

Interpretation of the hyperfine coupling constants of the boron trimer in rare-gas matrices

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By carrying out a systematic basis set and electron correlation investigation, we have determined accurately the isotropic and anisotropic parts of the hyperfine coupling tensor of the B₃ molecule using the multiconfiguration self-consistent-field restricted-unrestricted method. The anisotropy of the computed tensor is significantly larger than the experimental uncertainty. This indicates that the B₃ molecules must be freely tumbling in neon, argon, and krypton matrices at 4 K. The spin polarization of the 1s orbital on each B atom is found to be very small in the B₃ molecule. This implies that the isotropic hyperfine coupling is dominated by valence-orbital contributions rather than by 1s-orbital contributions.

I. INTRODUCTION

Electron-spin-resonance (ESR) spectra have recently been measured for B₃ in neon, argon, and krypton matrices at 4 K.¹ These ESR spectra confirm the earlier theoretical prediction of a D_{3h} B₃ radical with a ²A₁' ground electronic state in which the unpaired electron resides in an in-plane orbital of a₁' symmetry.² The hyperfine parameters of ¹¹B₃ inferred from this experimental data are isotropic in all of the rare-gas matrices. For the Ar matrix the hyperfine coupling constant (*A*) was found to be 130 MHz, and values differing only a few MHz were found both for the Ne and Kr matrices. The measured anisotropy was largest for Ne (−4 MHz) and only +2 MHz for Kr; both of these anisotropies are so small as to lie within the experimental error. From these facts it was concluded that either (i) the B₃ molecules are held rigidly but randomly oriented in the matrices yet have hyperfine coupling constants dominated by the (rigorously isotropic) Fermi contact (FC) term with negligible (potentially anisotropic) spin-dipole (SD) contributions, or (ii) the B₃ molecules are freely tumbling, thereby causing the (perhaps substantial) anisotropic SD contributions to be averaged to zero.

To further elucidate these matters, we carried out calculations of the FC and SD parameters for B₃ at and near its equilibrium geometry. From a theoretical point of view, evaluation of the FC and SD parameters is especially challenging in this case because B₃ is a highly correlated system due to the near degeneracy of the 2s and 2p orbitals in the B atom which, in turn, produces several low-lying excited electronic states. Our calculations show that the anisotropic contributions from the SD Hamiltonian are much larger than the uncertainty in the experimental measurements. The computed FC contributions are consistent with the experimentally observed isotropic coupling constant. Therefore, the most probable explanation for the isotropy of the experimentally observed hyperfine parameters is that the B₃ molecules are indeed tumbling freely¹ in all of the

noble-gas matrices in which measurements have been carried out.

We calculated the FC and SD parameters after carrying out a systematic basis set and correlation investigation, using the multiconfiguration self-consistent-field (MCSCF) restricted-unrestricted (RU) approach of Fernández *et al.*³ We have also compared our results with those obtained using conventional single- or multireference single- and double-excitation configuration-interaction (CISD and MCISD, respectively) calculations. These comparisons show that single-reference configuration-interaction approaches are inadequate for describing the ground state of B₃. Our results also show that spin polarization of the 1s-based orbitals of the B atoms is very small, contrary to what is found for the ground state of the B atom,⁴ and that the majority of the hyperfine coupling arises from valence-orbital contributions.

In the following section we briefly summarize our calculational procedure. Section III describes the results of our calculations, and in the last section we give our concluding remarks.

II. CALCULATIONAL PROCEDURE

We carry out systematic calculations of the hyperfine coupling tensor (*A*) for B₃. The hyperfine tensor represents the energy of interaction between the electrons and the nucleus, and contains an isotropic part (FC contribution), denoted *a*_{iso}, and an anisotropic part (SD contribution) denoted *A*^{*d*},

$$\mathbf{A} = a_{\text{iso}}\mathbf{1} + \mathbf{A}^d.$$

The principal values of *A*^{*d*} are named as *A*_{*x*}^{*d*}, *A*_{*y*}^{*d*}, and *A*_{*z*}^{*d*}. We report results for one B atom in a local coordinate system where *x* is perpendicular to the molecular plane and *z* is on the line that goes through the center of mass and the B atom, pointing away from the center of mass.

A. The restricted-unrestricted response function method

The RU approach³ employed for the B₃ hyperfine coupling calculation may be viewed as follows. In the absence of the FC or SD terms⁵ in the electronic Hamiltonian, we

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assume that the system can be described with a spin-restricted MCSCF wave function denoted $|0^{(0)}\rangle$. In the presence of the FC and SD Hamiltonian terms, which are triplet tensor operators in spin space, the wave-function spin relaxes, which thus necessitates using a spin-unrestricted description. The total energy of the system in the presence of the FC and SD couplings is then expressed in terms of the spin-relaxed wave function denoted $|\tilde{0}\rangle$,

$$E(\alpha) = \langle \tilde{0} | H + \alpha V | \tilde{0} \rangle. \quad (1)$$

Here H is the Born–Oppenheimer electronic Hamiltonian in the absence of the FC and SD terms, and the perturbation V denotes either the FC or SD Hamiltonian. The spin relaxation of $|\tilde{0}\rangle$ is achieved by introducing triplet operators in both the orbital and configuration spaces as described in Ref. 3.

Expanding $|\tilde{0}\rangle$ in powers of the perturbation gives

$$|\tilde{0}\rangle = |0^{(0)}\rangle + \alpha |0^{(1)}\rangle + \frac{1}{2}\alpha^2 |0^{(2)}\rangle + \dots, \quad (2)$$

and the first-order contributions to the energy, which relate to the molecular property of interest, are evaluated as

$$E^{(1)} = \langle 0^{(0)} | V | 0^{(0)} \rangle + \langle 0^{(1)} | H | 0^{(0)} \rangle + \langle 0^{(0)} | H | 0^{(1)} \rangle. \quad (3)$$

The first term in Eq. (3) is the standard *average value* expression (denoted *ave.* in the tables), whereas the last two terms are the *response terms* (denoted *resp.* in the tables) because they involve modification of the wave function induced by the perturbation. The latter terms appear because the zeroth-order wave function $|0^{(0)}\rangle$ is not optimized with respect to the triplet operators in the orbital space. In Ref. 3, details are given concerning evaluation of the response terms for such MCSCF wave functions.

B. Atomic basis sets

In our calculations we used as our primary basis sets Dunning's correlation-consistent polarized valence double-zeta (VDZ) $[9s4p1d/3s2p1d]$ and valence triple-zeta (VTZ) $[10s5p2d1f/4s3p2d1f]$ bases.⁶ Various calculations were carried out with slight modification of these bases. In some, all of the Cartesian components of the Gaussian functions were used; results of such calculations are denoted with the subscript *c*. In others, only $2L+1$ components were employed (e.g., the $3s$ function was removed from the $3d$ Gaussian functions), and the results are denoted by the subscript *s*. Calculations were also carried out in which all of the *s*-type basis functions were uncontracted, and the results are then denoted by the subscript *u*. In addition, calculations were performed in which diffuse functions and tight functions were added to the above bases. In this case, we provide explicit values for the orbital exponents (which, for the tight functions, were obtained by multiplying the most tight primitive exponent of the Dunning basis by 3, and, for the diffuse functions, by multiplying the most diffuse primitive exponent by $1/3$). Finally, to further test the adequacy of using the Dunning correlation consistent basis sets, we also carried out calcu-

lations using the $[10s6p2d/7s4p2d]$ basis that Chipman carefully designed to describe the hyperfine coupling constants.⁷

C. Configuration space choices

In these calculations, we used reference states $|0^{(0)}\rangle$ of the conventional spin-restricted single-configuration self-consistent-field (SCF) and complete-active-space (CAS) MCSCF forms. The CAS configuration spaces were chosen based on a CI natural orbital (CINO) occupation analysis using the VDZ_s basis. For lowering the number of configurations in the CINO calculation, we used the restricted-active-space (RAS) CI expansion,⁸ based on dividing the active orbital set into three subsets (RAS1, RAS2, and RAS3) in each of which the number of electrons is restricted. In this way, a CI wave function was determined by using the following number of orbitals in each space: the inactive (1,0,1,0,0,0), RAS1 (1,0,0,0,0,0), RAS2 (1,0,2,0,1,0), and RAS3 (4,3,7,1,2,4). Here the numbers in parentheses refer to the number of orbitals of symmetries ($a'_1, a'_2, e', a''_1, a''_2, e''$) in the respective spaces. The occupancies of the RAS1 and RAS3 spaces were both allowed to vary from 0 to 2 electrons, with the RAS2 space then accommodating the remaining electrons.

The orbitals used in the CI function were obtained from a valence CAS wave function (CASV) that has a total of three (1,0,1,0,0,0) inactive orbitals and twelve (2,1,3,0,1,1) active orbitals that contain the nine active valence electrons (98 278 determinants). These orbitals were chosen because we knew from previous calculations of Hernandez and Simons that the $^1A'_1$ ground state is highly correlated.²

The diagonalization of the one-electron density matrix for this CI wave function gives the CI natural-orbital (CINO) occupancies reported in Table I. These natural-orbital occupancies confirm that B_3 is a very highly correlated system with orbital occupancies as low as 1.840 in orbitals that are completely occupied in a SCF description and occupancies as large as 0.136 in orbitals that are empty in the SCF description. The SCF occupation is (3,0,2,0,1,0). The significant gap in the CINO occupancies near 0.01 shows that the orbital space denoted CASV earlier provides a balanced configuration space for all orbital symmetries.

An alternative balanced but improved description of B_3 can be obtained at an occupation number cutoff of 0.005, which adds two more orbitals of a'_1 symmetry and one of a''_2 symmetry. We denote this CAS space CAS2 (it contains 1 025 703 determinants). Yet a third configuration space at a *lower* correlation level than CASV can be obtained by using the CAS space of Hernandez and Simons.² We denote this space CAS1, which is a subset of the above CASV space in which the a'_1 orbital representing the symmetric combination of the three B-atom $2s$ orbitals is also kept inactive and a pair of e' orbitals are placed into the secondary orbital space. This choice gives a CAS MCSCF calculation that has four (2,0,1,0,0,0) inactive orbit-

TABLE I. Natural-orbital occupation numbers in various wave functions using the VDZ_s basis.

	A'_1	A'_2	E'	A''_1	A''_2	E''
CINO	2.000 00	0.014 78	2.000 00	0.00098	1.904 85	0.044 69
	1.967 57	0.000 63	1.840 05		0.008 23	0.003 55
	0.987 66	0.000 03	0.136 06		0.002 17	0.001 35
	0.008 66		0.013 72			0.000 21
	0.006 70		0.003 04			
	0.003 61		0.001 60			
	0.000 28		0.001 35			
			0.000 95			
			0.000 27			
			0.000 06			
CAS1	2.000 00	0.015 31	2.000 00		1.898 96	0.057 37
	2.000 00		1.852 55			
	0.993 26		0.136 31			
CASV	2.000 00	0.019 14	2.000 00		1.899 18	0.058 32
	1.975 55		1.848 22			
	0.988 56		0.136 85			
		0.015 39				
CAS2	2.000 00	0.018 45	2.000 00		1.893 24	0.056 40
	1.970 19		1.845 64		0.009 14	
	0.988 48		0.133 76			
	0.009 62		0.015 88			
	0.007 50					

als and nine (1,1,2,0,1,1) active orbitals that contain seven active electrons (2658 determinants).

In Table I we report the natural-orbital (NO) occupancies obtained for the CAS1, CASV, and CAS2 MCSCF calculations using the VDZ_s basis. The close agreement between the NO occupancies of these wave functions and those of the CINO calculation shows that we indeed have obtained balanced descriptions of the B₃ system with all of the above CAS configuration spaces. We also note that the

orbital occupancies in the calculations using larger basis sets are similar to the ones in Table I.

III. RESULTS

A. Basis-set dependence

In Table II we report results of a sequence of CAS1 RU calculations on the hyperfine tensor of B₃. Results are reported for various modifications of the VDZ and VTZ

TABLE II. Energies (hartrees), Fermi contact (FC), and spin-dipole (SD) hyperfine constants (MHz) for the B₃ molecule at the computed D_{3h} equilibrium geometry (Ref. 3).

Basis	Energy	FC a_{iso}	SD		
			A_x^d	A_y^d	A_z^d
VDZ _s	-73.906 250	149.6	-14.3	-27.3	41.6
VDZ _c	-73.906 715	138.3	-14.2	-27.3	41.5
VDZ _{us}	-73.906 918	148.0	-14.3	-27.3	41.6
VDZ _{uc}	-73.907 174	146.4	-14.2	-27.3	41.5
VTZ _s	-73.919 234	147.8	-15.8	-30.2	46.0
VTZ _c	-73.919 760	146.0	-15.9	-30.3	46.2
VTZ _{us}	-73.919 958	148.7	-15.8	-30.2	46.0
VTZ _{uc}	-73.920 282	148.1	-15.8	-30.3	46.1
VTZ _s +s(0.02870) +p(0.02566) +d(0.06633)	-73.919 505	146.4	-15.8	-30.1	45.9
VTZ _s +s(16419.0)	-73.919 372	149.1	-15.8	-30.2	46.0
VTZ _s +s(16419.0, 49257.0)	-73.919 805	151.7	-15.8	-30.2	46.0
VTZ _s +s(16419.0, 49257.0,147771.0)	-73.919 808	151.9	-15.8	-30.2	46.0
Chipman _s	-73.905 588	141.4	-15.6	-29.1	44.7
Chipman _c	-73.905 990	142.2	-15.7	-29.0	44.7

TABLE III. Fermi contact (FC) and spin-dipole (SD) contributions (MHz) for B₃ at the D_{3h} equilibrium geometry using the VTZ_s basis.

Energy (a.u.)	SD												
	FC												
	aver.	a_{iso} resp.	tot.	aver.	A_x^d resp.	tot.	aver.	A_y^d resp.	tot.	aver.	A_z^d resp.	tot.	
SCF	-73.759 978	18.2	2343.1	2361.3	-21.6	89.8	68.2	-19.5	-186.4	-205.9	41.0	96.6	137.6
CAS1	-73.919 234	201.8	-54.1	147.8	-15.0	-0.8	-15.8	-24.9	-5.2	-30.1	40.0	6.0	46.0
CASV	-73.968 175	132.8	6.8	139.6	-16.7	0.0	-16.7	-24.5	-3.7	-28.2	41.2	3.8	45.0
CAS2	-74.006 135	138.1	0.4	138.5	-16.7	0.3	-16.4	-25.2	-1.9	-27.1	41.8	1.7	43.5
Vib.cor. ^a				0.2			0.0			0.5			-0.6
Expt. ^b				ca.130									

^aVibrational corrections evaluated with the VDZ_s basis set.

^bThe values given in Ref. 1 range from 126 to 135 MHz and show anisotropy of at most 4 MHz.

basis sets using Cartesian (*c*) and spherical (*s*) Gaussians and where the *s* functions are completely uncontracted (*u*). The results show that with a VTZ basis, the FC contribution is nearly the same independent of whether Cartesian or spherical Gaussians are used or the *s* functions are completely uncontracted or not. The VDZ basis does not display this stability. For either the VDZ or VTZ basis, the SD contributions are adequately described and vary little.

To examine the effect of diffuse and tight functions, we also report in Table II results of VTZ_s calculations where we added a set of diffuse *s*, *p*, and *d* functions and tight *s* functions whose exponents are given in parentheses in Table II. Very little effect is observed on the computed hyperfine tensor when these functions are added, with the tight *s* functions having the largest effect. Finally, calculations are also reported in Table II with a basis that Chipman used in earlier work on B.⁷ The results obtained differ by only a few percent from those obtained with the VTZ_s basis. We therefore feel that the VTZ_s basis is appropriate to describe the hyperfine coupling tensor within a few percent; this was thus our basis of choice in all subsequent calculations.

B. SCF vs CAS results

In Table III we report hyperfine tensors computed using the VTZ_s basis for SCF and various CAS wave functions using the RU approach described earlier. As discussed in Sec. II A, the RU calculations have both average value and response FC and SD contributions to the hyperfine coupling tensor. Each of these contributions are reported in Table III. These results clearly show that an SCF description of the B₃ molecule is inadequate. The SCF FC average-value term, which represents the contribution of the electron in the singly occupied orbital, is 18.2 MHz, only ca. 15% of the total value. The response term is thus unable to describe the residual part of the property and gives a total FC value of 2361 MHz. In previous calculations on BH₂ we found that the response term provides accurate treatment of the wave function's spin polarization when it was small compared to the average value term.³

At the CAS1 level, we observe that the FC and SD values are qualitatively correct but still not within reasonable range of the experimental numbers. The CASV wave

function provides a better description of the B₃ molecule, so we expect the hyperfine tensor to be better. We also report in Table III the result of the even higher-quality CAS2 calculation. The changes in the hyperfine tensor from the CASV to CAS2 functions are very small, indicating that we are approaching saturation with respect to correlation treatment. The RU values for the hyperfine tensor show a clear monotonic converging trend with increasing correlation treatment. A similar converging trend is not found for the average value part of the RU values. It is therefore important to calculate the response contribution even though it may vanish as in the CAS2 calculation.

From Table II it is seen that uncontraction of the *s* functions and addition of tight functions does not change the FC value. Spin polarization of the core 1s orbital can be adequately described when the *s* functions are uncontracted and tight *s* functions are added, and the results in Table II therefore indicate that the spin polarization of the 1s orbital is small. The average-value term describes the spin polarization of the valence space better and better when the CAS spaces are enlarged. At the CAS2 level the average-value contribution to the FC constant gives a rather complete description of the valence-spin polarization and the response term, which describes the spin polarization of the 1s orbital, as expected is very small (see Table III). Our best estimates, before vibrational averaging is taken into consideration, are $a_{\text{iso}}=138.5$, $A_x^d=-16.4$, $A_y^d=-27.1$, and $A_z^d=43.5$ MHz.

C. CI level results

In order to compare with results of more conventional configuration-interaction treatments, we report in Table IV results obtained with the VDZ_s basis using the RU approach and employing CISD and MCISD wave functions. In the CISD calculations, a single reference function is used and all single and double excitations are formed (38 986 determinants). For the MCISD calculation, a multiconfiguration reference function is employed and all single and double excitations are then included (4 418 193 determinants). The CI wave function of the MCISD calculation was the same as that used in the CINO calculation mentioned earlier except that the inactive orbitals were put into the RAS1 space that now contains between 6 and 8

TABLE IV. Calculations of the Fermi contact (FC) and spin-dipole (SD) contributions to A for B_3 at the D_{3h} equilibrium geometry using the VDZ_s basis set.

	Energy	FC			SD								
		a_{iso}			A_x^d			A_y^d			A_z^d		
		aver.	resp	tot.	aver.	resp	tot.	aver.	resp.	tot.	aver.	resp.	tot.
SCF	-73.747 092	24.3	1439.6	1463.9	-19.8	66.1	46.3	-17.8	-140.5	-158.3	37.6	74.4	112.0
CAS1	-73.906 250	188.8	-39.2	149.6	-14.0	-0.3	-14.3	-23.5	-3.8	-27.3	37.5	4.0	41.5
CASV	-73.954 029	136.8	8.2	145.0	-15.6	0.6	-15.0	-23.2	-2.4	-25.6	38.8	1.8	40.6
CAS2	-73.986 659	142.5	0.0	142.5	-15.6	0.8	-14.8	-23.5	-1.0	-24.5	39.1	0.2	39.3
CISD	-73.994 578	78.3	0.0	78.3	-18.1	0.0	-18.1	-21.9	0.0	-21.9	39.9	0.0	39.9
MCISD(1s)	-74.029 407	141.9	0.0	141.9	-15.7	0.0	-15.7	-23.7	0.0	-23.7	39.4	0.0	39.4
MCISD	-74.033 365	140.5	0.0	140.5	-15.7	0.0	-15.7	-23.8	0.0	-23.8	39.5	0.0	39.5

electrons. We will also report results of the “frozen 1s” CI calculation denoted MCISD (1s) that use the same CI wave function as in the CINO calculation (534 500 determinants).

The results of Table IV show that the single-reference CISD function cannot properly describe the hyperfine tensor. The CAS2 and the MCISD results are very similar and are expected to give a rather accurate description for a VDZ_s basis. Comparison of the MCISD and MCISD (1s) results confirms that the spin polarization of the 1s orbital is small. We should point out that using the MCISD calculation is much more involved than the RU CAS approach, and that the RU approach provides a very efficient way of describing both the spin polarization of the valence and the core orbitals. For these reasons, the RU CAS method is preferable.

D. Effect of zero-point vibrational motion

To investigate the vibrational corrections to the FC and SD terms, we evaluated these properties in the vicinity of the minimum-energy geometry and at geometries corresponding to the classical (zero-point) turning points obtained within the harmonic approximation. In doing so, we considered several choices of the degenerate modes (i.e., because the two modes q_1 and q_2 are degenerate, any combinations $q_1 \cos \theta \pm q_2 \sin \theta$ are equally acceptable) and evaluated the A tensor at the turning points. We find that the largest changes in A , relative to A at the minimum-energy geometry, are essentially independent of the choice of θ . On the other hand, we observed substantial changes in the A tensor's values as functions of the magnitude of the distortion (small for the nondegenerate symmetric mode, but up to 43% for the degenerate mode). These observations made it necessary to further investigate the vibrational corrections to these terms.

Within the Born–Oppenheimer approximation, the vibrationally averaged A tensor has elements given by

$$\langle X_0 | A_{\text{el}} | X_0 \rangle, \quad (4)$$

where X_0 is the vibrational wave function of the ground state (appropriate for the low-temperature matrix experiments) and A_{el} is the tensor element computed as the average value and response terms for the SD or FC operator for the MCSCF electronic function. Expanding this A_{el} in

terms of the geometrical vibrational distortions about the equilibrium geometry ($\alpha_i=0$, $i=1,2,3$) gives

$$\begin{aligned} A_{\text{el}} &= A_{\text{el}}^0 + \sum_i \left(\frac{\partial A_{\text{el}}}{\partial \alpha_i} \right)_0 \alpha_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 A_{\text{el}}}{\partial \alpha_i \partial \alpha_j} \right)_0 \alpha_i \alpha_j + \dots \\ &= A_{\text{el}}^0 + \sum_i a_i \alpha_i + \frac{1}{2} \sum_{i,j} b_{ij} \alpha_i \alpha_j + \dots \end{aligned} \quad (5)$$

Insertion of Eq. (5) into Eq. (4) gives

$$\begin{aligned} \langle X_0 | A_{\text{el}} | X_0 \rangle &= \langle X_0 | A_{\text{el}}^0 | X_0 \rangle + \sum_i a_i \langle X_0 | \alpha_i | X_0 \rangle \\ &\quad + \frac{1}{2} \sum_{i,j} b_{ij} \langle X_0 | \alpha_i \alpha_j | X_0 \rangle + \dots, \end{aligned} \quad (6)$$

where the first term in the expansion corresponds to the A values we obtained at the equilibrium geometry. The next two terms (vibrational corrections) were evaluated within the harmonic approximation, giving

$$\langle X_0 | \alpha_i | X_0 \rangle = 0 \quad \text{and} \quad \langle X_0 | \alpha_i \alpha_j | X_0 \rangle = \delta_{ij} \frac{109\,738.29}{\bar{\nu}_i m_B}, \quad (7)$$

where $\bar{\nu}_i$ is the wave number (in cm^{-1}) of the normal mode i and m_B the mass of the boron atom in atomic units (where the electron has unit mass). To calculate the a_i and b_{ij} values, small distortions ($\alpha_i = \pm 0.005$, $\alpha_{j \neq i} = 0.0$ a.u., $i, j = 1, 2, 3$) were taken from the equilibrium geometry and the property A_{el} was evaluated at these points using the *ab initio* method described in Sec. II A (with the VDZ_s basis because it is computationally feasible). Using these data, and neglecting terms of order higher than two in Eq. (5), we obtain a set of systems of two equations whose solution produces the values of a_i and b_{ij} . Substituting these a_i and b_{ij} into Eq. (6) gave zero for the second term in Eq. (6) and insignificantly small values for the third (see Table III). We have not calculated the contribution to the vibrational average originated from the anharmonicity of the vibrational wave function, but expect this contribution also to be insignificant.

In addition to taking into account the above changes in the A tensor values as functions of the geometry, we examined the effects of more complete geometry optimization which affect the value for the first term in Eq. (5). All of

the CASV calculations reported in Tables II–IV were carried out at the equilibrium geometry determined with the CAS1 wave function and the VDZ_s basis.² We therefore reoptimized the geometry with the CASV higher-level wave function and the VTZ_s basis. This gave a B–B internuclear distance of 1.583 Å compared with 1.587 Å in the CAS1 calculation. As a result of these small changes in the interatomic distance, the CASV-level FC parameter changed from 139.6 MHz to 139.0 MHz and no changes were obtained in the SD values. We therefore believe that the vibrationally corrected CAS2-level results (a_{iso} : 138.5 + 0.2 = 138.7; A_x^d : -16.4 + 0.0 = -16.4; A_y^d : -27.1 + 0.5 = -26.6; A_z^d : 43.5 - 0.6 = 42.9) represent our final and best data.

IV. OVERVIEW AND DISCUSSION

The RU approach has been used to carry out a systematic basis set and correlation investigation of the hyperfine tensor of the $^1A_1'$ ground state of B₃. We have shown that a valence CAS calculation is capable of giving an accurate description of the hyperfine tensor. We obtain a vibrationally averaged FC contribution of $a_{\text{iso}} = 138.7$ MHz and a SD contribution of $A_x^d = -16.4$, $A_y^d = -26.6$ and $A_z^d = 42.9$ MHz. The experimental hyperfine coupling constant of B₃ (Ref. 1) was found to be isotropic within the experimental uncertainty in the rare-gas matrices at 4 K: for Ar to equal 130 MHz, and values differing in only a few MHz were found for both the Ne and Kr matrices. Our prediction for the FC contribution is in close agreement with the experimental tensor. However, the calculated

principal values of A^d are far beyond the experimental uncertainty, indicating that the observed isotropy of A is inconsistent with fixed, random orientations of B₃ in the rare-gas matrices. Rapid rotation of B₃ around the C₃ axis would produce an average A^d tensor with principal values -16.4, 8.2, and 8.2 MHz, which are still much larger than the experimental uncertainty. Hence our calculations indicate that the spin-dipole contribution to the hyperfine coupling is completely averaged out by free tumbling of B₃ in the rare-gas matrices. This result supports the speculation made in Ref. 1.

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