 1996, Smith *et al.*⁵ reported trapping the products of the laser vaporization of boron/carbon pellets in solid neon at 6 K and studying the absorption and laser-induced emission spectra of the trapped diatomic BC molecule. The $B^4\Sigma^- - X^4\Sigma^-$ absorption and emission spectra and the $B^4\Sigma^- - A^4\Pi$ and $d^2\Sigma^+ - a^2\Pi$ (through intersystem crossing) near-infrared emission spectra were observed and the vibrational constants of these five low-lying states were reported. In 1998, Wyss *et al.*⁶ reported a new band system of BC in neon matrices at 5 K and assigned the system of

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near-UV bands as $C^4\Pi-X^4\Sigma^-$, although we prefer to label it as $E-X$, based on more recent theoretical calculations (*vide infra*).

Most recently (2011), Ng, Pang, and Cheung⁷ reported the observation of laser-induced fluorescence of gas phase BC. The authors produced the boron carbide molecule by the complex reaction of 0.5% B_2H_6 and 3% CH_4 in argon in the presence of laser-ablated magnesium atoms. They recorded laser-induced fluorescence spectra of the 2-0, 1-0, and 0-0 bands (^{11}BC and ^{10}BC) of the $B^4\Sigma^-X^4\Sigma^-$ system, with marginally resolved spin fine structure. The bands were rotationally analyzed and fitted, but the spin-spin constants were fixed at the values reported by Fernando *et al.*⁴ Equilibrium vibrational and rotational constants were reported for both isotopologues.

BC has received considerable theoretical attention.^{3,8-13} The most extensive calculations to date are those of Tzeli and Mavridis^{12,13} in which large correlation consistent basis sets (up to quintuple zeta) and multireference variational methods were used to predict the molecular properties. The potential energy curves and spectroscopic constants of 29 excited electronic states of BC were calculated, providing excellent guidelines for future experimental studies.

In the present work, we have reinvestigated the $B^4\Sigma^-X^4\Sigma^-$ band systems of ^{11}BC and ^{10}BC by laser-induced fluorescence and wavelength resolved emission spectroscopy. The $E^4\Pi-X^4\Sigma^-$ band system of both isotopologues has also been thoroughly studied by a variety of experimental techniques including optical-optical double resonance (OODR) spectroscopy through the $B^4\Sigma^-$ state.

II. EXPERIMENT

The ^{11}BC and ^{10}BC free radicals were produced in a discharge free jet expansion¹⁴ using precursor mixtures of 1% $B(CH_3)_3$ (in boron natural abundance or enriched in ^{10}B) in high pressure argon. The gas mixture was injected at a pressure of 30–40 psi through the 0.8 mm orifice of a pulsed molecular beam valve (General Valve, Series 9) into the vacuum chamber. After a short time delay, a pulsed electric discharge was struck between a pair of ring electrodes mounted in a cylindrical Delrin flow channel attached to the exit to the valve, fragmenting the precursors and producing BC by secondary reactions. The radicals were cooled to low rotational temperatures (~ 10 K) by collisions downstream of the discharge. A 1.0 cm reheat tube¹⁵ was attached to the exit of the discharge flow channel to increase the number of collisions, which both enhanced the production of the radicals and suppressed the background glow from electronically excited argon atoms.

Low-resolution laser induced fluorescence (LIF) spectra were recorded by exciting the jet-cooled radicals with the collimated beam of a pulsed tunable dye laser (Lumonics HD-500, linewidth 0.1 cm^{-1}) and imaging the resulting fluorescence signals onto the photocathode of a high gain photomultiplier (EMI 9816QB). The signals were sampled with a gated integrator and recorded with LabVIEW-based data acquisition software. The spectra were calibrated with optogalvanic lines from neon- and argon-filled hollow cathode

lamps to an accuracy of $\pm 0.1\text{ cm}^{-1}$. High resolution spectra were obtained in the same fashion but using a dye laser equipped with an intracavity angle-tuned etalon (Scanmate 2E), providing tunable radiation with a linewidth of 0.035 cm^{-1} . For the $E-X$ ultraviolet bands, the high resolution laser was frequency doubled, with a concomitant doubling of the linewidth. All high resolution spectra were calibrated with iodine LIF transitions.¹⁶

The LIF spectra were complicated by overlapping bands of ^{11}BC and ^{10}BC and fluorescence from various impurity species produced in the electric discharge. To circumvent these problems, we used the LIF synchronous scanning (sync-scan) technique described previously.¹⁷ In this method, the fluorescence is dispersed by a scanning monochromator, which is fixed on a prominent emission band of the isotopologue of interest. The excitation laser and the monochromator are scanning synchronously under computer control so that the resulting spectrum exhibits only those transitions that emit down to the chosen level, focusing on the spectrum of a subset of the molecular isotopologues and minimizing impurity emission. For example, we were able to obtain LIF spectra of ^{11}BC essentially free of ^{10}BC bands using this technique.

Single vibronic level emission spectra were obtained by laser excitation of the intensity maxima of the stronger bands observed in the LIF sync-scan spectra. The resulting fluorescence was focused onto the entrance slit of a 0.5 m scanning monochromator (Spex 500M) and the emission was detected with a cooled, red-sensitive photomultiplier (RCA C31034A), amplified by a factor of ~ 1000 , processed with a gated integrator, and then recorded digitally. The spectra were calibrated with emission lines from an argon discharge lamp to an estimated accuracy of $\pm 1\text{ cm}^{-1}$. The monochromator was equipped with a 1200 line/mm grating blazed at 750 nm and spectra were recorded with a bandpass of 0.1–0.4 nm, depending on the strength of the fluorescence.

In order to simplify the complex and badly overlapped high-resolution $E^4\Pi-X^4\Sigma^-$ 0-0 bands, we implemented an optical-optical double resonance scheme.¹⁸ This involved using one laser in the green to pump a single rotational “line” (actually a group of very closely spaced spin-components) of the $B^4\Sigma^-X^4\Sigma^-$ transition, a second counterpropagating red laser, spatially overlapped and temporally delayed by about 30 ns, to transfer population to the E state through the allowed $E^4\Pi-B^4\Sigma^-$ transition, and detection of the subsequent ultraviolet $E^4\Pi-X^4\Sigma^-$ fluorescence with the monochromator. By fixing the green laser and scanning the red laser (both with 0.1 cm^{-1} linewidth), we were able to record all the allowed rotational transitions from the B state level of known N to the various E state rotational levels. These OODR spectra contained many fewer transitions than the $E-X$ LIF spectra and were much easier to assign, ultimately facilitating a complete analysis of the $E^4\Pi-X^4\Sigma^-$ bands.

Trimethylborane was synthesized by the reaction of trimethylaluminum with boron tribromide as described in detail elsewhere.¹⁹ For experiments involving $^{10}B(CH_3)_3$ samples, we synthesized $^{10}BBr_3$ by the reaction of $^{10}BF_3$ (Ceradyne, $<96\%$ ^{10}B enrichment) with $AlBr_3$ by the procedure of Gamble.²⁰

III. EXPERIMENTAL RESULTS AND ANALYSIS

The low-lying boron carbide electronic states of quartet multiplicity are shown schematically in Fig. 1. The ground state molecular orbital configuration is $\dots 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^2 2\pi^0$ ($^4\Sigma^-$). In the simplest approximation, 3σ and 4σ are the $\sigma 2s$ and $\sigma^* 2s$ MO's, 5σ is $\sigma 2p_z$, 1π denotes the $\pi 2p_x$ and $\pi 2p_y$ MO's, and 2π includes the antibonding $\pi^* 2p_x$ and $\pi^* 2p_y$ orbitals. Promotion of the 4σ electron to the 1π orbitals yields the low-lying $A^4\Pi$ state. The $B^4\Sigma^-$ state is primarily due to the $\dots 3\sigma^2 4\sigma^1 5\sigma^2 1\pi^2$ configuration and the higher C and D states are both dominated by the $\dots 4\sigma^2 5\sigma^1 1\pi^1 2\pi^1$ configuration involving the higher energy 2π orbital.^{9,13} Finally, the E state is an admixture of the $\dots 4\sigma^1 5\sigma^1 1\pi^2 2\pi^1$ and $\dots 4\sigma^2 5\sigma^0 1\pi^2 2\pi^1$ configurations.⁹ The present work involves LIF and wavelength resolved emission spectroscopy of the $B^4\Sigma^- - X^4\Sigma^-$ and $E^4\Pi - X^4\Sigma^-$ electronic transitions and optical-optical double resonance experiments from the ground state to the E state through the intermediate B state. We have taken advantage of the two boron isotopes present in natural abundance ($^{11}\text{B} = 80.1\%$, $^{10}\text{B} = 19.9\%$) to study both ^{11}BC and ^{10}BC .

A. The $B^4\Sigma^- - X^4\Sigma^-$ band system

Ours is the first effort to produce BC spectra using a trimethylborane precursor. As shown in the top panel of Fig. 2, the initial total LIF spectra were rather congested and overlapped, due to the two BC isotopologues and the presence of C_2 bands in the same region. However, sync-scan LIF

FIG. 1. Schematic energy level diagram of the low-lying quartet states of the boron carbide diatomic molecule. Solid horizontal lines indicate states that have been observed experimentally; dashed lines are states that have been predicted by *ab initio* theory. The vertical arrows indicate LIF, emission, and OODR transitions observed in the present work.

FIG. 2. Low resolution LIF spectra of the $B^4\Sigma^- - X^4\Sigma^-$ band system of BC. The top trace is the spectrum obtained by detecting the total LIF signal through a longpass filter. The middle trace is the sync-scan LIF spectrum of ^{11}BC with a monochromator offset of 1150 cm^{-1} , corresponding to the ground state $v = 1 - v = 0$ interval. The bottom trace is the sync-scan LIF spectrum of ^{10}BC with a monochromator offset of 1190 cm^{-1} .

spectra, in which we detected only the ^{11}BC emission down to $v'' = 1$ (a 1150 cm^{-1} offset from the laser), were much cleaner as shown in the second panel of Fig. 2. Changing the sync-scan offset to 1190 cm^{-1} (the ^{10}BC $v = 1 - v = 0$ ground state interval) allowed us to record a similar spectrum of ^{10}BC in natural abundance (see Fig. 2, bottom panel). There is nothing new here as these spectra were previously studied in emission⁴ and LIF with jet-cooling.⁷

In the ground $^4\Sigma^-$ electronic state, each rotational level of a given $N > 2$ consists of four very closely spaced spin components labeled F_1 ($J = N + 3/2$), F_2 ($J = N + 1/2$), F_3 ($J = N - 1/2$), and F_4 ($J = N - 3/2$). Here, N is the quantum number for end-over-end rotation of the molecule exclusive of electron spin and J is the total angular momentum including electron spin. For a given N , the spin components cluster together and their order depends on the signs of the spin-spin constant λ and the spin-rotation constant γ . A convenient energy level diagram, with greatly exaggerated spin splittings, for the $B^4\Sigma^- - X^4\Sigma^-$ transition is given in Fig. 3 of Ref. 4.

Using $\text{B}(\text{CH}_3)_3$ and enriched $^{10}\text{B}(\text{CH}_3)_3$ precursors, and our highest resolution laser (0.035 cm^{-1}) with sync-scan detection, we recorded high resolution rotationally resolved $B-X$ sync-scan LIF 0-0 band spectra of jet-cooled ^{11}BC and ^{10}BC , the latter shown in Fig. 3. The insets show that the low- N lines exhibit partially resolved spin-splittings, for the first time. The spin-splittings are very small and clearly correspond to Hund's case (b).

Focusing on the $R(0)$ line, three components are evident, as expected for a transition from $N'' = 0$ with only a single $J = |N + \Sigma| = 1.5$ spin-rotational level to three upper state levels with $N' = 1$ and $J = 2.5$ (F_1), 1.5 (F_2), and 0.5 (F_3). The relative intensities are controlled almost solely by line strength factors,²¹ which indicate that the transitions should be in the ratio $1:0.62:0.34$, with the weaker transition terminating on $J = 0.5$. Comparing to experiment, this locates the upper state $N = 1$ energy levels with $J = 0.5$ (F_3) $<$ $J = 2.5$ (F_1) $<$ $J = 1.5$ (F_2), which can only be the case if the spin-spin

FIG. 3. A high resolution sync-scan LIF spectrum of the $B^4\Sigma^- - X^4\Sigma^-$ 0-0 band of ^{10}BC . The insets show the partially resolved spin structure of the $P(1)$, $R(0)$, and $R(1)$ rovibronic transitions. The vertical arrow in the $R(1)$ inset indicates an extra line due to a perturbation in the upper state. The asterisks identify lines of ^{11}BC that show up weakly in the sync-scan spectrum.

splitting constant $\lambda' > 0$. In a similar fashion, an examination of the spin-splittings of the $P(1)$ line (see Fig. 3) shows that the ground state $N = 1$ levels are in the energy order $J = 0.5 (F_3) > J = 2.5 (F_1) > J = 1.5 (F_2)$, necessitating that $\lambda'' < 0$. Both of these conclusions are exactly the opposite of that of previous analyses,^{4,7} which fitted the spectrum with $\lambda' < 0$ and $\lambda'' > 0$. We defer further analysis of this spectrum until we discuss our studies of the $E^4\Pi - X^4\Sigma^-$ band system, which confirm our conclusions about the signs of spin-spin constants and provide reliable ground state constants.

B. The $E^4\Pi - X^4\Sigma^-$ LIF spectrum

Based on previous matrix work,⁵ the $E - X$ band system of BC was expected to occur at 291 nm. Experiments using the trimethylborane precursor and detecting the near-UV fluorescence back down to the ground state readily yielded LIF spectra in this region. High resolution LIF sync-scan spectra (offsets of 1150 cm^{-1} and 1190 cm^{-1} , respectively) of the 0-0 bands of ^{11}BC and ^{10}BC were recorded and are shown in Fig. 4. It is important to note that the rotational structure of the two bands is unexpectedly different, perhaps signaling perturbations in one or the other. Although these spectra are highly congested and contain multiple overlapping rovibronic lines, detailed rotational analysis proved possible for the 0-0 band of the ^{11}BC isotopologue. First, we review the salient features of the rotational structure of the excited electronic state.

In the $E^4\Pi$ state, the spin splittings are substantially larger than in the ground state due to the nonzero spin-orbit coupling, so that the $F_1 - F_4$ components form separate groups of levels slightly displaced from each other, as shown in Fig. 5. In this figure, the rotational energy levels of the $^4\Pi$ state are drawn to scale using our final E state constants (*vide infra*) but the Λ -doubling has been neglected. The X state levels are not to scale and have greatly exaggerated spin splittings, while the $N'' = 5$ levels have been further magnified in order to show the spin substructure. The transitions allowed by the $\Delta J = 0, \pm 1$ selection rule to the upper state F_4 component

FIG. 4. High resolution sync-scan LIF spectra of the $E^4\Pi$ and $X^4\Sigma^-$ 0-0 bands of ^{11}BC (top) and ^{10}BC (bottom). The top spectrum was recorded using the mixed isotope $\text{B}(\text{CH}_3)_3$ precursor, with a sync-scan offset of 1150 cm^{-1} . The bottom spectrum was obtained using an enriched $^{10}\text{B}(\text{CH}_3)_3$ precursor, with a 1190 cm^{-1} sync-scan offset.

are shown on the right hand side of the diagram. Generally, such transitions are labeled $^{\Delta N} \Delta J_{F'F''}$ but in the present case, for the sake of clarity, ΔN has been neglected. The strongest branches are those in which $F' - F'' = 0$ and these are labeled less redundantly as P_4 , etc. It is obvious that there are a total

FIG. 5. A schematic diagram of the rotational energy levels of the $E^4\Pi$ and $X^4\Sigma^-$ electronic states of ^{11}BC . The lower state levels are not drawn to scale and the spin splittings have been exaggerated. The upper state levels are drawn to scale but the small Λ -doublings have been neglected. The allowed transitions between $N'' = 5$ levels of the ground state and the F_4 levels of the excited state are indicated by vertical lines. The rectangle isolates levels with the same value of N in the $E^4\Pi$ excited state.

of twelve branches terminating on a given upper state spin-orbit component, which yields 48 branches in total. However, because of the very small spin splittings (less than 0.1 cm^{-1}) in the lower state, transitions in Fig. 5, which terminate on the same upper state level, such as Q_4 and P_{43} , or R_4 , Q_{43} , and P_{42} , will of necessity overlap each other, so that many of the observed lines in the spectrum (Fig. 4) must have multiple assignments.

We began our analysis of the ^{11}BC high resolution 0-0 band using the very convenient graphical program PGOPHER²² to simulate the general contour of the band. Starting with the ground state constants obtained from the BC emission spectrum,⁴ the *ab initio* excited state B value,⁹ and an estimate of the band origin, the E state spin-orbit coupling constant A was manually varied until a reasonable simulation was obtained. This allowed a few lines to be assigned and then the constants were slowly varied, adding more lines as the simulation improved. Attempts to vary the ground state constants improved the overall standard deviation but invariably led to a negative value of the spin-spin constant λ'' , contrary to previous analyses which gave $\lambda = +0.0282 \text{ cm}^{-1}$.

In order to check our analysis, we formed ground state combination differences from the assigned lines, initially assuming $\lambda'' > 0$. This led to some degree of difficulty for certain transitions, again suggesting that the ground state spin-spin constant was negative. The analysis was then repeated from the beginning inverting the order of the ground state components within a given N as required by a negative value of λ'' , and this greatly improved the overall standard deviation of fit to 0.015 cm^{-1} for 104 transitions with N' and $N'' \leq 10$. In the ground state, B and λ were varied with the spin-rotation constant γ fixed at the *ab initio* value, as suggested in the analysis of the $B-X$ transitions (*vide infra*). For the excited state, B , A , λ , γ , the Λ -doubling constant o , and the band origin, T_0 , were varied. The resulting constants are summarized in Table I.

The good agreement between the observed and simulated spectra for the central portion of the 0-0 band of ^{11}BC is shown in Fig. 6. The very strong features in the center of the band are the P_1 , Q_1 , and R_1 branches, as designated by the vertical leaders in the figure. Many of the weaker lines in this region can be assigned to the $\Delta F = 0$ branches involving F_2 , F_3 , and F_4 , and they are displaced relative to the F_1 transitions due to the small but significant value of $A = 4.58 \text{ cm}^{-1}$.

The weaker $E^4\Pi-X^4\Sigma^-$ 1-0 band of ^{11}BC was also studied at high resolution and analyzed in a similar fashion.

FIG. 6. The central portion of the $E^4\Pi-X^4\Sigma^-$ high resolution sync-scan LIF spectrum of ^{11}BC (top) and the simulation of the spectrum at a rotational temperature of 40 K and linewidth of 0.065 cm^{-1} (bottom). Some of the prominent transitions are identified in the top trace. Weak features in the experimental spectrum that are not evident in the simulation are due to residual ^{10}BC transitions.

The ground state constants were fixed at those obtained for the 0-0 band and the excited state constants were varied, with only γ' fixed at the $v' = 0$ value. A total of 77 transitions with N' and $N'' \leq 7$ were fitted to a standard error of 0.018 cm^{-1} yielding the constants presented in Table I. The correspondence between the upper state constants of the 1-0 and 0-0 bands is quite reasonable, lending credence to the analysis. It was evident that both Λ -doubling components of the $N = 3$, $J = 1.5$ and 2.5 , and $N = 5$, $J = 3.5$ and 6.5 upper state levels are perturbed, although the assignments were readily verified by ground state combination differences.

Building on our success with the $E-X$ bands of ^{11}BC , we attempted to understand the high-resolution spectrum of the 0-0 band of ^{10}BC . In a sense, this is the cleanest spectrum as it was produced from isotopically enriched $^{10}\text{B}(\text{CH}_3)_3$ so does not have an underlying background of weak transitions from the other isotopologue. Despite these encouraging preliminaries, it proved not possible to obtain a realistic simulation or set of assignments for this spectrum, which appears to be extensively perturbed. We shall return to this topic in Sec. III C.

TABLE I. Molecular constants (cm^{-1}) of ^{11}BC .

	$X^4\Sigma^- v=0$	$X^4\Sigma^- v=1$	$B^4\Sigma^- v=0$	$B^4\Sigma^- v=1$	$E^4\Pi v=0$	$E^4\Pi v=1$
B	1.310 11(45) ^a	1.295 11(20)	1.367 65(17)	1.354 30(19)	1.080 72(51)	1.075 88(51)
λ	-0.029 0(69)	-0.025(22)	0.030 2(45)	0.050(22)	0.036 6(75)	0.050 6(78)
$10^6 D$		9.23(36)		8.71(31)		
A_{SO}	...	...	...	...	4.585(11)	4.091(15)
$10^3 \times \gamma$	-1.3(fixed)	...	...	...	-4.01(78)	-4.01(fixed)
o	...	...	...	...	-0.048 5(54)	-0.036 0(72)
T_0	...	...	17 904.870 8(69)	18 025.585 9(36) ^b	34 353.112 9(78)	35 317.051(13)

^aThe numbers in parentheses are 3σ error limits.

^bThis is T_0 for the 1-1 band.

C. Optical-optical double resonance spectroscopy

Due to the complexity and multitude of overlapping lines in the high resolution $E^4\Pi-X^4\Sigma^-$ bands, lingering doubts about our rotational analyses, and our inability to assign the ^{10}BC 0-0 band spectrum, we decided to attempt OODR experiments to clarify the assignments. The basic idea was to excite a “single” well-defined, readily assigned rotational line in the $B^4\Sigma^- - X^4\Sigma^-$ 0-0 band with a green laser, then use a second scanning red dye laser to promote the allowed $E^4\Pi - B^4\Sigma^-$ transitions and detect them by monitoring the subsequent $E-X$ fluorescence in the ultraviolet region. The green laser had a linewidth of 0.1 cm^{-1} so it simultaneously populated all the available (and precisely known!) B state levels of a given N (this includes all four F_1-F_4 levels at higher values of N'). Scanning the red laser mapped out the $E-B$ OODR spectrum, promoting transitions to the more widely separated and therefore resolvable F_1-F_4 components of the E state.

Some examples of typical OODR spectra for the $E^4\Pi - B^4\Sigma^-$ 0-0 band of ^{11}BC are presented in Fig. 7. Consider, with reference to Fig. 5, the top very informative OODR spectrum, which involves pumping the $P(1)$ line of the $B-X$ band, populating the single $N = 0$, $J = 1.5$ (F_1e) B state level. Following the $\Delta J = 0, \pm 1$ selection rule, and working from lower to higher wavenumbers, we see that there are three transitions to the three lowest ($J = 0.5, 1.5$, and 2.5) levels of $N' = 1$. The relative spacing of the transitions follows that

FIG. 7. Example observed (upwards) and simulated (downwards) OODR spectra of ^{11}BC . The identity of the intermediate $B-X$ transition is given in the corner of each panel and the assignments of the $E^4\Pi$ final state levels are given below the simulations. The simulations were done using the constants given in Table I.

shown in Fig. 5. At slightly higher energy, the pattern is repeated for transitions to $N' = 2$. Finally, there is a two-line pattern, which is readily attributed to transitions to $N' = 3$ for which the $J = 0.5$ level does not exist. There is also a very weak transition to $N' = 4$, $J = 2.5$ expected at 16469.36 cm^{-1} but its intensity is calculated to be a factor of 10 smaller than the weakest observed transition in the spectrum so it is not surprising that it was not detected. In conclusion, the topmost OODR spectrum immediately shows the moderate spin-orbit splittings of the various J components of a given N' , that the E state spin-orbit constant $A > 0$ (because the energy increases with J for a given N'), and that the disposition of the rotational levels is as depicted in Fig. 5, largely validating our rotational analysis of the $E-X$ bands.

Using the non-Boltzmann population options in PGOPHER, we were able to simulate the OODR spectrum using the B and E state constants (see Table I) with the result shown below the top spectrum in Fig. 7. The line positions precisely match those of the experiment providing further convincing confirmation of our $E-X$ 0-0 band rotational analysis. The relative intensities of the weaker OODR lines appear to be underestimated in the simulation, which we believe is due to experimental saturation effects. In effect, the scanning red dye laser saturates the stronger transitions so that they are attenuated relative to the weaker unsaturated lines.

The middle panel of Fig. 7 shows a more complicated OODR pattern obtained by pumping the $B-X$ $P(4)$ line, populating the four B state $N = 3$ ($J = 1.5 F_4f < J = 4.5 F_1e < J = 2.5 F_3e < J = 3.5 F_2f$) levels, which span a range of only 0.07 cm^{-1} . Note that the order of the levels is opposite to that of the X state in Fig. 5 because $\lambda > 0$ in the B state. In the E state, the various spin components of a given N tend to group together, as illustrated by the box around the $N = 6 F_1-F_4$ levels in Fig. 5, so that the transitions form groups with a common N' and this is how they are denoted on the OODR spectrum. With the same caveats about the intensities, the simulation is again very satisfactory.

The OODR spectrum from pumping the $R(5)$ $B-X$ line [B state $N = 6$, $J = 4.5 F_4f < J = 7.5 F_1e < J = 5.5 F_3e < J = 6.5 F_2f$] shown in the bottom panel of Fig. 7 consists of a series of doublets. This is because the clustering of the E state levels is even more pronounced at high values of N . The most prominent features in the spectrum are the $\Delta N = -1, 0$, and $+1$ transitions, accompanied by weaker $\Delta N = \pm 2$ satellite lines, all of which are very well accounted for by the simulation. The results of these and many other OODR experiments convincingly confirmed our rotational analysis of the ^{11}BC $E-X$ 0-0 band.

We had hoped to use the same techniques to unravel our difficulties with assigning and fitting the $E-X$ 0-0 band of ^{10}BC , but it soon became obvious that the OODR spectra were not nearly as well-behaved. Fig. 8 shows a plot of the lowest rotational energy levels of the E state ($v = 0$) of ^{11}BC and ^{10}BC derived from our easily interpretable OODR spectra. It is readily apparent that the ^{10}BC levels are perturbed and we were unable to fit them in any reasonable fashion using the standard $^4\Pi$ Hamiltonian.

FIG. 8. A comparison of the low-lying $E\ 4\Pi$ levels of ^{11}BC and ^{10}BC as determined from OODR spectra.

Finally, we did a series of OODR experiments to determine the sign of λ in the B state of boron carbide. These involved using our high resolution (0.035 cm^{-1}) laser to pump individual partially resolved spin components of the $B-X\ R(0)$ [$N' = 1 \leftarrow N'' = 0, J = 1.5$] line (see inset of Fig. 9) and then using a second laser to drive the $E-B$ OODR transitions. In this case, a single spin component (a specific J) of the $N = 1$ level of the B state is primarily but not exclusively populated, so the OODR spectrum should predominantly reflect the J value of the intermediate spin component. If the J' values of the three partially resolved features of the $R(0)$ line (see inset of Fig. 9) can be determined, then the sign of λ is determined.

The top trace in Fig. 9 is the OODR spectrum obtained by broadband excitation (0.1 cm^{-1}) of the $^{10}\text{BC}\ R(0)$ line, populating the three B state components of $N = 1$ [$J = 2.5, J = 1.5$, and $J = 0.5$]. The various OODR transitions are readily assigned and the small center doublet can be attributed to transitions from the B state $J = 0.5$ level. Narrow band excitation of the lowest wavenumber, partially resolved component A (see inset of Fig. 9) yields the OODR spectrum labeled A, which accentuates these two features. The spectrum also contains weaker contributions from the central peak B since A and B are poorly resolved. However, narrow band excitation of peaks B and C yields OODR spectra (those labeled B and C) that do not have any appreciable contribution from the centre doublet. Analysis of the OODR spectra A, B, and C shows that they originate from the $J = 0.5$ (F_3) $< J = 2.5$ (F_1) $< J = 1.5$ (F_2) levels of the B state, respectively, and this pattern of levels can only occur for a positive value of λ' , entirely in accord with our previous

FIG. 9. ^{10}BC OODR spectra recorded after pumping the $B-XR(0)$ line, which is shown in the inset. The top trace is the overall spectrum obtained by pumping the $R(0)$ line with a broadband (0.1 cm^{-1}) dye laser. Transitions from the B state $J = 0.5$ levels are identified in this spectrum. Trace A is the spectrum obtained by narrow band (0.035 cm^{-1}) laser pumping of feature A of the $R(0)$ line (see inset). The B state $J = 0.5$ doublet is accentuated. Trace B is the OODR spectrum obtained by high resolution pumping of the central maximum (B) of the $R(0)$ line and trace C is that obtained by pumping feature C. The vertical dashed lines mark the position of the $J = 0.5$ doublet in all four spectra.

analysis (see Section III A) of the intensity pattern of the $R(0)$ line.

D. The $E\ 4\Pi-X\ 4\Sigma^-$ emission spectrum

Ultraviolet dye laser excitation of the central maximum in the 0-0 band LIF spectra of ^{11}BC and ^{10}BC gave the emission spectra shown in Fig. 10 with the measured energy

FIG. 10. Emission spectra obtained by pumping the $E\ 4\Pi-X\ 4\Sigma^-$ 0-0 bands of ^{11}BC (top) and ^{10}BC (bottom).

TABLE II. Vibrational energy levels, residuals, and constants (all in cm^{-1}) for the ground states of ^{11}BC and ^{10}BC .

v''	^{11}BC		^{10}BC	
	Energy	Observation–calc.	Energy	Observation–calc.
1	1147.1	–1.7	1180.3	0.3
2	2278.4	0.8	2338.5	0.2
3	3387.2	0.7	3474.3	–0.6
4	4474.9	–0.5	4590.1	0.3
ω_e	1168.8(14) ^a	[1161.1] ^b	1201.7(5)	
$\omega_e x_e$	10.0(3)	[11.0] ^b	10.8(1)	

^aThe numbers in parentheses are 1 σ error limits.^bMRCI results, Ref. 13.

levels collected in Table II. We can compare our ^{11}BC energy levels (Table II) to those obtained previously by rotational analyses of high resolution spectra:^{4,7} $v'' = 1$: 1147.1 vs 1149.84 cm^{-1} , $v'' = 2$: 2278.4 vs 2279.34 cm^{-1} , suggesting that our low resolution numbers underestimate the band origins by 1–3 cm^{-1} . We have fitted the observed energy levels for both isotopologues to the usual anharmonic relationship and obtained the vibrational constants and residuals given in Table II. These are in accord with previously reported values for the $v'' = 0, 1$, and 2 levels obtained from the LIF study⁷ of jet-cooled ^{11}BC .

IV. DISCUSSION

A. Reanalysis of the B - X bands

Now that the signs of the spin-spin constants λ has been determined experimentally (from the relative intensities of the partially resolved spin components, Section III A, from the analysis of the $E^4\Pi-X^4\Sigma^-$ spectrum Section III B, and from OODR experiments, Section III C), we return to the rotational analysis of the $B^4\Sigma^--X^4\Sigma^-$ 0-0 band. We have fixed the ground state ^{11}BC constants at those obtained from the $E^4\Pi-X^4\Sigma^-$ 0-0 band (with $\lambda'' < 0$, see Table I) and varied only B , λ , and T_0 of the excited state, starting with $\lambda' > 0$. This gave a much better fit to the observed data than any scheme with $\lambda'' > 0$ and did not improve significantly if the ground state constants were allowed to vary. Tests showed that the ground state spin-rotation constant γ was necessary to describe the partially resolved splittings at higher N , but that the constant could not be varied independently in both states. The value obtained by varying γ'' with $\gamma' = 0$ was very close to the value we calculated from density functional theory (DFT) [B3LYP/aug-cc-pVTZ value using the Gaussian 09 program],²³ so in the final analysis, we simply fixed γ'' at the theoretical value. A total of 59 transitions from the $P(8)$ through $R(9)$ lines were fitted with a standard deviation of 0.012 cm^{-1} . The constants are summarized in Table I.

Subsequently, we also analyzed the high resolution spectrum of the $B^4\Sigma^--X^4\Sigma^-$ 0-0 band of ^{10}BC . In this case, we did not have ground state constants from the $E^4\Pi-X^4\Sigma^-$ spectrum since it was perturbed (see Section III C), so we varied the constants in both states, again fixing the ground state spin-rotation constant at the DFT value. In the least

TABLE III. Molecular constants (cm^{-1}) of ^{10}BC .

Constant	$X^4\Sigma^- v=0$	$B^4\Sigma^- v=0$
B	1.378 70(42) ^a	1.439 31(42)
λ	–0.028 9(66)	0.033 2(66)
$10^3 \times \gamma$	–1.4(fixed)	...
T_0	...	17 906.271 3(60)

^aThe numbers in parentheses are 3 σ error limits.

squares analysis, we fitted 52 transitions encompassing the $P(8)$ through $R(7)$ lines with an overall standard deviation of 0.0095 cm^{-1} . The resulting constants are given in Table III. The derived constants are very similar to those of ^{11}BC .

Finally, in order to obtain r_e bond lengths, we reanalyzed the data for the 1-1 band of ^{11}BC reported by Fernando and co-workers,⁴ reversing the assignments to correspond to a negative value of λ in the ground state. A total of 184 assignments were fitted, with the inclusion of the centrifugal distortion constant D in both states, to an overall standard deviation of 0.025 cm^{-1} . Due to the fact that the lines appear as doublets, each with at least two assignments, the spin constants, especially λ'' , were only barely determined. Nevertheless, the B values should be quite reliable. The resulting constants are reported in Table I.

B. Bond lengths and comparison to MO theory

The bond lengths in the various electronic states have been calculated from the B values and are summarized in Table IV. For the X and B states, the agreement between the r_0 bond lengths of the ^{11}BC and ^{10}BC isotopologues is reasonable, and average values are $r_0(X) = 1.4969(1)$ and $r_0(B) = 1.4650(1)$ Å. The equilibrium bond lengths, derived from ^{11}BC data, are $r_e(X) = 1.4927(2)$ and $r_e(B) = 1.4616(1)$ Å, about 0.005 Å shorter than the corresponding *ab initio* r_e values¹³ of 1.499 and 1.466 Å, respectively. Theory predicts a 0.03 Å decrease in the bond length in the B state, due to the promotion of an electron from the $4\sigma^*$ to the 5σ bonding orbital, precisely as is observed. The *ab initio* vibrational frequency and anharmonicity¹³ of the ^{11}BC ground state agree very well with the same quantities derived from the B - X emission spectra (see Table II). In a similar fashion, $\omega_e = 1265.4$ cm^{-1} and $T_e = 17\,830$ cm^{-1} calculated¹³ for the B state are in reasonable agreement with the experimental parameters⁷ $\omega_e = 1290.59$ cm^{-1} and $T_e = 17\,965.1$ cm^{-1} . There is a rather large discrepancy of unknown origin in the calculated B state multi-reference configuration interaction (MRCI) anharmonicity constant [$\omega_e x_e = 2.45$ cm^{-1}] compared to the experimental value [obtained from the rotational analysis of $v = 0$ –2 in the excited state] of 9.98 cm^{-1} , which agrees well with previous neon matrix values^{5,6} of 10.5 cm^{-1} and 8.5 cm^{-1} . There can be little doubt that the excited state accessed by the B - X transition is that labeled in the theoretical study¹³ as $7^4\Sigma^-$, which is the second excited state of quartet multiplicity and thus labeled the B state.

In an effort to see if better agreement between theory and experiment can be achieved for the ground state bond length, we have used the Gaussian 09 program²³ and coupled cluster theory with singles, doubles and triples included perturbatively

TABLE IV. Bond lengths (in Å) of boron carbide derived from the B values given in Tables I and II compared to *ab initio* values from the literature.

	^{11}BC			^{10}BC	
	$X^4\Sigma^- v=0$	$B^4\Sigma^- v=0$	$E^4\Pi v=0$	$X^4\Sigma^- v=0$	$B^4\Sigma^- v=0$
r_v (expt.)	1.4970(1) ^a	1.4652(1)	1.6483(2)	1.4967(1)	1.4648(1)
r_e (expt.)	1.4927(2)	1.4616(1)	1.6464(2)	...	...
r_e (theory) ^b	1.499	1.466	1.654	1.499	1.466

^aThe numbers in parentheses are 1σ error limits.^bMRCI+Q results from Ref. 13.

[CCSD(T)] with progressively larger basis sets to extrapolate to the complete basis set (CBS) limit using a simple exponential extrapolation function.²⁴ Two sets of results are given in Table V: calculations involving only correlation of the valence electrons with aug-cc-pVnZ; $n = 3, 4, 5$ basis sets, and calculations that included full correlation of all the electrons with the appropriate aug-cc-pCVnZ; $n = 3, 4, 5$ basis sets. The results of the CBS extrapolation with valence shell correlation are still about 0.006 Å too large but it is gratifying that inclusion of core correlation and extrapolation to the CBS limit yields a bond length within 0.0003 Å of experiment.

The upper state of the $E-X$ transition corresponds to the $E\ 15^4\Pi(2)$ excited state found by Tzeli and Mavridis¹³ whose calculated vibrational frequency and electronic energy [$\omega_e = 958.5\text{ cm}^{-1}$ and derived $T_0 = 33\ 820\text{ cm}^{-1}$] agree reasonably well with our experimental data [vibrational fundamental = 963.9 cm^{-1} , $T_0 = 34\ 353.11\text{ cm}^{-1}$]. In the E state, we have B values for $v = 0$ and $v = 1$ of ^{11}BC , allowing a calculation of $r_e = 1.6464(2)\text{ Å}$, about 0.005 Å shorter than the *ab initio* value of 1.654 Å. The theoretically predicted 0.151 Å increase in the bond length on promoting an electron from the 5σ bonding orbital to the 2π antibonding orbitals is nicely corroborated by the 0.154 Å elongation measured from the experimental data. The $C\ 11^4\Delta$ state [calc. $r_e = 1.856\text{ Å}$, $\omega_e = 555.1\text{ cm}^{-1}$, and $T_e = 32\ 180\text{ cm}^{-1}$], the $D\ 13^4\Sigma^+$ state [calc. $r_e = 1.872\text{ Å}$, $\omega_e = 530.2\text{ cm}^{-1}$, and $T_e = 32\ 880\text{ cm}^{-1}$] states are also in the vicinity,¹³ with the $F(17^4\Pi_g)$ state predicted to be much higher at $T_e = 45\ 120\text{ cm}^{-1}$. However, the calculated vibrational frequencies of the C and D states are more than 400 cm^{-1} lower than that observed in the $E-X$ spectrum and our rotational analysis is entirely consistent with a $^4\Pi$ upper state, confirming our assignment.

C. The sign of λ in the $X^4\Sigma^-$ state

In the original analysis of the $B-X$ emission spectrum,⁴ in which the spin splittings were very poorly resolved, the authors

TABLE V. *Ab initio* calculations of the ground state bond length of ^{11}BC .

Basis set	CCSD(T)/valence ^a	CCSD(T)/core ^b	Expt.
$n = 3$	1.5071	1.5017	
$n = 4$	1.5003	1.4937	
$n = 5$	1.4990	1.4926	
CBS limit	1.4987	1.4924	1.4927(2)

^aBasis set aug-cc-pVnZ.^bBasis set aug-cc-pCVnZ.

rationalized the choice of $\lambda'' > 0$ (and therefore $\lambda' < 0$) based on the use of perturbation theory to calculate the second-order spin-orbit interaction parameter $\lambda^{\text{SO}(2)}$. They argued that the interaction of the ground state with nearby $^2\Sigma^+$ and $^2\Pi$ states both give a positive contribution to λ'' .

In fact, we find that $\lambda'' < 0$, which seems to contradict the above argument, which turns out to be slightly in error. Experimentally, the spin-spin constant is proportional to the difference in energies of the purely electronic spin components of the $^4\Sigma^-$ state as

$$\lambda_{\text{eff}} = [E(^4\Sigma_{3/2}^-) - E(^4\Sigma_{1/2}^-)]/4. \quad (1)$$

The effective spin-spin parameter λ_{eff} has a direct spin-spin contribution and a second-order spin orbit contribution,

$$\lambda_{\text{eff}} = \lambda^{\text{SS}} + \lambda^{\text{SO}(2)}. \quad (2)$$

According to Lefebvre-Brion and Field,²⁵ the direct spin-spin contribution (λ^{SS}) for a $^4\Sigma^-$ state arising from a $\sigma\pi^2$ configuration is zero, so it is only necessary to consider the second-order spin-orbit mixing of the boron carbide $X^4\Sigma^-$ state with higher excited states, following the $\Delta\Omega = 0, + \leftrightarrow -, \Delta\Sigma = -\Delta\Lambda = 0$ or ± 1 or ± 2 selection rules. The main contributions are from energetically nearby excited states, which may belong to the same configuration as the state of interest (the so-called isoconfigurational second-order spin-orbit effect) or may arise from a different configuration (nonisoconfigurational second-order spin-orbit effect). In the present case, the lowest $4\sigma^2 5\sigma^1 1\pi^2$ configuration yields the $X^4\Sigma_{3/2,1/2}^-$ ground state along with $^2\Delta_{5/2,3/2}$, $^2\Sigma_{1/2}^+$, and $^2\Sigma_{-1/2}^-$ excited states. In addition, there is the very low-lying $a^2\Pi_{3/2,1/2}$ state, which, in order to make the calculation tractable, we attribute solely to the $4\sigma^2 1\pi^3$ configuration.^{9,13} The possible interactions that satisfy the spin-orbit selection rules are shown in Fig. 11 and consist of the nonisoconfigurational interaction with the $a^2\Pi_{3/2,1/2}$ state with an *ab initio* (MRCI + Q) energy difference¹³ of $\sim 3500\text{ cm}^{-1}$ and the isoconfigurational interaction with the $d^2\Sigma_{1/2}^+$ state, which has been experimentally measured⁵ to be $11\ 210\text{ cm}^{-1}$ above the a state.

A semiempirical estimate of the sign and approximate magnitude of the second-order spin-orbit coupling constant yields²⁶

$$\lambda^{\text{SO}(2)} = \left(\frac{1}{6}\right) \frac{[A_{\text{SO}}(^2\Pi)]^2}{E(^2\Sigma^+) - E(^4\Sigma^-)} + \left(\frac{1}{24}\right) \frac{[A_{\text{SO}}(^2\Pi)]^2}{E(^2\Pi_{1/2}) - E(^4\Sigma_{1/2}^-)} - \left(\frac{1}{8}\right) \frac{[A_{\text{SO}}(^2\Pi)]^2}{E(^2\Pi_{3/2}) - E(^4\Sigma_{3/2}^-)}, \quad (3)$$

FIG. 11. Schematic diagram showing the various interactions that affect the sign and magnitude of the spin-spin constant λ in the ground state of boron carbide. The relative energies of the various electronic states are drawn to scale but the splittings of the X and a states are greatly exaggerated.

where $A_{SO}(^2\Pi)$ is the *unknown* spin-orbit constant for the $a^2\Pi$ electronic state. The isoconfigurational interaction (first term) displaces the $X^4\Sigma_{1/2}^-$ component downwards, increasing the splitting, giving a positive contribution to λ . The nonisoconfigurational interaction with the $a^2\Pi_{1/2}$ state (second term) also increases λ , but the 3 times larger $^2\Pi_{3/2}-^4\Sigma_{3/2}^-$ interaction (third term) effectively decreases the splitting, a negative contribution to λ . Assuming the energy denominators in the last two terms are equal (a very good approximation) and the energy values given above, we obtain

$$\lambda^{SO(2)} = -1.25 \times 10^{-5} [A_{SO}(^2\Pi)]^2. \quad (4)$$

Clearly, due to the relative energies of the interacting states, the ground state spin-spin constant is expected to have a negative sign validating our analysis of the $B-X$ bands. If we approximate the spin-orbit constant as the average of the atomic spin orbit coupling constants²⁵ of boron ($\zeta = 10.7 \text{ cm}^{-1}$) and carbon ($\zeta = 29.0 \text{ cm}^{-1}$) then $A_{SO}(^2\Pi) \sim 19.9 \text{ cm}^{-1}$ and $\lambda^{SO} = -0.005 \text{ cm}^{-1}$, about a factor of 6 smaller than the experimental value of $\lambda'' = -0.0290(69) \text{ cm}^{-1}$. It is gratifying that the magnitude of our ground state ^{11}BC spin-spin constant is in very good agreement with the ESR neon matrix value³ of $|\lambda| = D/2 = 0.028 \text{ cm}^{-1}$.

D. Perturbations

There is evidence that both the B and E state bands we have recorded are perturbed to some extent. The $R(1)$ inset of Fig. 3 shows an extra line that cannot be assigned as part of the spin substructure of the transition and a similar feature occurs in the $P(3)$ line (not shown). The emission

spectrum obtained on pumping the extra line clearly indicates that the feature is due to ^{10}BC , but the fluorescence lifetime (as observed qualitatively on an oscilloscope) is longer than that of the $R(1)$ line, suggesting that it arises by the mixing of a B state level with a nearby dark background level. The occurrence of a perturbation requires that the nearly coincident levels have the correct electronic symmetry and the same J rotational quantum numbers. From the calculations of Tzeli and Mavridis,¹³ the only nearby state is $6^2\Pi$, which lies approximately 2800 cm^{-1} below the B state. Energetically, the $v = 3$ level of the lower $^2\Pi$ state occurs in approximately the right region, but in the absence of more information about the perturbations, further speculation is unwarranted.

Fig. 8 shows that the $E^4\Pi v = 0$ rotational levels of ^{10}BC are considerably displaced compared to the regular pattern observed for the $E^4\Pi v = 0$ and $v = 1$ (not shown in the figure) levels of ^{11}BC . It appears that the perturbations affect all of the spin components, although the evidence in Fig. 8 is not conclusive. *Ab initio* calculations show that there are the $13^4\Sigma^+$ and $14^2\Sigma^-$ states both $\sim 1000 \text{ cm}^{-1}$ below the E state and one or the other is perhaps responsible for the interaction.

V. CONCLUSIONS

In spectra with small spin splittings, it is often difficult to determine the sign and magnitude of the spin constants. Boron carbide is a case in point where the original data obtained from a hollow cathode source at relatively high temperatures exhibited only spin doublets, which contain little reliable information about the signs of the constants in the combining states.⁴ Our success in recording LIF spectra of the $B^4\Sigma^- - X^4\Sigma^-$ bands of jet-cooled boron carbide made this a much more tractable problem since the first lines of the P - and R -branches exhibit further splittings and characteristic intensity patterns that give the signs and magnitudes directly. In the present case, we were able to confirm these by analysis of the $E^4\Pi - X^4\Sigma^-$ bands, which give an independent and corroborative value of λ for the ground state.

Optical-optical double resonance from the X to the E states through the intermediate B state proved invaluable in our study of boron carbide. The ability to optically populate a single level of the B state and then detect the allowed transitions from that level to the various levels of the E state was a great aid in untangling the complex and overlapping rotational structure of the $E-X$ bands. The sampling of OODR data in Fig. 7 and the corresponding simulations very convincingly show that our rotational analysis of the ^{11}BC $E-X$ 0-0 band is correct. In addition, careful studies of the OODR spectra obtained by pumping single spin-rotational levels of the B state conclusively proved that the $\lambda' > 0$, as we previously determined from the $B-X$ LIF spectrum.

This work revises the signs of the spin constants in the X and B states of boron carbide and presents the first rotational analysis of the $E^4\Pi - X^4\Sigma^-$ bands, from which reliable molecular constants and bond lengths have been derived. We have also shown that the negative sign of the spin-spin constant in the ground state is entirely consistent with the predictions of an empirical estimate based on second order perturbation theory.

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