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Theoretical investigation of weakly-bound complexes of B with H₂

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Continuing an earlier study [M. H. Alexander, J. Chem. Phys. **99**, 6014 (1993)] of the B(²P)⋯H₂ complex, we report here a further investigation into the adiabatic→diabatic transformation for this system, characterized by three potential energy surfaces (PES's) which become asymptotically degenerate. The diabatic PES's are used to determine the energies of the lowest bend–stretch levels of complexes of B(²P) with either *o*- or *p*H₂. The predicted dissociation energies (*D*₀) are 27.9 and 38.6 cm^{−1} for the complexes with *p*H₂ and *o*H₂, respectively, and 37.3 and 48.5 cm^{−1} for the complexes with *o*D₂ and *p*D₂, respectively. The motion of the *o*H₂ moiety within the cluster cannot be described accurately using a single electronic potential energy surface. In addition, new *ab initio* calculations are reported for the complex of H₂ with B in its first electronic excited state (...2s²3s). The PES for this B(²S)⋯H₂ complex is repulsive and nonreactive, at least in the region sampled by vertical electronic excitation of the B(²P)⋯H₂ complex. © 1995 American Institute of Physics.

I. INTRODUCTION

Over the past few years, the B+H₂ system has been the object of several experimental investigations. These have included reactions of electronically excited B with H₂,¹ the spectroscopy of B in H₂ matrices,² the reaction of translationally hot B atoms with H₂ codeposited in an Ar matrix,³ and, more recently, the formation and detection of the binary B⋯H₂ complex.⁴

The complicating, and challenging, feature of the B⋯H₂ system, as compared to the interaction of an *S*-state atom [Li(2s) or Mg(3s²)] with H₂, is the additional complexity introduced by the threefold degeneracy of the 2*p* orbital, which gives rise to three adiabatic PES's (two of *A'* symmetry and one of *A''* symmetry in *C_s* geometry) which become degenerate at large B–H₂ distances. Prior theoretical investigations of the interaction of an atom in a *P* electronic state with H₂ have been reported for a number of atoms; F(²P),^{5–9} C(³P),¹⁰ Be(³P),¹¹ Na(²P),^{12–15} Mg(³P),¹⁶ Cd(^{1,3}P).¹⁷ Several years ago we reported¹⁷ the determination of the potential energy surfaces (PES's) which are accessed by the approach to H₂ to B in its ground (2s²2*p* ²P) electronic state.

In *C_{2v}* geometry, the two B(²P)H₂ states of *A'* symmetry become ²A₁ and ²B₂ and the unique state of *A''* symmetry, ²B₁. The BH₂ molecule is strongly bound [*D*₀=349±65 kJ/mol (Ref. 18)] with a bent structure¹⁹ (H–B–H angle 131°, BH distance 1.18 Å, and electronic symmetry ²A₁). Notwithstanding, we have argued¹⁷ on the basis of complete-active-space, self-consistent-field (CASSCF) (Ref. 20) calculations that there will be a significant barrier to molecule formation upon approach of B(²P) to H₂, for two reasons. First, the H₂ molecule must be significantly stretched before insertion of the B atom can occur. In addition, substantial orbital rearrangement must accompany formation of the BH₂ molecule. In the present article we shall report multireference, configuration-interaction (MRCI) calculations which confirm our earlier prediction of a barrier to molecule formation.

Except in the two high symmetry geometries (*C_{2v}* and

C_{∞v}), the two B(²P)H₂ states which are symmetric (*A'*) with respect to reflection of the wave function in the triatomic plane, represent, in the simplest picture, an orthogonal transformation of the two in-plane orientations of the B 2*p* orbital. In a treatment of the nuclear motion of the B(²P)+H₂ system it is most convenient to consider a *diabatic* representation of the interaction potential, in which the three states are characterized by the three Cartesian orientations of the B 2*p* orbital with respect to the vector *R* which joins the atom to the center-of-mass of the H₂ molecule.^{6,17,21}

In our earlier paper,¹⁷ we followed the pioneering work of Rebentrost and Lester⁵ on the F(²P)+H₂ system and used the matrix elements of the electronic orbital angular momentum *l* to define the approximate adiabatic→diabatic transformation. Alternatively, one can use the CI coefficients of the dominant configurations to define the adiabatic→diabatic transformation.²² As will be described in Sec. II below, this results in a transformation unchanged from what was determined previously.¹⁷ In addition, both transformations predict derivative coupling matrix elements which are nearly identical to those calculated numerically, directly from the adiabatic electronic wave functions.

Using our diabatic B(²P)H₂ diabatic PES's,¹⁷ we then predict the energies and structures of the lowest bend–stretch levels of the B(²P)⋯H₂ complex. To do so, we make use of the recent general treatment by Dubernet and Hutson²¹ of complexes between open-shell atoms and closed-shell diatomic molecules. We shall report on the results of these calculations in Secs. III and IV below.

In a recent experimental investigation, Yang *et al.*,⁴ excited electronically the B(²P)⋯H₂ complex to the B(²S)⋯H₂ complex, which is unbound and promptly dissociates. The fluorescence of the dissociated B(²S) atom provides an action spectrum of the B(²P)⋯H₂ complex, as a function of the frequency of the excitation laser. To model this experiment requires, in addition, a knowledge of the PES's of the B(²P)⋯H₂ complex. We shall report calculations of these PES's in Sec. II C. The simulation of the excitation spectrum is described in the accompanying paper.⁴

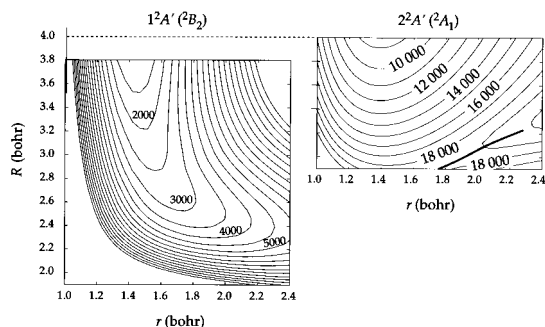


FIG. 1. Contour plots of the lowest MRCI $B(^2P)\cdots H_2$ potential energy surfaces of A' symmetry as a function of the H–H bond distance r and the distance R of the B atom from the center of mass of the BH_2 molecule. The left-hand panel, with contours every 1000 cm^{-1} , depicts the lower $1A'$ potential energy surface, which in C_{2v} symmetry corresponds to the 2B_2 surface, in which the B $2p$ orbital is oriented *parallel* to the H_2 bond. The right-hand panel, with contours every 2000 cm^{-1} , depicts the higher $2A'$ potential energy surface. In C_{2v} symmetry this corresponds to the 2A_1 surface, in which the B $2p$ orbital is oriented *perpendicular* to the H_2 bond and in the triatomic plane. The barrier on the $2^2A'$ surface due to an avoided crossing is indicated by the thick gray contour. The equilibrium geometry of the BH_2 molecule is T-shaped (C_{2v} symmetry) with $R=0.923$ bohr, $r=4.06$ bohr, and an electronic wave function of 2A_1 symmetry.

II. AB INITIO INVESTIGATIONS

A. Barrier to molecular formation in encounters of $B(^2P)$ with H_2

In our previous study,¹⁷ we used complete-active-space, self-consistent-field (CASSCF) (Ref. 20) calculations to predict a substantial barrier to formation of the BH_2 molecule upon approach of ground state B atoms to H_2 . These CASSCF calculations are here supplemented by multireference, configuration-interaction (MRCI) calculations. As an atomic orbital basis we used the augmented correlation-consistent valence-triple-zeta (*avtz*) basis of Dunning and co-workers^{23,24} ($11s6p3d2f$ contracted to $5s4p3d2f$ for B and $6s3p2d$ contracted to $4s3p2d$ for H). We found¹⁷ earlier that the *avtz* basis yielded $B(^2P)$ interaction potentials which were virtually identical to those determined with larger basis sets.

With this *avtz* basis set, complete-active-space, self-consistent-field (CASSCF) (Ref. 20) calculations were performed, with seven electrons in a space (exclusive of the $1s$ orbital on B) of four a' and one a'' orbitals. This excludes the H_2 antibonding σ orbital. As discussed previously,¹⁷ over the full range of configuration space explored it was not possible to include this orbital consistently while simultaneously excluding higher atomic orbitals on the B atom which contribute significantly to the correlation of the $2s$ electrons. All calculations were carried out with the MOLPRO suite of *ab initio* programs.²⁵

Figure 1 presents contour plots of the lowest BH_2 potential energy surface of A' symmetry for perpendicular (C_{2v}) approach of the B atom. The $B\cdots H_2$ system will be described by the usual Jacobi coordinates, R , r , and θ . The topologies of the PES's are qualitatively unchanged from the earlier¹⁷ CASSCF PES's. Approach on the $2^2A'$ surface (right-hand panel) is steeply repulsive. Approach to the molecular mini-

mum, which lies at $R=0.923$ bohr and $r=4.06$ bohr—far beyond the lower right hand corner of the plots—involves passage over a high barrier. This barrier is an avoided crossing indicative of orbital rearrangement prior to formation of the BH_2 molecule. The electron occupancy of the lowest state of 2A_1 symmetry of the $B\cdots H_2$ complex is $1a_1^2 2a_1^2 3a_1^2 4a_1$, where the $3a_1$ and $4a_1$ designate, respectively, the H_2 bonding orbital and the B $2p_z$ orbital. This electron occupancy does not correlate adiabatically with that of the lowest 2A_1 state of BH_2 , which is $1a_1^2 2a_1^2 1b_2^2 4a_1$.¹⁹ The barrier found here in our CI calculations, $\sim 19\,000\text{ cm}^{-1}$, is lower than what we reported earlier from the CASSCF calculations, $\sim 33\,000\text{ cm}^{-1}$, but still large.

As seen in the left-hand panel of Fig. 1, the lower surface of A' symmetry, which corresponds in C_{2v} geometry with the first excited 2B_2 state of BH_2 , is less repulsive as the atom approaches the molecule, since the electron occupancy of this state is nominally the same for both the molecule and the van der Waals complex. The topology of this PES is comparable to what was seen in our earlier CASSCF calculations (Fig. 2 of Ref. 17), although the surface is less repulsive.

Consequently, based on our earlier CASSCF calculations and the present MRCI calculations, we believe that molecule formation will not occur for approach of $B(^2P)$ to H_2 at thermal velocities. Notwithstanding, the recent matrix studies by Tague and Andrews,³ involving laser ablated B atoms, indicate that reaction of $B(^2P)$ with H_2 can occur at hyperthermal velocities.

B. Determination of the adiabatic→diabatic transformation for $B(^2P)H_2$

Asymptotically, without loss of generality one can choose the three degenerate states of the B atom to correspond to a nominal orientation of the B $2p$ orbital along \mathbf{R} (P_z), perpendicular to \mathbf{R} but still in the triatomic plane (P_x), and, finally, perpendicular both to \mathbf{R} and to the triatomic plane (P_y). As the B atom approaches the H_2 molecule, the lowest two adiabatic states of A' symmetry can, to a good approximation, be thought of as representing a 2×2 orthogonal transformation of the two, asymptotically degenerate, diabatic states of A' symmetry (P_x and P_z). This transformation can be represented by a single transformation angle $\gamma(R, r, \theta)$, as follows:

$$\begin{bmatrix} 1A' \\ 2A' \end{bmatrix} = \begin{bmatrix} \cos \gamma & \sin \gamma \\ -\sin \gamma & \cos \gamma \end{bmatrix} \begin{bmatrix} P_x \\ P_z \end{bmatrix}. \quad (1)$$

A physically more meaningful, but equivalent, interpretation identifies the angle γ with an orthogonal *rotation* of the pair of in-plane orbitals p_x and p_z . The magnitude of this rotation depends on the position of the H_2 molecule. For perpendicular, C_{2v} , geometry the A_1 state (P_z) always lies above the B_2 state (P_x), so that the rotation angle in Eq. (5) is always 0° . For linear geometry the angle γ is 90° at long

range, where the Σ state (P_z) lies below the Π state (P_x), but switches to 0° at shorter range, where the Π state crosses below the Σ state.¹⁷

The van der Waals interaction of an atom with a single p electron outside a closed shell and a closed shell molecule will not involve bond formation. In this case the orthogonal rotation of the two configuration state functions corresponding to $B(2p_z)H_2$ and $B(2p_x)H_2$ will be reflected by the matrix of the x (or z) component of the electronic orbital angular momentum L_x .¹⁷ Correspondingly, following the original suggestion of Rebentrost and Lester,⁵ we proposed¹⁷

$$\gamma = \tan^{-1} \langle 1A' | L_x | 1A'' \rangle / \langle 2A' | L_x | 1A'' \rangle. \quad (2)$$

Here the states $|1A'\rangle$ and $|2A'\rangle$ designate, respectively, the wave functions for the upper and lower electronically adiabatic states of A' symmetry, and $|1A''\rangle$ designates the wave function for the sole state of A'' symmetry [$B(2p_y)H_2$].

An alternative approach to the determination of the adiabatic→diabatic transformation, proposed several years ago by Werner and co-workers,²² is to assume, following Eq. (1), that the transformation angle is given by a relationship similar to Eq. (2), namely,

$$\gamma = \sin^{-1} \left(C_{p_x}^{1A'} / \sum_i C_i^2 \right), \quad (3)$$

where C_i denotes the coefficient of the i th configuration state function (csf) in the MRCI wave function and $C_{p_x}^{1A'}$ is the coefficient of the csf with electron occupancy $(1a')^2(2a')^2(3a')^24a'$, where the $1a'$ and $2a'$ orbitals correspond to the B $1s$ and $2s$ orbitals, the $3a'$ orbital corresponds to the H₂ $1\sigma_g$ orbital, and the $4a'$ orbital corresponds to the B $2p_x$ orbital. In order to ensure that the information on the 2×2 rotation of the B $2p_x$ and $2p_z$ orbitals is mirrored in the CI coefficients, rather than in the CASSCF orbitals, at the end of each CASSCF calculation the orbitals of the $1A'$ and $2A'$ wave functions are rotated to achieve maximum overlap with the comparable orbitals at a reference geometry where there is no p_x – p_z mixing.²² In the case of BH₂ this reference geometry could be either collinear or T-shaped. Here we used a collinear reference geometry, since a conical intersection occurs in collinear geometry.¹⁷

A comparison of the calculated transformation angle calculated by Eqs. (2) and (3) is given in the upper panels of Figs. 2 and 3. In Fig. 2, γ is plotted as a function of θ , for several values of R and, in Fig. 3, as a function of P for $\theta=0.5^\circ$. In both cases r was held fixed at its equilibrium value ($r=1.402$ bohr). The plot in Fig. 3 displays the transformation angle very near the point of conical intersection, which occurs in collinear geometry at $R=6.712$ bohr (again, for $r=1.402$ bohr). In both plots we observe nearly perfect agreement between the diabatic transformations given by Eqs. (2) and (3).

Both these diabatic transformations are approximate. A measure of their accuracy is a comparison of the derivative of the transformation angle with the corresponding off-diagonal derivative matrix element, in the adiabatic basis. These will be equal for the true diabatic transformation, so that

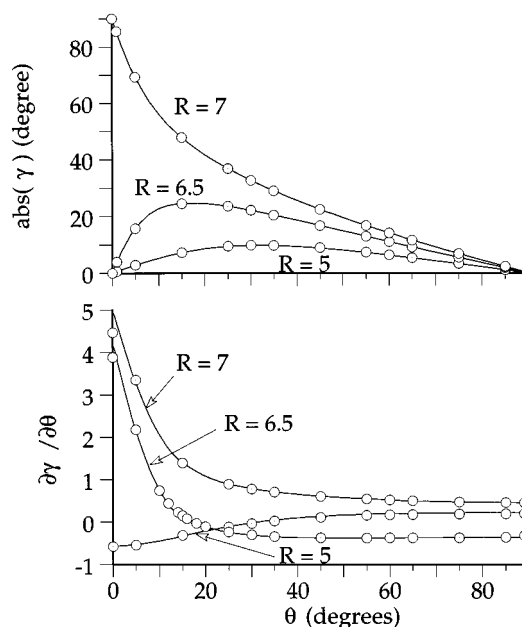


FIG. 2. (Upper panel) Calculated adiabatic→diabatic transformation angle γ as a function of the B \cdots H₂ angle for three different values of R . The value of the H₂ distance r was kept fixed at its equilibrium value of 1.402 bohr. The solid curves represent the values of γ from Ref. 17 determined using the matrix elements of the electronic orbital angular momentum L_x . The open circles represent the values of γ given by the transformation of Eq. (3), based on the expansion coefficients in the CI wave function. (Lower panel) Comparison, for the same geometries, of the off-diagonal derivative matrix element $\langle 1A | \partial/\partial\theta | 2A' \rangle$ (open circles) with the derivative of the transformation angle $\partial\gamma/\partial\theta$ (solid curves) from Ref. 17.

$$\partial\gamma/\partial q = \langle 1A' | \partial/\partial q | 2A' \rangle, \quad (4)$$

where q designates any nuclear coordinate (R , r , or θ). The lower panels of Figs. 2 and 3 compare the derivatives of the transformation angle, obtained from Eq. (2), with the corresponding derivative matrix element. Again, we observe near perfect agreement.

The comparisons of Figs. 2 and 3 validate the adiabatic→diabatic transformation carried out in our earlier paper,¹⁷ and suggest that one can use our published diabatic B(²P)H₂ PES's with confidence.

C. Investigation of the B(²S)H₂ PES

As mentioned in the Introduction, Yang *et al.* have reported⁴ the experimental observation of the B(²P) complex, using laser fluorescence excitation in the region of the B(²S←²P) atomic transition. The excited state, accessed in these experiments, corresponds to the complex of B($\dots 2s^2 3s$) with H₂. To investigate the topology of the single PES corresponding to this electronically nondegenerate complex, we have carried out some additional *ab initio* calculations.

In these new MRCI calculations, the *avt**z* basis set, used in the earlier investigation of the B(²P) \cdots H₂ complex,¹⁷ was expanded by addition of two diffuse s , and one diffuse p , functions on the B-atom with exponents ($\zeta_s=0.010\ 013$ and $0.003\ 685$, $\zeta_p=0.005\ 457$). Test calculations showed that the calculated interaction energies changed insignifi-

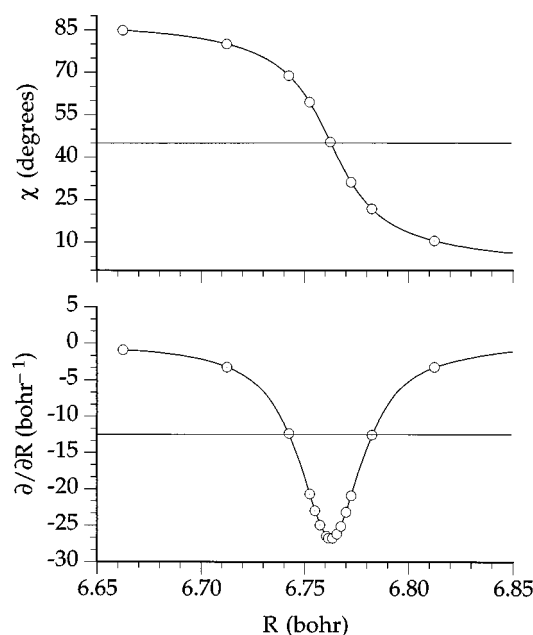


FIG. 3. (Upper panel) Calculated adiabatic→diabatic transformation angle γ as a function of the B...H₂ distance in the neighborhood of the conical intersection. The values of the H₂ distance r and the B...H₂ angle were kept fixed at 1.402 bohr and 0.05°, respectively. For this value of r the conical intersection occurs at $R=6.762$ bohr and $\theta=0$. The solid curves represent the values of γ from Ref. 17 determined using the matrix elements of the electronic orbital angular momentum l_x . The open circles represent the values of γ given by the transformation of Eq. (3), based on the expansion coefficients in the CI wave function. (Lower panel) Comparison, for the same geometries, of the off-diagonal derivative matrix element $\langle 1A' | \partial/\partial R | 2A' \rangle$ (open circles) with the derivative of the transformation angle $\partial\gamma/\partial R$ (solid curves) from Ref. 17.

cantly with addition of a diffuse d function; hence these were not included in the calculations of the full PES. The determination of the PES involved first CASSCF calculations, with seven electrons in a space (exclusive of the $1s$ orbital on B) of five a' and one a'' orbitals. Subsequently, internally-contracted^{26,27} MRCI calculations were carried out. The contribution of higher-order excitations was estimated using the internally-contracted multireference version of the Davidson correction (MRCI+Q).²⁸ Standard counterpoise²⁹ and size-consistency corrections were made.

To allow for stretching of the H₂ bond which might accompany incipient breaking of the molecule, calculations of the B(²S)H₂ PES were carried out at three different value of r ; 1.352, 1.402, and 1.452 bohr. Figure 4 displays plots of the interaction potential, $V(R, r, \theta)$, for $r=1.402$ bohr and $\theta=0^\circ, 30^\circ, 60^\circ$, and 90° . The inset in this plot, compares the interaction potentials at $\theta=90^\circ$ calculated for r fixed at 1.402, and at the value of r which minimizes V , for a given value of R . As can be seen in this inset, the effect of stretching the H₂ bond on the interaction energy is negligible.

Over the range of configuration space explored here, for collinear approach of the H₂ molecule the interaction is purely repulsive. For perpendicular approach, however, the behavior of the interaction potential is reminiscent of what we found earlier for the interaction of B(²S) with Ne;³⁰ a broad, gradually repulsive shoulder, and then, at smaller R , a

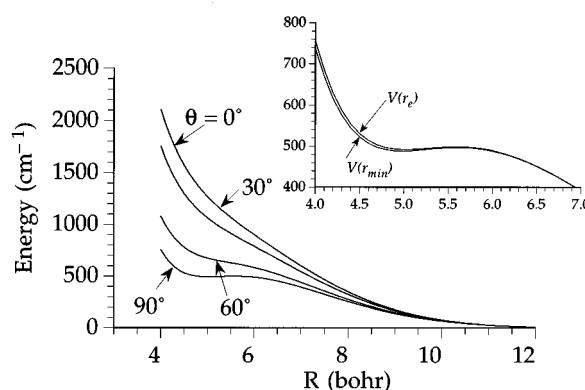


FIG. 4. Dependence on R of the B(²S)H₂ interaction potential $V(R, r, \theta)$ for $r=1.402$ (the equilibrium internuclear separation of the isolated H₂ molecule) and fixed values of θ . The inset panel displays $V(R, r, \theta=90^\circ)$ evaluated at the equilibrium internuclear separation of the H₂ molecules ($r=1.402$ bohr) and at the value of r which minimizes $V(R, r, \theta=90^\circ)$, for R fixed.

steep repulsive wall. Notwithstanding, a quantitative comparison of the fixed angle B(²S)H₂ potential curves in Fig. 4, with our earlier B(²S)Ne (Ref. 30) potential curve, shows substantial differences.

The PES for interaction of an atom in an S state with a closed-shell diatomic is conventionally expanded in terms of regular Legendre functions of the angle,^{31,32} namely,

$$V(R, \theta) = \sum_{\lambda=0}^{\lambda_{\max}} V_{\lambda}(R) P_{\lambda}(\cos \theta). \quad (5)$$

For the B(²S)H₂ PES, only the $V_{\lambda}(R)$ terms with $\lambda=0$ and 2 were found to be significant. These are displayed in Fig. 5.

III. VIBRATIONAL WAVE FUNCTIONS OF THE B(²P)H₂ COMPLEX

A. Expansion of the PES's

As discussed in Sec. II, in our previous investigation of the B(²P)H₂ system,¹⁷ we expressed the interaction potential in a diabatic basis defined by the orientation of the Cartesian $2p$ orbitals of the B atom with the H₂ molecule lying in the xz -plane. There exist three diagonal PES's— $V_{xx}(R, r, \theta)$,

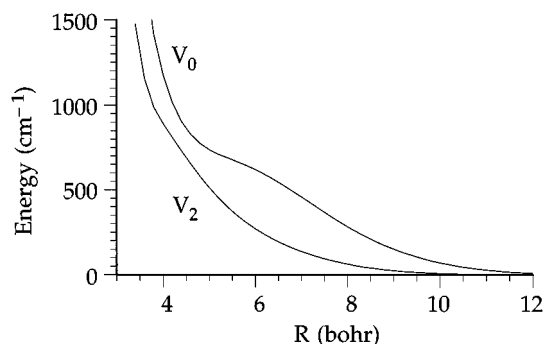


FIG. 5. Dependence on R of the $V_0(R)$ and $V_2(R)$ coefficients in the body-frame expansion of the B(²S)H₂ interaction potential [Eq. (5)].

$V_{yy}(R, r, \theta)$, and $V_{zz}(R, r, \theta)$ —which are the interaction potentials between H₂ and a B atom with the $2p$ orbital oriented along the body-frame (BF) x , y , and z axis, respectively. The coordinate system is unchanged from that defined in Sec. II B above. The two in-plane orientations of the $2p$ orbital, which form the diabatic basis, are mixed, except in linear and perpendicular geometry. This mixing is described by an additional PES, which we denote $V_{xz}(R, r, \theta)$. Finally, it is more appropriate to use the sum and difference of the xx and yy PES's, which we denote as $V_s(R, r, \theta)$ and $V_d(R, r, \theta)$, which are defined by¹⁷

$$V_{yy} = V_s + V_d \quad (6a)$$

and

$$V_{xx} = V_s - V_d. \quad (6b)$$

For notational simplicity, in what follows we shall suppress the dependence on the H₂ bond distance r unless explicitly necessary.

The angular dependence of these PES's can be expanded in terms of reduced rotation matrix elements,³³ or equivalently, regular and associated Legendre polynomials, as follows:

$$V_{zz}(R, \theta) = \sum_{\lambda=0} V_{\lambda}^{zz}(R) d_{00}^{\lambda}(\theta), \quad (7a)$$

$$V_s(R, \theta) = \sum_{\lambda=0} V_{\lambda}^s(R) d_{00}^{\lambda}(\theta), \quad (7b)$$

$$V_{xz}(R, \theta) = \sum_{\lambda=1} V_{\lambda}^{xz}(R) d_{10}^{\lambda}(\theta), \quad (7c)$$

and

$$V_d(R, \theta) = \sum_{\lambda=2} V_{\lambda}^d(R) d_{20}^{\lambda}(\theta). \quad (7d)$$

The reader should note that for interactions involving a homonuclear diatomic, only the even- λ terms are nonvanishing.¹⁷

To determine the bound bend–stretch states of the B(²P)H₂ complex, we follow an important paper by Dubernet and Hutson (DH).²¹ Extending earlier work of Launay and Flower,^{9,34} DH described several general expansions for the nuclear–electronic wave function describing the interaction of an open-shell atom with a closed-shell molecule, and then derived explicit formulas for the matrix elements of the interaction potential in these bases. In addition, DH explored several decoupling schemes defined by the neglect of various off-diagonal matrix elements.

The interaction potential can be expanded in either a space-fixed (SF) or body-fixed (BF) frame. Adopting, wherever possible, the notation of DH, we write the BF expansion as

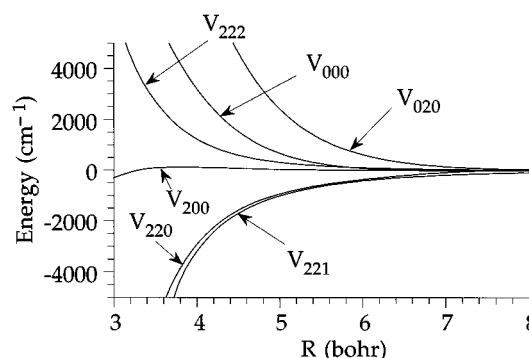


FIG. 6. Dependence on R of the $V_{\lambda_r \lambda_a \mu}(R)$ coefficients in the body-frame expansion of the B(²P)H₂ interaction potential [Eq. (8)].

$$V(R, \theta, \phi, \theta_a, \phi_a)$$

$$= \sum_{\lambda_r \lambda_a \mu} V_{\lambda_r \lambda_a \mu}(R) C_{\lambda_a - \mu}(\theta, \phi) C_{\lambda_r \mu}(\theta_a, \phi_a), \quad (8)$$

where $C_{\lambda \mu}$ is an unnormalized spherical harmonic,³³ and $\{\theta_a, \phi_a\}$ represent the orientation of the $2p$ orbital of the B atom with respect to R . The index μ is restricted to $0 \leq \mu \leq \min(\lambda_a, \lambda_r)$. For interactions involving an atom with a p^1 (or p^5) electron occupancy, only the terms with $\lambda_a = 0$ and 2 are nonvanishing. Again, for notational simplicity, we have suppressed the dependence on r of the $V_{\lambda_r \lambda_a \mu}(R)$ expansion coefficients.

The relationship between these $V_{\lambda_r \lambda_a \mu}(R)$ expansion coefficients and the Cartesian based expansion coefficients we have defined previously [Eq. (7)] is

$$V_{\lambda_r 00}(R) = [2V_{\lambda_r}^s(R) + V_{\lambda_r}^{zz}(R)]/3, \quad (9a)$$

$$V_{\lambda_r 20}(R) = 5[V_{\lambda_r}^{zz}(R) - V_{\lambda_r}^s(R)]/3, \quad (9b)$$

$$V_{\lambda_r 21}(R) = 5V_{\lambda_r}^{xz}(R)/\sqrt{6}, \quad (9c)$$

and

$$V_{\lambda_r 22}(R) = 5V_{\lambda_r}^d(R)/\sqrt{6}. \quad (9d)$$

Again, for interactions involving a homonuclear diatomic, only the even λ_r terms are nonvanishing. For B(²P)H₂, Fig. 6 displays the variation with R of the $V_{\lambda_r \lambda_a \mu}(R)$ expansion coefficients with $\{000\} \leq \{\lambda_r \lambda_a \mu\} \leq \{222\}$. The $V_{\lambda_r 00}(R)$ terms describe the interaction between H₂ and B, averaged over the three orientations of the $2p$ orbital. The anisotropy of this average interaction with respect to the rotation of the H₂ molecule is expressed by the $V_{\lambda_r 00}(R)$ terms with $\lambda_r \neq 0$. We see that these are very small. The $V_{\lambda_r 20}(R)$ terms describes the difference between the interaction when the $2p$ orbital is pointed parallel, as compared to perpendicular, to R . We observe in Fig. 6 that of all the anisotropic terms (those with at least one of the $\lambda_r \lambda_a \mu$ coefficients $\neq 0$), the largest is the 020 term, which expresses the variation of the PES's with the orientation of the B $2p$ orbital, averaged over the orientation of the H₂ moiety.

The $V_{2,21}(R)$ term, which is also large, is proportional to the coupling between the x and z orientations of the $2p$

orbital induced by approach of the H₂. Finally, the $V_{\lambda_r 22}(R)$ terms describe the difference in the interaction between the two possible perpendicular orientations of the 2p orbital; in-plane (x) and out-of-plane (y).

Alternatively, as discussed by DH, one can expand the interaction potential in a SF basis, with expansion indices λ_r , λ_a , and λ_{12} . The relationship between the SF expansion coefficients, designated $V^{\lambda_r \lambda_a \lambda_{12}}(R)$ and the BF expansion coefficients, defined by Eq. (9), is given by

$$V^{\lambda_r \lambda_a \lambda_{12}}(R) = \sum_{\mu} (\lambda_r \mu \lambda_a - \mu | \lambda_{12} 0) V_{\lambda_r \lambda_a \mu}(R), \quad (10)$$

where $(\cdots | \cdots)$ is a Clebsch–Gordan coefficient.³³

B. Full (close-coupled) expansion of the wave function

In the full, or close-coupled (CC), treatment the wave function describing the nuclear motion of the B(²P)H₂ complex is developed by vector coupling the total electronic angular momentum of the atom \mathbf{j}_a with that of the molecule \mathbf{j} to form \mathbf{j}_{12} , which is then coupled with the orbital angular momentum of the B–H₂ pair \mathbf{L} to form the total angular momentum \mathbf{J} . Explicitly, the wave function is expanded in terms of the form

$$\begin{aligned} \Psi_{lsj_a jj_{12} LJM}(R, \beta_r, \alpha_r, \beta_a, \alpha_a) \\ = |lsj_a jj_{12} LJM\rangle = \sum_{m_a m m_{12} M_L} (j_a m_a j m | j_{12} m_{12}) \\ \times (j_{12} m_{12} L M_L | J M) |lsj_a m_a\rangle |j m\rangle |L M_L\rangle, \end{aligned} \quad (11)$$

where the SF projections of the various angular momenta are designated by Roman *m*'s. Here $\{\beta_r, \alpha_r\}$, and, similarly, $\{\beta_a, \alpha_a\}$, designate the SF orientations of the molecular axis \mathbf{r} and the B 2p orbital. The wave function of the atom, $|lsj_a m_a\rangle$ corresponds to vector coupling the electronic \mathbf{l} and the spin \mathbf{s} angular momenta of the atom, namely,

$$|lsj_a m_a\rangle = \sum_{m_l m_s} (l m_l s m_s | j_a m_a) |l m_l\rangle |s m_s\rangle. \quad (12)$$

The total wave function, which is independent of M , is then written as

$$\Psi^{JM} = (1/R) \sum_{j_a jj_{12} L} C_{j_a jj_{12} L}^J(R) |lsj_a jj_{12} LJM\rangle. \quad (13)$$

The expansion coefficients $C_{j_a jj_{12} L}^J(R)$ satisfy the standard close-coupled (CC) equations

$$\begin{aligned} \left[\frac{d^2}{dR^2} - L(L+1)/R^2 + k_{aj}^2 \right] C_{j_a jj_{12} L}^J(R) \\ = (2\mu/\hbar^2) \sum_{j'_a j' j'_{12} L'} V^J(j'_a j' j'_{12} L', j_a jj_{12} L) C_{j'_a j' j'_{12} L'}^J(R), \end{aligned} \quad (14)$$

where k_{aj} denote the asymptotic wave vectors.³⁵ For convenience later we designate the CC equations in matrix notation as

$$\left[\frac{d^2}{dR^2} + W(R) \right] C^J(R) = 0, \quad (15)$$

where the definition of the $W(R)$ matrix follows directly from Eq. (14). To determine the matrix elements of the interaction potential in Eq. (14), it is most convenient to use the SF expansion of the potential. Explicit expressions for these matrix elements have been given previously by DH [see Eq. (17) of Ref. 21].

C. Body-frame and centrifugal-decoupled expansions of the wave function

Alternatively, it is possible to use a number of different BF expansions of the wave functions. Most useful in the physical interpretation of the states of the B(²P)H₂ complex is the expansion denoted “case 1A” by DH, in which the angular momentum of both the atom and the molecule are projected onto \mathbf{R} . We follow DH and denote the BF projections of \mathbf{j}_a and \mathbf{j} as ω and k , respectively. The case 1A basis functions are²¹

$$\Phi_{lsj_a \omega j k}^{JM} = \left(\frac{2J+1}{4\pi} \right)^{1/2} D_{MP}^{J*}(\alpha_R, \beta_R, 0) Y_{jk}(\theta, \phi) |lsj_a \omega\rangle. \quad (16)$$

Here $P = \omega + k$ is the projection of the total angular momentum along \mathbf{R} and D_{MP}^{J*} is a rotation matrix element³³ whose arguments define the SF orientation of \mathbf{R} .

With a BF expansion of the wave function, it is most convenient to use the BF expansion of the interaction potential. Explicit expressions for the matrix elements of the interaction potential have been given previously by DH [see Eqs. (22) and (23) of Ref. 21]. The matrix of the interaction potential is diagonal in P .

By contrast, however, the matrix of the B–H₂ orbital angular momentum \mathbf{L} is no longer diagonal in a BF expansion. In general, however, the matrix elements of \mathbf{L} which couple different values of P , are proportional to J .²¹ Under conditions where a weakly-bound complex is formed in a supersonic expansion, only low values of J will be populated. It is then often reasonable to neglect the off-diagonal matrix elements of \mathbf{L} . This defines the so-called centrifugal decoupling (CD) approximation.

Using either a BF or SF expansion of the wave function, we can obtain the energies and eigenfunctions of the bound states of the B(²P)H₂ complex by determination of the $C^J(R)$ expansion coefficients in Eq. (15). This can be done either variationally or by numerical solution of the CC equations.

D. Adiabatic bender approximation

Considerable qualitative insight can be obtained by examination of the adiabatic potentials associated with the eigenvalues $w^{\text{ad}}(R)$ of the Hamiltonian exclusive of the R -dependent kinetic energy term.^{35–38} These are defined by

$$w^{\text{ad}}(R) = T(R) W(R) T(R)^T, \quad (17)$$

where $T(R)$ is the matrix which diagonalizes the $W(R)$ matrix [Eq. (15)] at each value of R . Since the BF and SF

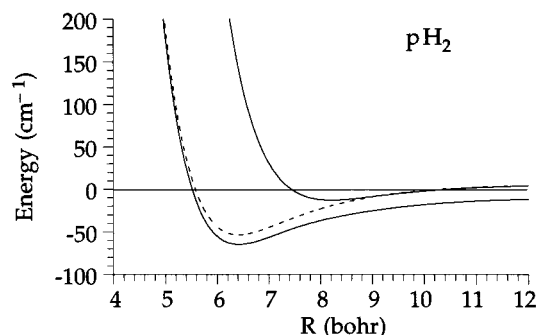


FIG. 7. Dependence on R of the adiabatic bend potentials for $B(^2P)pH_2$ within the CD approximation for $J=P=0.5$ (solid) and $J=P=1.5$ (dashed).

expansion states are related by an orthogonal transformation,³⁹ the locally adiabatic states are identical whether the Hamiltonian is constructed in a BF or SF basis.

Within the CD approximation, the $W(R)$ matrix is block diagonal in P and independent of the sign of P .^{21,40,41} In this case, additional physical insight can be gained by an examination of the definite- P adiabatic energies, obtained by diagonalization of the unique block of the BF $W(R)$ matrix corresponding to the chosen value of P .

Figure 7 displays the radial adiabatic bend potentials for $B(^2P)pH_2$ within the CD approximation for both $P=0.5$ and 1.5 . Each of the two spin-orbit states of B gives rise to an attractive potential, which correspond to the degenerate $^2\Pi$ state of $B(^2P)pH_2$.¹⁷ As has been discussed previously,^{42,43} the splitting between the lower two bend curves at the molecular minimum is quenched to $\sim 2/3$ of the atomic value, even though the spin-orbit constant of the B atom is kept fixed [10.17 cm^{-1} (Ref. 44)]. Figure 8 displays the radial adiabatic bend potentials for $B(^2P)oH_2$ within the CD approximation for both $P=0.5$ and 1.5 . The three-fold rotational degeneracy of the H₂ molecule in $j=1$ renders more complex the relatively simple structure of the adiabatic bend potentials for $B(^2P)pH_2$ (Fig. 7). In particular, the coupling between the three internal angular momenta (l , s , and j) gives rise to a complex avoided crossing between the three lowest $B(^2P)oH_2$ adiabatic bend potentials with $P=0.5$.

These radial adiabatic bend potentials can be used to investigate the vibrational motion along the van der Waals stretching coordinate R . The energies of these vibrational levels can be obtained by solution of a one-dimensional Schrödinger equation with potential $w_{\text{ad}}(R)$. To the extent that off-diagonal matrix elements of the radial kinetic energy operator can be ignored, these energies will provide a good approximation to the bend-stretch states of the complex.

IV. BEND-STRETCH LEVELS OF THE $B(^2P)H_2$ COMPLEX

We carried out variational determinations of the $B(^2P)H_2$ bend-stretch energies, within the exact CC description, and within a CD approximation in the DH case 1A basis. We used the distributed Gaussian method of Hamilton and Light⁴⁵ which we exploited in our earlier studies of hy-

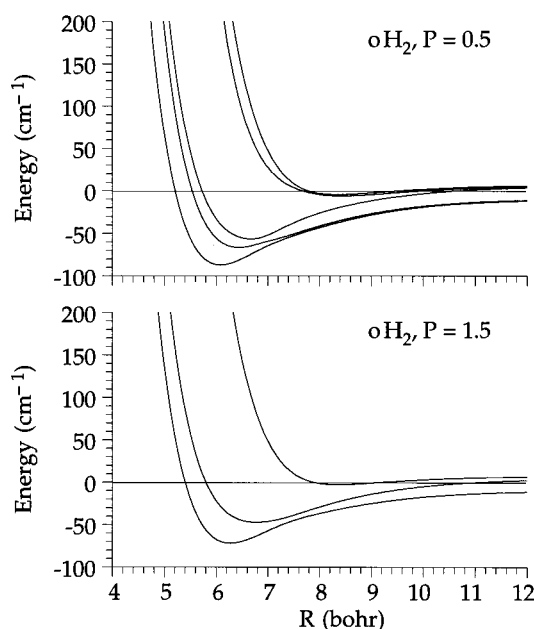


FIG. 8. Dependence on R of the lower (attractive) adiabatic bend potentials for $B(^2P)oH_2$ within the CD approximation for $J=P=0.5$ (upper panel) and $J=P=1.5$ (lower panel).

dride van der Waals complexes.^{35,37,38,46} For oH_2 in its lowest rotational level ($j=1$), the anisotropy in the $B(^2P)H_2$ potential will preferentially orient the H₂ molecule so that \mathbf{r} lies perpendicular to \mathbf{R} (see Fig. 6 of Ref. 17). Consequently, in the expansion of the molecular wave function, the $k=\pm 1$ terms in Eq. (16), for which \mathbf{r} lies preferentially perpendicular to \mathbf{R} , will have a larger weight. For pH_2 in its lowest rotational level ($j=0$), the H₂ molecule appears spherical, so no orientation can occur. Notwithstanding, if the anisotropy is large enough, higher rotational levels of pH_2 ($j=2,4,\dots$) will contribute to the total wave function, and hence lead to some degree of orientation.

Because the rotational spacing of the H₂ molecule is so large [$B_e=60.85\text{ cm}^{-1}$ (Ref. 47)], the contribution of the higher rotational levels will be small. In a previous study of BH_2 , Vegiri and co-workers⁴⁸ pointed out that, to second order in perturbation theory, the coefficients of the higher j states are given by, schematically

$$C_j = \langle j | V(\theta) | j=0 \rangle / (E_j - E_{j=0}). \quad (18)$$

For $B(^2P)pH_2$ the perturbation theory estimate was⁴⁸ $C_2 \approx 0.05$. This should be compared with $C_2=0.055$, given by analysis of the exact variational wave function.⁴⁸ Further, the contribution of all higher rotational states ($j=4,6,\dots$) was found to be negligible. From perturbation theory, inclusion of the $j=2$ level will lower the predicted energy of the complex. For complexes with oH_2 , whose lowest rotational level is $j=1$, the contribution of the higher rotational levels ($j=3,5,\dots$) will be smaller for oH_2 because the energy denominator in Eq. (18) is larger ($10 B_e$ rather than $6 B_e$ where B_e is the H₂ rotational constant). Vegiri and co-workers⁴⁸ report that rotational levels with $j>1$ make a contribution of less than 0.1% to the wave function.

TABLE I. Energies (cm⁻¹) of lowest ($v_s=0$) levels of B(²P)pH₂.^a

Method	$J=0.5$	$J=1.5$	$J=2.5$
$P=0.5$			
Adiabatic bender	-38.7		
CD	-38.06	-35.85	-32.20
CC (av)	-38.07	-36.02	-32.61
ΔE_{CC}^J ^b	0.38	0.75	1.09
$P=1.5$			
Adiabatic bender		-26.4	
CD		-26.29	-22.57
CC (av)		-26.23	-22.44
ΔE_{CC}^J ^b		0.03	0.11

^aThe separated B+pH₂ system has an energy of -10.17 cm⁻¹, the energy of the lowest ($j_a=1/2$) spin-orbit state of B(²P).

^bEquation (19).

The calculations reported here show that the addition of the $j=2$ rotational levels to the basis lowers the calculated energy of the lowest vibrational levels of the B(²P)pH₂ complex by $\sim 10\%$, compared to what might be denoted a “free rotation” model, in which only the $j=0$ levels of H₂ were included, so that the rotation of the H₂ moiety is not quenched in the complex. However, for the B(²P)oH₂ complex addition of the $j=3$ rotational levels lowers the vibrational energies by only $\sim 2\%$. In both cases inclusion of still higher levels was found to make a negligible contribution.

In the exact (CC) treatment, the even and odd parity levels, which correspond to the two possible linear combinations of the $\pm P$ BF projection states, are split. Rather than report the energies separately for both sets of parity states, we report the average, for a given J , CC energy, and the parity splitting, which we define as

$$\Delta E_{CC}^J = E_f^J - E_e^J. \quad (19)$$

In analogy with the convention in diatomic molecule spectroscopy,^{42,49} we use the label e to identify states whose parity is equal to $(-1)^{J-1/2}$ and as f to identify states whose parity is equal to $-(-1)^{J-1/2}$.

Table I lists the energies of the lowest vibrational levels of the complex of B(²P) with pH₂, calculated including both the $j=0$ and 2 rotation levels of H₂ in the expansion of the wave function. The calculated energies correspond to the lowest vibrational level of the two attractive adiabatic bender potentials shown in Fig. 7. The agreement between the adiabatic bender and CD energies is excellent. This indicates that there is very little nonadiabatic mixing between the various adiabatic bender states. In addition, the CD and CC energies are in excellent agreement. This indicates that Coriolis coupling is unimportant, at least at the low values of J studied.

Because of the light reduced mass (1.70 amu), the centrifugal barrier is significant, even at low values of J . From the average CC energies in Table I we extract a rotational constant of 0.68 cm⁻¹ for the lowest vibrational level of B(²P)pH₂. To second order in perturbation theory, the parity splitting should vary as $p(J+1/2)$ for the nominally $P=0.5$ levels, but vary as $q(J-1/2)(J+1/2)(J+3/2)$ for the nominally $P=1.5$ levels, where p and q are constants.^{37,50,51} The nominally $P=0.5$ B(²P)pH₂ energies do exhibit the

TABLE II. Energies (cm⁻¹) of lowest ($v_s=0$) levels of B(²P)oH₂.^a

Method	$J=0.5$	$J=1.5$	$J=2.5$
$P=0.5$			
Adiabatic bender	-51.6		
	-37.8		
	-24.4		
CD	-48.63	-46.16	-42.09
	-37.54	-35.46	-32.02
	-31.99	-29.92	-26.49
CC (av)	-48.72	-45.69	-41.80
	-37.57	-35.54	-32.19
	-31.91	-29.97	-26.65
ΔE_{CC}^J ^b	-0.89	-1.76	-2.53
	-0.32	-0.34	-0.30
	0.52	0.80	0.79
$P=1.5$			
Adiabatic bender		-41.1	
		-22.9	
CD		-40.21	-36.38
		-23.57	-20.33
CC (av)		-40.49	-37.53
		-23.14	-19.18
ΔE_{CC}^J ^b		-0.04	-0.10
		-0.001	-0.06
$P=2.5$			
Adiabatic bender			-28.6
CD			-28.54
CC (av)			-28.46
ΔE_{CC}^J ^b			-0.02

^aThe separated B+oH₂ system has an energy of -10.17 cm⁻¹, the energy of the lowest ($j_a=1/2$) spin-orbit state of B(²P).

^bEquation (19).

predicted linear dependence on $(J+1/2)$ with $p=0.415$ cm⁻¹. As expected, the parity splitting for the nominal $P=1.5$ levels is much smaller. Because of the light reduced mass, the magnitude of the parity splitting is large.^{37,50}

Table II lists the energies of the lowest vibrational levels of the complex of B(²P) with oH₂, calculated including both the $j=1$ and 3 rotation levels of H₂ in the expansion of the wave function. The calculated energies correspond to the lowest vibrational level of the attractive adiabatic bender potentials shown in Fig. 8. The agreement between the adiabatic bender and CD energies is good, with a small error however for the $P=0.5$ levels. This error indicates the importance of nonadiabatic mixing between the adiabatic bender states corresponding to the three attractive $P=0.5$ curves shown in the upper panel of Fig. 8.

For the complexes with oH₂, as was seen to be the case for the complexes with pH₂, the CD and CC energies are in excellent agreement. The predicted rotational constant for the lowest (nominally $P=0.5$) level is 1.14 cm⁻¹. This is considerably larger than what was found for the B(²P)pH₂ complexes, which would indicate a more compact structure for the oH₂ complex. However, from the adiabatic bender wave functions, one can compute an effective rotational constant as $B=\langle R^{-2} \rangle / 2\mu$, which yields $B=0.74$ and 0.81 cm⁻¹, respectively, for the lowest vibrational states of the pH₂ and oH₂ complexes.

These values are quite different from the phenomeno-

TABLE III. CC energies (cm⁻¹) of lowest (*v_s*=0) levels of B(²*P*)D₂.^a

	CC (av)	ΔE_{CC}^J ^b
<i>o</i> D ₂	-47.44	0.17
<i>p</i> D ₂	-58.69	-0.67

^aEnergies of the nominally *P*=0.5 levels with *J*=0.5. The separated B+D₂ system has an energy of -10.17 cm⁻¹, the energy of the lowest (*j_a*=1/2) spin-orbit state of B(²*P*).

^bEquation (19).

logical values of *B*, obtained from fitting the *J* dependence of the calculated energies, especially for the *o*H₂ complex. From this we conclude that the rotational mixing between the lowest vibrational levels of the *o*H₂ complex may be too complicated to use the phenomenological rotational constant to make quantitative predictions about the structure of the complex.

We further observe that the variation with *J* of the calculated parity splitting, especially for the second and third of the nominally *P*=0.5 levels, does not follow the expected linear dependence on *J*. Again, this is likely indicative of rotational mixing. Since the reduced mass of the complexes is so small, these rotational couplings will be proportionally more important than for many previously studied van der Waals complexes.

In our calculations, the lowest dissociation asymptote [B(²*P*_{1/2})+H₂] is defined to lie at -10.17 cm⁻¹. Thus the dissociation energy of the complexes will be lower than the bound-state energies given in Tables I and II. Specifically, we predict dissociation energies (*D*₀) of 27.9 and 38.6 cm⁻¹, respectively, for the *p*H₂ and *o*H₂ complexes.

Because of the larger reduced mass, the complexes of B(²*P*) with D₂ will have larger dissociation energies. Table III lists the energies of the lowest vibrational states of the complex with ortho (*j*-even) and para (*j*-odd) D₂. The corresponding dissociation energies are 37.3 and 48.5 cm⁻¹, respectively, ~10 cm⁻¹ larger than those of the complexes with H₂.

V. COMPARISON WITH PREVIOUS WORK

In an earlier investigation of complexes of B with multiple H₂ molecules,⁴⁸ based on the *ab initio* PES's of Ref. 17, Vegiri *et al.* modeled the complex of B(²*P*) with *o*H₂ by ignoring the electronic structure of the atom and assuming that the interaction was governed solely by the lowest B(²*P*)H₂ adiabatic electronic potential energy surface (1*A*' ; *D_e*=121 cm⁻¹). Within this approximation, the system is equivalent to the interaction of a structureless atom with H₂. A dissociation energies of 70.2 cm⁻¹ was predicted for the lowest state, which corresponds to a state with *P*=1, in which the H₂ moiety rotates nominally in a plane perpendicular to **R**.

We now see that this greatly overestimates the dissociation energy of the complex, by a factor of 2. Because of its light mass, the H₂ moiety does not move purely adiabatically on the lowest B(²*P*)H₂ PES. Rather, the motion of the H₂ moiety samples, to a considerable extent, the other two PES's, which are less attractive (2*A*' ; *D_e*=68 cm⁻¹ and

1*A*' ; *D_e*=75 cm⁻¹). The substantial contribution of these electronically excited potential energy surfaces implies that accurate simulations of clusters of B with multiple *o*H₂ molecules cannot be done accurately with methods which assume only a single electronic potential energy surface.

VI. CONCLUSION

In this paper we have presented additional *ab initio* studies of complexes of B in both its ground (²*P*) and first excited (²*S*) electronic state with both ortho and para H₂. In our original study of the B(²*P*)H₂ system,¹⁷ we used matrix elements of the electronic angular momentum to formulate the transformation into an electronically diabatic representation. The accuracy of this transformation was confirmed here by comparison with a totally different transformation, based on the expansion coefficients of the MRCI wave function,²² and by comparison of the predicted derivatives of the transformation with the corresponding derivative matrix elements, in the electronically adiabatic representation.

Using our diabatic B(²*P*)H₂ potential energy surfaces, and a recent general treatment of weakly-bound complexes of open-shell atoms with molecules by Dubernet and Hutson,^{21,51} we then determined the energies of the lowest vibrational states of these clusters. For the low values of the total angular momentum characteristic of clusters produced in a supersonic expansion, Coriolis coupling was found to be negligible, so that centrifugally decoupled expansions of the wave function gave accurate predictions of the bound-state energies. A simpler, adiabatic bender model^{35,36} also gives a good first approximation to these energies, although, in the case of complexes with *o*H₂, there is significant nonadiabatic mixing involving interplay between the spin-orbit coupling in the atom and the rotational anisotropy of the H₂ molecule.

The complexes with *o*H₂ were found to be more strongly bound by ~10 cm⁻¹, as compared with those of *p*H₂. This, coupled with the enhanced statistical abundance of *o*H₂ (3:1), implies that preparation of B(²*P*)H₂ complexes in a supersonic expansion will give rise primarily to complexes involving *o*H₂.

MRCI calculations were also carried out for the interaction of H₂ with the first electronically excited (...2*s*²3*s* ²*S*) state of B. In the region of configuration space sampled by the B(²*P*)H₂ complex, the potential energy surface of the B(²*S*)H₂ complex was found to be purely repulsive. Thus electronic excitation of the B(²*P*)H₂ complex in the region of the 3*s*←2*p* atomic transition should lead to dissociation of the unbound B(²*S*)H₂ complex with subsequent fluorescence of the free B(²*S*) atoms. In the accompanying paper, Yang *et al.*⁴ describe an experimental study of the B(²*P*)H₂ complex, using just this free←bound excitation to monitor complex formation. These authors use the calculated BH₂ PES's and vibrational wave functions described in the present paper to simulate the observed fluorescence excitation spectrum, obtaining excellent agreement. The synergy between theory and experiment, expressed in these two papers, provides a full and complete understanding of the novel B...H₂ complex.

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