Characterization of the molecular iodine electronic wave functions and potential energy curves through hyperfine interactions in the $B0_u^+(3\Pi_u)$ state

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Received October 18, 2004; revised manuscript received December 5, 2004; accepted December 13, 2004

We present a high-resolution analysis of the six electronic states that share the same dissociation limit with the second excited electronic state $B$ in molecular iodine. These six states are coupled to the $B$ state via hyperfine interactions. The four hyperfine parameters, $C_B$, $\delta_B$, $d_B$, and $eqQ_B$, are calculated with the available potential energy curves and wave functions constructed from the separated-atom basis set. We obtain a maximum separation of the respective contributions from all six electronic states and compare each individual contribution with high-precision spectroscopic data, providing an independent verification of the relevant electronic structure. © 2005 Optical Society of America

1. INTRODUCTION

Comprehensive and high-precision measurements on hyperfine spectra in the $B-X$ system of molecular iodine provide a unique opportunity for a detailed examination of the molecule’s electronic structure relevant to the second dissociation limit, $^2P_{3/2} + ^2P_{1/2}$. Molecular iodine is a rare case in that the hyperfine spectra in the $B-X$ system have been recorded not only with high precision at the kilohertz level but also for a large set of rovibrational levels, extending from $\nu' = 2$ to just below the dissociation limit ($\nu' = 82$) in the excited $B0_u^+(3\Pi_u)$ electronic state.1–17 Precise empirical–interpolation formulas have been developed to describe the hyperfine interaction.2,3 These interpolation forms present a detailed frequency map for precision measurements relying on the hyperfine spectrum of molecular iodine. The vibrational levels studied cover a broad range of internuclear separation, with $R$ centroid ($R_c$, the mean of internuclear separations weighted by the $B$-state vibrational wave function) ranging from approximately 3 to 12 Å. Because hyperfine interactions can exert large influences on electronic structure, experimentally determined hyperfine parameters over a large range of $R_c$ allow a sensitive test of the relevant electronic wave functions and potential energy curves.

Precise measurement of hyperfine interactions has been applied to test several relevant electronic states, i.e., $X$, $B$, and $E$ in molecular iodine,4,18–25 and in other diatomic molecules.26 In the case of the $B0_u^+(3\Pi_u)$ state in molecular iodine, second-order contributions to the four hyperfine parameters, the electric quadrupole parameter $eqQ_B$, spin–rotation parameter $C_B$, tensorial spin–spin parameter $d_B$, and scalar spin–spin parameter $\delta_B$, have been calculated for several vibrational levels ($\nu' \sim 40–82$) in the $B$ state.4,18,19,22–24 In these analyses, the molecular wave functions involved were constructed from a separated-atom basis set because the molecule spends much of its time at large internuclear separations for high-lying vibrational levels close to the dissociation limit. The good agreement between the experimental data and these calculations justifies the separated-atom model as a simple and effective tool in characterizing the electronic structure at large internuclear separations. Nonetheless, there is room to extend this approach. First, the same calculation can be carried out with improved resolution for vibrational levels lower than $\nu' \sim 40$ as well as for the detailed rotational dependence in each vibrational level. This approach has become particularly relevant given the latest spectroscopic data with an extensive coverage of vibrational and rotational dependence of the hyperfine interactions.6,17 In addition, detailed information on the short- and intermediate-range ($R < 7 \text{ Å}$) potential energy curve (PEC) of the perturbing electronic state, obtained either empirically or theoretically, was largely unavailable when these earlier calculations were performed, and therefore the property of the molecular wave function of the corresponding electronic state could not be independently inferred from these analyses. In contrast, with adequate constraints on the PECs, a correct account of the hyperfine parameters permits either the determination of the admixture of the basis wave functions in the separated-atom model or the verification of more sophisticated molecular wave functions.

In this paper, we extend the calculation of hyperfine parameters to low vibrational levels and to rotational dependence at each vibrational level, using electronic wave functions derived from the separated-atom basis set and the related empirical or theoretical PECs. Our aim is to
take advantage of our recently measured hyperfine parameters covering an extensive range of rovibrational levels near the dissociation limit and combine them with other published experimental data to test the PECs, the electronic wave functions, and the separated-atom model. In doing so, we are able to quantitatively address several issues such as (1) to what extent the separated-atom wave functions can be extrapolated to small internuclear separations, (2) the estimation of the admixture of the basis wave functions in the separated-atom model, and (3) the sensitivity of the dependence of hyperfine parameters on the choice of PECs. For the spin–rotation parameter $C_B$, the calculated dependence on both vibrational and rotational quantum numbers is in good agreement with the experimental data for $v'\approx 42$. Subsequently, the admixture of the two $1_u$ states is independently determined. Moreover, calculations of the other three parameters, $eqQ_B$, $d_B$, and $\delta_B$, place a stringent constraint on the long-range PECs of the relevant electronic states. Here we consider the smooth second-order contributions. Thus the calculation does not cover the abnormal variations of the hyperfine parameters around $v'=57-60$ and $v'=76-78$, for which the existence of the strong hyperfine coupling has already been analyzed in a great detail.4,16,23

In Section 2 we introduce the explicit form of the second-order contributions to the hyperfine parameters in Hund’s case c coupling scheme, along with a discussion of the PECs and the electronic wave functions in the separated-atom model. We present results for the four effective hyperfine parameters at various internuclear separations in Section 3. These results are discussed in three steps to demonstrate the maximum separation of contributions from different perturbing electronic states. First, a detailed analysis of $C_B$ is required for the determination of the admixture of the two $1_u$ states. Then, through the calculation of $\delta_B$, contributions from the other two states (0_u and 0_g) are separated from the rest (two 1_g states), and the corresponding long-range PECs are tested. Finally, we present results for $eqQ_B$ and $d_B$, which are in part based on the information derived in the previous two steps. Conclusions are provided in Section 4.

2. THEORY

The hyperfine interaction, which is not included in the Born–Oppenheimer molecular Hamiltonian, can couple the $B0^+_u$ state to several electronic states sharing the same $2P_{3/2}^42P_{1/2}^4$ dissociation limit. Consequently, the hyperfine spectra of the $X\rightarrow B$ transitions are altered to various degrees depending on the coupling strength and the energy differences between the $B0^+_u$ and the perturbing states. An effective Hamiltonian based on second-order perturbation theory was developed by Broyer et al.23 to treat these couplings. Except for levels at which strong coupling is present, perturbed hyperfine spectra can generally be described by the effective hyperfine Hamiltonian with high precision by use of the four effective hyperfine parameters, $eqQ_B$, $C_B$, $d_B$, and $\delta_B$, extracted from fitting the spectroscopic data to the effective Hamiltonian. Moreover, second-order calculations of these parameters relate their experimental values to the relevant PECs and the admixture of the basis wave functions, imposing stringent constraints on the relevant electronic structure.

The detailed derivation of the matrix elements of this effective hyperfine Hamiltonian and the associated effective hyperfine parameters can be found in the literature.24,25 For clarity of the notation and discussion, we provide an overview of this derivation before we list the explicit expressions. Then we proceed to describe several computational issues concerning the preparation of the PECs, the electronic wave functions constructed from the separated-atom basis set, and the electronic matrix elements.

A. Matrix Element of the Hyperfine Hamiltonian

The hyperfine Hamiltonian of the iodine molecule can be formally written as

$$H_{hf} = H_{hf}(a) + H_{hf}(b) + H_{hf}(a,b),$$

(1)

where $a$ and $b$ denote the two iodine nuclei and $H_{hf}(a)$ and $H_{hf}(a,b)$ represent the nucleus-electron and nucleus-nucleus hyperfine interactions, respectively. The last term in the above Hamiltonian is left out in the following discussion because it contains only nuclear coordinates and thus cannot couple different electronic states.

With the last term dropped, this Hamiltonian can be expressed in tensorial form:

$$H_{hf} = \sum_{a=b} \sum_{k} (-1)^k Q_k^a(I_a) V_k^{a}\epsilon_k,$$

(2)

where the rank-$k$ spherical tensor operators $Q_k^a(I_a)$ and $V_k^{a}\epsilon_k$ act, respectively, on the nuclear spin $I_a$ and the electronic degrees of freedom.

Considering the strong spin-orbit interaction in this heavy molecule, Hund’s case c coupling scheme at large internuclear separations is appropriate for the molecular basis set, which we denote by

$$|\psi\rangle = |\Omega wMM_F\rangle,$$

(3)

where $\Omega$ is the projection of the total angular momentum $J$ onto the molecular axis connecting the two nuclei, $w$ is the vibrational quantum number, $I$ is the total nuclear spin, $F=I+J$, and $M_F$ is the projection of $F$ onto a quantization axis. Note that in the energy continuum, the discrete level index $\nu$ is replaced by a continuous energy spectrum $E$. Averaging explicitly over the molecular rotation in the laboratory frame gives matrix elements of this hyperfine Hamiltonian in terms of $3\nu$ (parentheses) and $6\nu$ (curly brackets) symbols and electronic matrix elements:

$$\langle \psi|H_{hf}^k(a)|\psi\rangle = \delta_{FF'}\delta_{MM_F}\langle -1 \rangle^{F+3\nu} J' k J \langle [2J'+1] \times (2J+1)(2I'+1)(2I+1)\rangle^{1/2} f_k(a, \Omega', \nu', \Omega, \nu),$$

(4)

where $\Delta J=J'-J$, $\Delta F=I'-I$, $\Delta \Omega=\Omega'-\Omega$, and $f_k(a, \Omega', \nu', \Omega, \nu)$ encapsulates the averaging over the
electronic motion in the molecular frame and the molecular vibration, which is written as
\[ f_k(\alpha, \Omega', v', \Omega, v_j) = (-1)^{1/2} \frac{C_k}{(k \ I_a \ I_u \ 0 \ I_a - I_u)} (\Omega' v' | \Omega \ I_a) (\Omega' v' | \Omega \ I_u). \]  
(5)

Here \( C_k = \mu_s g_I I_a \) is the nuclear magnetic dipole moment, where \( \mu_N \) is the nuclear magneton, \( g_I \) is the Landé factor for the iodine nucleus, and \( C_2 = \frac{1}{5} \sigma Q_{I_a} \) is the nuclear electric quadrupole moment with \( e \) the proton charge and \( Q_{I_a} \) defined as
\[ Q_{I_a} = e (I_a, M_{I_a} = I_a, \sum_p (3z_p^2 - r_p^2) I_a, M_{I_a} = I_a), \]  
(6)

where \( z_p \) and \( r_p \) refer to the coordinates of the protons \( p \) in the iodine nucleus.

For \( \Omega \neq 0 \), the projection of the angular momentum \( J \) onto the molecular axis can take either the positive or the negative direction, a degeneracy that is lifted by the coupling with external states. In this case the molecular wave function is represented by
\[ |\psi_u\rangle = \left(\frac{1}{\sqrt{2}}\right) |[\Omega, uJFM_F] + e[-\Omega, uJFM_F]|, \]  
(7)

where \( e \) can take on the values of 0 (\( \Omega = 0 \)) and \( \pm 1 \) (\( \Omega > 0 \)). The net effect of this \( \Omega \) doubling on the matrix element \( \langle \psi'_u | H_{K\alpha}^k (a) | \psi_u\rangle \) is to replace the \( f_k(a, \Omega', v', \Omega, v_j) \) defined in Eq. (5) by
\[ \left(\frac{1}{\sqrt{2}}\right)^{|\psi|} [1 + e(-1)^{J'} f_k(a, \Omega', v', \Omega, v_j) + C(\Omega^*)[e + e'(-1)^{J'} f_k(a, \Omega', v', -\Omega, -v_j)], \]  
(8)

where
\[ C(\Omega^*) = \begin{pmatrix} J' & k & J \\ -\Omega' & \Omega^* - \Omega \\ J' & k & J \\ -\Omega' & \Delta \Omega & \Omega \end{pmatrix}. \]

and \( \Omega^* = \Omega' + \Omega \).

Expression (8) is equivalent to Eq. (6) in Ref. 24 when \( e = 0 \). For the case of the \( B0^+_u \) state, expression (8) is reduced to
\[ \left(\frac{1}{\sqrt{2}}\right)^{|\psi|} [1 + e(-1)^{J'} f_k(a, \Omega', v', 0^*_u, v_j)]. \]  
(9)

The matrix element for the second nucleus \( b \) is related to that of the first nucleus \( a \) because of symmetry considerations\textsuperscript{24,28}:
\[ \langle \psi'_{a_u} | H_{K\alpha}^k (b) | \psi_{a_u}\rangle = (-1)^{3J'} \langle \psi'_{a_u} | H_{K\alpha}^k (a) | \psi_{a_u}\rangle, \]
\[ \langle \psi'_{a_u} | H_{K\alpha}^k (b) | \psi_{b_u}\rangle = (-1)^{3J'-1} \langle \psi'_{a_u} | H_{K\alpha}^k (a) | \psi_{b_u}\rangle, \]  
(10)

where the \( u (g) \) symmetry refers to the odd (even) electronic wave functions under reflection with respect to the center of the molecule. Another component capable of coupling external electronic states to the \( B0^+_g \) state is the off-diagonal part of the rotational Hamiltonian \( V^0 \), defined as
\[ V^0 = -\frac{\hbar^2}{2\mu R^2} [J_+(L_+ + S_+) + J_-(L_+ + S_+)], \]  
(11)

where \( \mu \) is the reduced mass of two nuclei and \( R \) is the internuclear separation. It can couple only states with \( \Delta \Omega = \pm 1 \) and the same \( u (g) \) symmetry, and therefore the \( B0^+_u \) state is coupled by \( V^0 \) to only two \( 1_u \) states. The matrix element of \( V^0 \) between the \( B0^+_u \) state and such a \( 1_u \) state with \( \Omega \) doubling (\( e' = 1 \)) is evaluated as
\[ \langle V^0 \rangle = \langle 1_{u, e' = 1} | V^0 | 0_u^* \rangle \]
\[ = -2J(J + 1)^{1/2} \frac{1}{\sqrt{2}} \times \begin{pmatrix} 1 \ (\Omega' = 1), v_j' \left[ \frac{\hbar^2}{2\sqrt{2}R^2} (L_+ + S_+) \right] 0^*_u v_j \\ 1 \ (\Omega' = 1), v_j' \left[ \frac{\hbar^2}{2\sqrt{2}R^2} (L_+ + S_+) \right] 0^*_u v_j \end{pmatrix} \]
\[ = -2J(J + 1)^{1/2} \frac{1}{\sqrt{2}} \times \begin{pmatrix} 1 \ (\Omega' = 1), v_j' \left[ \frac{\hbar^2}{2\sqrt{2}R^2} (L_+ + S_+) \right] 0^*_u v_j \end{pmatrix} \]
\[ = -2J(J + 1)^{1/2} \frac{1}{\sqrt{2}} \frac{\hbar^2}{2\sqrt{2}R^2} (L_+ + S_+) 0^*_u v_j. \]  
(12)

The factor \( \sqrt{2} \) in the last line of Eq. (12) arises from the \( \Omega \) doubling of the \( 1_u \) state.

B. Second-Order Contributions to Hyperfine Parameters

With the coupling matrix elements for \( V^0 \), \( V^1 \), and \( V^2 \) given in Subsection 2A, the hyperfine parameters are calculated by second-order perturbation theory to include the contributions from all rovibrational levels allowed by the selection rules in each of the six perturbing states \([C: 1_u, 1_u, 1_u(1/2)^2], 1_g(3/2)^2, 0_g(3/2)^2 \), and \( 3_0^u \). In the derivation of these parameters (see Appendix I in Ref. 28), a weak \( J' \) dependence of \( f_k(a, \Omega', v', \Omega, v_j) \) across neighboring rotational levels is assumed when the summation on \( J' \) is performed. However, to account for the \( \Omega \) doubling, one must replace \( f_k(a, \Omega', v', \Omega, v_j) \) defined in Eq. (5) with expression (9). In fact, this modification does not interfere with the just-mentioned assumption because the coupling selection rules for \( \Delta J = -1 \) are different for \( e' = +1 \) and \( -1 \); hence their combined effect adds no extra \( J' \) dependence to the modified \( f_k(a, \Omega', v', \Omega, v_j) \). After summations on \( I' \) and \( J' \) and reorganization of various terms according to their angular momentum dependence, the explicit expressions for the four effective parameters are obtained and are listed below\textsuperscript{28}:

\[ C_B = C_D - \frac{4}{[I_a(d_a + 1)(2I_a + 1)]^{1/2}} \times \sum_{l_a} \sum_{\nu'} \frac{f_0(\nu',0_a^0_0,1\nu')}{E_{0_a^0_0} - E_{1\nu'}} \]
\[ + \frac{2}{\pi} \left( \frac{\mu}{2\hbar^2} \right)^{1/2} \int_{E_0}^{\infty} dE \frac{f_0(1\nu',0_a^0_0,1\nu')}{\sqrt{E_a(E_{0_a^0_0} - E_{1\nu'})}} \right], \]

(13)

\[ \delta_B = -\frac{2}{3I_a(d_a + 1)(2I_a + 1)} \times \sum_{\Omega'} \chi(1 + |\epsilon'|) \left[ \sum_{\nu'} \frac{|f_1(\nu',\Omega',0_a^0_0)|^2}{E_{0_a^0_0} - E_{1\nu'}} \right] \]
\[ + \frac{2}{\pi} \left( \frac{\mu}{2\hbar^2} \right)^{1/2} \int_{E_0}^{\infty} dE \frac{|f_1(\nu',\Omega',0_a^0_0)|^2}{\sqrt{E_a(E_{0_a^0_0} - E_{1\nu'})}} \right], \]

(14)

\[ eqQ_B = eqQ_0 - 4\sqrt{2} \sum_{l_a} \sum_{\nu'} \frac{4f_0(1\nu',0_a^0_0,1\nu')}{E_{0_a^0_0} - E_{1\nu'}} \]
\[ + \frac{2}{\pi} \left( \frac{\mu}{2\hbar^2} \right)^{1/2} \int_{E_0}^{\infty} dE \frac{4f_0(1\nu',0_a^0_0,1\nu')}{\sqrt{E_a(E_{0_a^0_0} - E_{1\nu'})}} \right] \]
\[ + 10 \sum_{k,k'=1,2} \sum_{1\Omega'} (1 - |\epsilon'|) \]
\[ \times \left[ \sum_{\nu'} \frac{2f_0(\nu',\Omega',0_a^0_0,1\nu')}{E_{0_a^0_0} - E_{1\nu'}} + \frac{2}{\pi} \left( \frac{\mu}{2\hbar^2} \right)^{1/2} \int_{E_0}^{\infty} dE \frac{2f_0(\nu',\Omega',0_a^0_0,1\nu')}{\sqrt{E_a(E_{0_a^0_0} - E_{1\nu'})}} \right] \]
\[ \times \left[ \Delta\Omega - \Delta\Omega \begin{pmatrix} 1/2 1/2 \\ 1/2 1/2 \end{pmatrix} \right] \]

(16)

\[ C_D \] and \( eqQ_0 \) are the first-order contributions to the corresponding parameters in Eqs. (13) and (16), respectively. In Eqs. (14)–(16), \( \Omega' \gg 0 \) and \( \epsilon' \) can take on the values of \( 0(\Omega' = 0) \) and \( \pm 1(\Omega' > 0) \). For each perturbing electronic state \( \Omega' \), \( \chi = 1 \) \((-1)\) if the state has \( g(u) \) symmetry and the state’s contribution to the hyperfine parameters comes from both discrete levels \( \nu',J \) and the energy continuum \( E_{1\nu'} \), whose density of state is \((2/\pi)(\mu/2\hbar^2E_{1\nu'})^{1/2}\), where \( E_a \) is the radial kinetic energy. \( E_0 \), the lower limit of the integrals for the energy continuum, is the energy just above the last discrete rovibrational level that an attractive potential can support. In the expressions for \( \delta_B \), \( d_B \), and \( eqQ_B \), the extra factor \( (1 + |\epsilon'|) \) arises from the \( \Omega \) doubling of the perturbing state \( \Omega' \).

C. Preparation of Potential Energy Curves and Electronic Wave Functions

We use the available empirical and theoretical I\(_2\) PECs to construct the rovibrational structure and the associated wave functions inside each electronic state. The B-state empirical PEC is adopted from the analysis performed by Gerstenkorn et al., \(^{28}\) in which the PEC was constructed from Fourier spectroscopic data by use of an inverted perturbation approach method. For the six states that perturb the \( 0_2^0_0 \) state, we adopt the empirically improved relativistic PECs in Ref. 30, and these PECs are used in the short and intermediate internuclear separations (\( R \approx 6.5 \) Å). Figure 1 plots these PECs over the range 2.5 Å < \( R < 6.5 \) Å, along with the B-state empirical PEC and the other three PECs belonging to the same dissociation limit. Apart from these PECs, the \( 1_2^1(10) \) empirical PEC determined from the optical–optical double-resonance experiment by Jewsbury et al. \(^{31}\) is also tested in the calculation. For large internuclear separations (\( R > 7 \) Å), the PECs take the inverse-power form, \( V(R) = C_0/R^6 \) + \( C_6/R^3 \) + \( E_{\text{diss}} \), which includes quadrupolar electrostatic and dispersion energy terms, with the corresponding coefficients \( C_5 \) and \( C_6 \) determined by Saute and Aubert-Frécon. \(^{32}\) Figure 2 shows these long-range PECs for all ten electronic states that share the same dissociation limit, \( 2P_3/2 + 2P_1/2 \). To make a smooth transition between the two PEC segments, each short-range PEC is shifted vertically to match the corresponding long-range PEC at around \( R = 7 \) Å. The matched short- and long-range PECs are illustrated in Fig. 3.

The matrix element \( \langle \Omega',\nu',0_a^0_0|\psi_{\Omega,\nu}|0_a^0_0,\nu \rangle \) in the functions \( f_0(\nu',\Omega',0_a^0_0) \) in Eqs. (13)–(16) is approximated as a product of an electronic matrix element and a Franck–Condor in-
Chen et al. and the vibrational levels inside a perturbing state.

Energy continua, respectively. As an example, a portion of the vibrational spectrum is shown in Fig. 5. A special case arises when a potential barrier is present. As a result, their energy spectra can be broadened significantly and can no longer be treated as discrete or quasi-discrete levels. We isolate these levels from the residual discrete levels and treat them instead as part of the energy continuum.

At large internuclear separations (R > ~7 Å), the molecular wave functions can be constructed from symmetrized products of two atomic wave functions. Each molecular wave function constructed in this way is a linear combination of the separated-atom basis functions (see Table I in Ref. 32). For example, the two 1g states, 1g(3Σg+) and C:1u(3Σu0), also designated as 1g and 1g*, respectively, are mixtures of the two basis functions |1g⟩ and |1g*⟩:

\[ |1g⟩ = α|1g⟩ + \sqrt{1−α^2}|1g*⟩, \]

\[ |1g*⟩ = α|1g⟩ + \sqrt{1−α^2}|1g*⟩, \]

with α as the admixture of the two basis functions. Likewise, the two 1u states, 1u(1Πu) and 1u(1Σu0), are linear combinations of the two basis functions |1u⟩ and |1u*⟩:

\[ |1u⟩ = β|1u⟩ + \sqrt{1−β^2}|1u*⟩, \]

\[ |1u*⟩ = β|1u⟩ + \sqrt{1−β^2}|1u*⟩, \]

Fig. 2. Long-range PECs for the ten electronic states, adopted from Ref. 32. Dashed line, the 3P3/2 + 3P1/2 dissociation limit. Note that 1g and 1g* refer to the C:1a(3Σg) and 1g(3Σg) states, respectively.

Fig. 3. Combining the short- and long-range potentials. Solid curves, the short-range (R < 7 Å) PECs from the ab initio calculation30; dashed curves, the ab initio long-range PECs from Ref. 32. To make a smooth connection between two segments of the PEC, each short-range PEC has been shifted vertically to match the corresponding long-range one. The unchanged B-state empirical PEC30 and ab initio long-range PEC are also included.

The electronic matrix element is assumed to have a weak R dependence over the range sampled by the vibrational wave function. FORTRAN codes LEVEL33 and BCONT34 developed by Le Roy and Kraemer are used to calculate the Franck–Condor integrals for the discrete levels and energy continua, respectively. As an example, a portion of the B-state rovibrational structure is sketched in Fig. 4, and the vibrational levels inside a perturbing state C:1a are shown in Fig. 5. A special case arises when a potential can support rotational levels above its asymptotic energy because of a potential barrier located at the PEC outer limit. Wave functions of such levels can tunnel through the potential barrier. As a result, their energy spectra can be broadened significantly and can no longer be treated as discrete or quasi-discrete levels. We isolate these levels from the residual discrete levels and treat them instead as part of the energy continuum.

At large internuclear separations (R > ~7 Å), the molecular wave functions can be constructed from symmetrized products of two atomic wave functions. Each molecular wave function constructed in this way is a linear combination of the separated-atom basis functions (see Table I in Ref. 32). For example, the two 1g states, 1g(3Σg+) and C:1u(3Σu0), also designated as 1g and 1g*, respectively, are mixtures of the two basis functions |1g⟩ and |1g*⟩:

\[ |1g⟩ = α|1g⟩ - \sqrt{1−α^2}|1g*⟩, \]

\[ |1g*⟩ = α|1g⟩ + \sqrt{1−α^2}|1g*⟩, \]

with α as the admixture of the two basis functions. Likewise, the two 1u states, 1u(1Πu) and 1u(1Σu0), are linear combinations of the two basis functions |1u⟩ and |1u*⟩:

\[ |1u⟩ = β|1u⟩ + \sqrt{1−β^2}|1u*⟩, \]

\[ |1u*⟩ = β|1u⟩ - \sqrt{1−β^2}|1u*⟩, \]

Fig. 4. B-state rovibrational structure. Thick solid curves are the empirical B-state rotationless potential.29 Vibrational levels ν = 57–68 are indicated as short-dashed lines. The rotational levels at several vibrational levels are also drawn as short bars. The curve of long dashes is the effective potential (a sum of the rotationless and centrifugal potentials) associated with a rotational level (ν = 60, J = 83). The probability distributions of the molecular vibration for levels (ν = 60, J = 0) and (ν = 60, J = 83) are plotted as thin solid curves for comparison of the internuclear separations populated by the two levels.

Fig. 5. Two 1g PECs used in the calculation of Cg. Also plotted is the B-state empirical potential,27 which is used for all internuclear separations. C:1g, and 1g PECs (R < 7 Å) are constructed from theoretical30 (R < 7 Å) and long-range PECs33 (R > 7 Å). The PECs from ab initio calculation are shifted vertically to match the corresponding long-range ones. Dashed lines, the vibrational levels of the C:1a state. The 1g and C:1u states are also denoted by 1u* and 1u, respectively.
\[ |1^\sigma_u\rangle = \beta |1^\sigma_d\rangle - \sqrt{1 - \beta^2} |1^\sigma_d\rangle, \]

where \(1^\sigma_u\) and \(1^\sigma_d\) refer to \(1^\sigma(1^1\Sigma_u^{+})\) and \(1^\sigma(3^\Sigma_d^{+})\) states, respectively. The \(R\) dependence of the mixing parameters \(\alpha\) and \(\beta\) will be examined in Section 3. The other two states, \(0^\Sigma_c(1^1\Pi_d)\) and \(0^\Sigma_c(6^3\Sigma_u)\), each consist of only one basis function. With molecular wave functions derived from the separated-atomic basis functions, the electronic matrix element \((\Omega | V^2_{\text{mol}}(\alpha)/W_0^0 \rangle)\) can be readily determined from the experimental values of atomic hyperfine constants.\textsuperscript{18,24}

3. RESULTS AND DISCUSSIONS

In this section we present results for the calculated effective hyperfine parameters, \(e\)\(q_{\text{B}}, C_B, d_B, \) and \(\delta_B, \) together with a detailed analysis of the electronic structure of the associated states. The calculation covers nearly all the vibrational levels \((3 \leq \nu \leq 82)\) in the \(B0^+_u\) state, with \(R_c\) extending from \(\sim 3.5\) to \(\sim 12.5\) Å. Additionally, to demonstrate the numerical analysis on a finer energy scale, we show the calculated rotational dependence of the hyperfine parameter \(C_B\) for two vibrational levels. We also compare calculations with experimental results.

A. Spin–Rotation Parameter \(C_B\) and the Admixture of Two \(1^\sigma_u\) States

The states that contribute to \(C_B\) are restricted to the \(1^\sigma\) states by the coupling selection rule associated with the off-diagonal rotational Hamiltonian \(V^0\). Thus the calculation of \(C_B\) automatically isolates the second-order contributions of the two \(1^\sigma\) states from those of the other four perturbing states. Furthermore, this allows a determination of the mixing parameter \(\alpha\) between the two \(1^\sigma\) states that, in turn, can serve as a consistency check of the relevant \(ab \text{ initio}\) calculation based on the separated-atom model. The details of the PECs and molecular wave functions used in Eq. (13) have already been described in Section 2. Here we stress that, in the calculation, we are able to use the same value for mixing parameter \(\alpha\) at a wide range of internuclear separations, especially in the intermediate and long ranges and this value is adjusted until a global agreement with experimental results is achieved.

Figure 6 summarizes the comparison between calculations and experiments. In the figure, filled circles are experimental data, and open circles and squares are calculations performed with the mixing parameter \(\alpha=0.99\) and 0.9, respectively. To the best of our knowledge, we incorporated all available experimental data reported in previous publications.\textsuperscript{1–17} First, the result shows a sensitive dependence on the mixing parameter \(\alpha\) at large internuclear separations \(R \geq \sim 7\) Å, as shown in Fig. 6(a). In contrast, we verify that the uncertainty in the two \(1^\sigma\) PECs has merely a small influence on the calculation at large \(R\). For instance, we intentionally decrease the potential depths of the two \(1^\sigma\) states by 50 and 30 cm\(^{-1}\) and repeat the calculation. While this modification results in a noticeable reduction of \(C_B\) between 4.0 and 5.5 Å, as indicated by triangles in Fig. 6(b), it induces less than a 2% change of \(C_B\) at \(R_c > \sim 7\) Å. Additional diagnostic tests on the different parts of the two \(1^\sigma\) PECs produce similar outcomes. Consequently, the mixing parameter \(\alpha\) is essentially constant and takes on the value of 0.99 for internuclear separation \(R > 7\) Å. Moreover, a calculation that uses the same \(\alpha\) at even shorter \(R_c\) is in good agreement with the experiment until \(R_c\) reaches 4 Å, as shown in Figs. 6(b) and 6(c). On the other hand, a close examination of \(C_B\) at \(R_c < 4\) Å in Fig. 6(c) shows that the calculated results gradually deviate from the experiment, quantitatively illustrating a transition from the separated-atom model to the overlapped and distorted charge distribution that calls for a description employing more sophisticated molecular wave functions.

Fig. 6. Second-order calculations of the spin–rotation parameter \(C_B\). Filled circles, spectroscopic data from the literature\textsuperscript{1–17}; other symbols and lines, calculations. (a) With a mixing parameter \(\alpha=0.99\) (open circles on solid curve) for two \(1^\sigma_u\) states, the calculations agree well with the experimental data,\textsuperscript{1–17} whereas changing \(\alpha\) to 0.9 (squares on dashed curve) results in a large global deviation from the experimental data. (b) A deliberate reduction of the potential depths of the two \(1^\sigma\) PECs (triangles on solid curve) produces a noticeable discrepancy at \(R_c=4.2–5.5\) Å but does not affect calculations at shorter and longer internuclear separations. (c) At \(R_c < 4\) Å, the calculation begins to depart from the experimental data.\textsuperscript{1–17}
Figure 7 plots the calculated rotational dependence for two vibrational levels, \(v' = 70\) and \(v' = 47\), with the mixing parameter \(\alpha = 0.99\). Considering a large energy difference between the two levels and the use of a fixed mixing parameter, the agreement with the experimental data\(^1\)–\(^7\) is reasonably good at both vibrational levels. Similar to the global trend exhibited in Fig. 6, the rotational dependence of \(C_B\) is due to the smooth variation of the Franck–Condon overlap and the energy denominator in Eq. (13).

This variation is also responsible for the perturbation-induced rovibrational dependence in the other three hyperfine parameters. When dealing with high-lying levels of the \(B0_u^+\) state, we estimate the possible contributions beyond second-order perturbation theory. The strength of the perturbation is characterized by the parameter \(\lambda = |\gamma/\Delta E|\), where \(\gamma\) is the coupling between the two discrete levels inside the \(B0_u^+\) and \(1_u\) states and \(\Delta E\) is their energy difference. Numerical estimation shows that \(\lambda\) is well below 1 for these high-lying levels. Moreover, when there is a possibility of energy coincidence, magnitude of the coupling between the two levels involved is verified to be below a few megahertz. Given this coupling strength, \(\Delta E\) has to be less than a few tens of megahertz for a strong perturbation to occur, which is unlikely because of the large mismatch in the rovibrational constants of the \(B0_u^+\) and \(1_u\) states. Thus second-order perturbation theory is sufficient for the calculation of \(C_B\) and the analysis of the related \(1_u\) states. However, for the other three hyperfine parameters, precautions should be taken because the \(B0_u^+\) state can be strongly coupled to a discrete level in a particular electronic state. We will discuss this case in Subsection 3.C.

### B. Separation of Contributions from \(0_u^+\left(^3II_g\right)\) and \((3)0_u^+\) States

Although only two \(1_u\) states contribute to \(C_B\), the other three parameters, \(\delta_B\), \(d_B\), and \(eqQ_B\), contain perturbations from all six perturbing states. In Subsection 3.A, we determined the mixing parameter \(\alpha\) associated with the two \(1_u\) states, and the sensitivity of \(C_B\) to the related PECs was investigated. With the help of this information, we decompose the hyperfine parameters into contributions from subsets of six states, or even from individual states when it is possible, allowing a sensitive characterization of the \(0_u^+\) and \(0_u^{-}\) states and the related long-range potentials.

We divide the six states into four groups: two \(1_u\) states, the \(0_u^+\) state, the \(0_u^{-}\) state, and two \(1_u\) states. Each of the three hyperfine parameters can be decomposed into terms that correspond to the contributions from these four groups of electronic states. For instance, the scalar spin–spin parameter \(\delta_B\) can be written as

\[
\delta_B = \delta(1_u) + \delta(1_u) + \delta(0_u^+) + \delta(0_u^-) .
\]  

From Eqs. (14) and (15), it follows that \(d_B\) is closely related to \(\delta_B\) by

\[
d_B = \frac{1}{2} \delta(1_u) + \frac{1}{2} \delta(1_u) - \delta(0_u^+) - \delta(0_u^-) .
\]

Using Eqs. (19) and (20), we can isolate the contributions of the \(0_u^+\) and \(0_u^-\) states from those of the other four states by

\[
[\delta(0_u^+) + \delta(0_u^-)] = \frac{1}{2}(\delta_B - 2d_B) ,
\]

where the right-hand side can be determined experimentally with the values of \(\delta_B\) and \(d_B\) from the spectroscopic fit.\(^1\)–\(^7\) The left-hand side of Eq. (21) is calculated and plotted (open squares on dashed curve) in Fig. 8(a). For comparison we also plot the experimental values (filled circles) according to the right-hand side of Eq. (21). Recall that in the calculation there is no adjustable parameter for the electronic wave functions of the \(0_u^+\) and \(0_u^-\) states. As can be seen in Fig. 8(a), there is a noticeable discrepancy between the experiment and the calculation, which increases with increasing \(R_c\).

To resolve the source of this discrepancy, the contributions from \(0_u^+\) and \(0_u^-\) need to be distinguished from each other. We notice that the last term in Eq. (16) for \(eqQ_B\) dominates when \(k\) and \(k'\) equal 1. Thus one can keep only these terms and compare them with Eq. (14). This leads to the following relation between \(eqQ_B\) and \(\delta_B\):

\[
\frac{1}{25}[eqQ_B - eqQ_0] = -\frac{1}{2} \delta(1_u) + \frac{1}{2} \delta(1_u) - \delta(0_u^+) + \delta(0_u^-) ,
\]

where \(eqQ_0\) is the first-order contribution, which is calculated in the separated-atom basis set at large internuclear separations. From Eqs. (19) and (20) and expression (22), the contributions from \(0_u^+\) and \(0_u^-\) are thus isolated from each other by

\[
[\delta(1_u) - 2\delta(0_u^-)] = d_B - \frac{1}{20}[eqQ_B - eqQ_0] ,
\]

\[
[\delta(1_u) + 2\delta(0_u^+)] = \frac{1}{2} d_B - \frac{1}{20}[eqQ_B - eqQ_0] ,
\]

where the right-hand side again can be determined experimentally by use of the values of \(\delta_B\), \(d_B\), and \(eqQ_B\) extracted from the spectroscopic fit. In Subsection 3.A we
determined the mixing parameter $\alpha$ related to $1_g$ states. This information is incorporated into the calculation of the left-hand side of Eqs. (23) that also involves the contribution from two $1_g$ states. Figures 8(b) and 8(c) show our results for the $0_u^-$ (open squares on dashed curves) and $0_u^-$ (open circles) states, respectively, along with the experimental data (filled circles) plotted in both panels according to the right-hand side of Eqs. (23). While the calculation of $0_u^-$ agrees with experimental data, a discrepancy exists for the $0_u^-$ state that is consistent with the discrepancy observed in Fig. 8(a). Evidently, the calculation of $0_u^-$ is the source of this discrepancy.

We perform additional diagnostic calculations of $\delta 0_u^-$. We verify that moderate modifications to the short- and intermediate-range potentials of the $0_u^-$ state cannot be responsible for the large discrepancy at $R_c \approx 8 \text{ Å}$, as shown in Fig. 8(b). Conversely, $\delta 0_u^-$ is sensitive to $C_5$ and $C_6$ of the $0_u^-$ long-range potential. In fact, at large $R_c$, the magnitude of $\delta 0_u^-$ has a steep increase that is dominated by perturbations from the last few discrete levels in the $0_u^-\text{state whose energies depend sensitively on the shape of the long-range potential. We therefore adjust $C_5$ and $C_6$ of the $0_u^-$ long-range potential to compensate for the error in the calculation of $\delta 0_u^-$. The modified long-range potential is then close to the $2_g$ long-range potential as shown in Fig. 2. In light of this observation, we repeat the calculation of $\delta 0_u^-$ with the $0_u^-$ long-range potential replaced with that of the $2_g$ state. These new results (open circles on the solid curve) are also presented in Figs. 8(a) and 8(b). The discrepancy is greatly reduced in comparison with the dashed curves that used the original $0_u^-$ long-range potential. We also estimate the coupling-strength $\lambda$ introduced in Subsection 3.A for each discrete level in the $0_u^-$ state to confirm the validity of the above analysis by use of second-order perturbation theory. We note that, although this comparison demonstrates a highly sensitive dependence of hyperfine interactions on the long-range PEC, the analysis alone does not provide a definitive answer to the preferred use of the $2_g$-state long-range PEC.

C. Strong Perturbation from the $1_g(11_2^n)$ State and Its Contributions to Hyperfine Parameters $\delta g_B$, $d_B$, and $eqQ_B$

In previous subsections we divided the six perturbing states that contribute to $\delta g_B$, $d_B$, and $eqQ_B$ into four groups, and the contributions from three groups were analyzed in detail. Once the contributions from the last two $1_g$ states are determined, the three hyperfine parameters $\delta g_B$, $d_B$, and $eqQ_B$ can be obtained by combination of contributions from all four groups. Among the two $1_g$ states, the outer branch of the $1_g(11_2^n)$ PEC is close to that of the $B0_u^-$ state (see Figs. 1 and 2), resulting in a strong coupling to high-lying levels ($70 \leq v_B \leq 82$) of the $B0_u^-$ state because of favorable Franck–Condon overlaps. Furthermore, this perturbation is enhanced because for each high-lying level in the $B0_u^-$ state, there is a nearby discrete level in the $1_g(11_2^n)$ state whose energy separation with the perturbed level is typically a few gigahertz. In calculating the contribution of the $1_g$ states, we monitor the coupling strength between the $B0_u^-$ and $1_g(11_2^n)$ states for high-lying levels ($70 \leq v_B \leq 82$). For $v_B = 78$, the coupling-strength $\lambda$ is verified to be below 0.1, whereas at the last four levels $v_B = 79–82$, $\lambda$ can be as large as 0.4. Therefore the second-order calculation for the $1_g(11_2^n)$ state is primarily restricted to levels below $v_B = 78$.

Despite the inadequacy of the second-order calculation for the $1_g(11_2^n)$ perturbation allows a high-resolution examination of the $1_g(11_2^n)$ long-range potential. We find that only a minor adjustment on the long-range PEC (see Fig. 2) is needed for the calculation of $\delta g_B$ to achieve good agreement with the experimental data,$^1$–$^3$ as shown in Fig. 9. In the calculation the value of the mixing parameter $\beta$ for the two $1_g$ states is taken from Ref. 4 and kept fixed.

Considering the linear independence of Eqs. (19) and (20) and expression (22), we perform calculations of $d_B$ and $eqQ_B$ to cross-check the $1_g$ long-range PEC and the mixing parameters $\alpha$ and $\beta$. The hyperfine parameter $d_B$ is calculated with Eq. (20). In the case of $eqQ_B$, our calculation includes both major contributions in expression (22) and other minor terms in Eq. (16). The results for $d_B$ and $eqQ_B$ agree reasonably well with experiment, as
shown, respectively, in Figs. 10 and 11. Compared with $d_B$, our calculation of $eqQ_B$ has a relatively large discrepancy because the residual error of $\delta_1$ is amplified by a factor of 10 in the case of $eqQ_B$ according to Eq. (19) and expression (22). Once the mixing parameter $\beta$ of the two $1_g$ states is independently determined, the calculation of $d_B$ and $eqQ_B$ can be further improved by a global fit of the $1_g(^2\Pi_g)$ long-range PEC to the three hyperfine parameters $d_B$, $d_B$, and $eqQ_B$.

Unlike $C_B$, $\delta_B$, and $d_B$, which result solely from perturbations of external electronic states over the whole range of internuclear separation, $eqQ_B$ has both first-order and second-order components that are important in different regions. Our numerical analysis makes it possible to locate more accurately the regions at which each component dominates. As shown in Fig. 11, at short internuclear separation ($R_c<5$ Å), the perturbation from the external states is negligible. The perturbation sets in at $R_c=5$ Å and increases along with the internuclear separation. Finally, it is worth noting that, at $R_c<5$ Å, the first-order component of $eqQ_B$ departs from the constant value determined by both the separated-atom basis and the linear combination of atomic orbitals models with the decreasing internuclear separation because of a combined effect of (1) the nuclear quadrupole–quadrupole interaction and (2) the distortion and overlapping of the two atomic electric charge distributions.

4. CONCLUSIONS

We have performed second-order calculations of the four hyperfine parameters $C_B$, $\delta_B$, $d_B$, and $eqQ_B$ by using the available molecular PECs and electronic wave functions derived from the separated-atom basis set. We have shown that, by dividing the six perturbing electronic states into four subgroups, their contributions to the hyperfine parameters can be separated and directly compared with the corresponding experimental data. For the spin–rotation parameter $C_B$, the results for both rovibrational dependence agree well with the experimental data for a wide range of internuclear separations ($R_c>\sim4$ Å), and the admixture of the two $1_g$ states is independently determined as $\alpha=0.99$. However, the calculations depart from the experimental data at short internuclear separations ($R_c<\sim4$ Å), indicating the breakdown of the separated-atom model. Moreover, calculations of the other three hyperfine parameters verify the mixing parameter of two $1_g$ states and place a stringent constraint on the long-range PECs of the relevant electronic states. On the basis of our investigations described here and earlier studies,\textsuperscript{1–17} the effective hyperfine Hamiltonian developed in Ref. 28 with second-order perturbation is proved to be sufficiently accurate to describe the experimental obser-
vations when strong perturbation from the $I_2$ state is absent. The study provides an independent and quantitative test on the separated-atom model and the related PECs.

ACKNOWLEDGMENTS

We thank J. L. Hall for his critical reading of the manuscript and W.-Y. Cheng for his contributions at an earlier stage of this paper. We acknowledge support from NASA, the National Science Foundation, the U.S. Office of Naval Research, and the National Institute of Standards and Technology.

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REFERENCES


19. B. Bacis, M. Broyer, S. Churassy, J. Vergés, and J. Vigué, "$\nu_4$ measurements in the $X_1\Sigma^+ \rightarrow B^1\Sigma^+$ state of $I_2$: a test of the electronic molecular eigenfunctions," J. Chem. Phys. 73, 2641–2650 (1980).


33. R. J. Le Roy, "LEVEL 7.5: a computer program for solving the radial Schrödinger equation for bound and quasibound levels," University of Waterloo Chemical Physics Research Rep. CP-635 (University of Waterloo, Waterloo, Ontario, Canada, 2002). The source code and manual for this program may be obtained from the Computer Programs link on the Internet site http://leroy.uwaterloo.ca.