Note: Deperturbation of the v3 band of BeD2

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Note: Deperturbation of the ν_3 band of BeD$_2$

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Beryllium dihydride is a favorite target molecule for *ab initio* theoretical calculations, and high quality experimental data on BeH$_2$ can serve as benchmarks for testing the accuracy of *ab initio* methods. We reported the first observation of gaseous BeH$_2$ in 2002 and recorded high resolution infrared emission spectra of BeH$_2$ in the ν_3 (antisymmetric stretching) region.[1] Analyses of the ν_3 fundamental band and several hot bands of BeH$_2$ and BeD$_2$ resulted in determination of molecular constants and equilibrium structure of BeH$_2$.[2,3] We also observed small local perturbations in the 001 (Σ_u^+) level of BeD$_2$ and attributed them to interactions with the nearby 030 (Π_u and Φ_u) levels.[2] Motivated by the availability of highly accurate molecular constants for BeH$_2$ and BeD$_2$, Koput and Peterson[4] and Li and Le Roy[5] performed very high level *ab initio* calculations on these molecules and computed vibrational energies which differed from experimental values by less than 0.5 cm^{-1}. In this Note, we report the deperturbation of the 001 level of BeD$_2$, which results in an experimental value for the vibrational energy of the 030 level.

Perturbations are observed in the high rotational levels of the 001 (Σ_u^+) state of BeD$_2$ through interactions with the nearby 030 vibrational level, which has 03^{1}0 (Π_u) and 03^{3}0 (Φ_u) states. Rotational levels of the 001 (Σ_u^+) state with $J \leq 30$ are shifted toward higher energies, whereas the $J \geq 31$ levels are shifted toward lower energies (Fig. 1). Although the magnitudes of these perturbations are relatively small, i.e., the largest term value shifts being +0.24 cm^{-1} at $J = 30$ and −0.12 cm^{-1} at $J = 31$, they are quite significant compared to the absolute accuracy of the observed spectral line positions (∼0.002 cm^{-1}). The perturbation pattern observed in BeD$_2$ (Fig. 1) clearly indicates that the perturbing state has a larger effective $B_{[v]}$ value and a smaller vibrational energy. The effective $B_{[v]}$ values of the 03^{1}0 (Π_u) and 03^{3}0 (Φ_u) states were estimated using the $B_{[v]}$ values of the 000, 01^{1}0, 02^{0}0, and 02^{2}0 states.[2,3] The 03^{1}0 (Π_u) and 03^{3}0 (Φ_u) states have the e and f parity components, but only the e parity levels can interact with the 001 (Σ_u^+) rotational levels. Due to the large rotational ℓ-type doubling in the 03^{1}0 (Π_u) state,[6] the effective $B_{[v]}$ value of its e parity component becomes smaller than that of the 001 (Σ_u^+) state. In addition, because the vibrational g_{22} constant of BeD$_2$ is larger than the $B_{[v]}$ values,[3] the rotational levels of 03^{3}0 (Φ_u) lie above those of the 03^{1}0 (Π_u) state. Therefore, the 03^{3}0 (Φ_u) state is responsible for the observed perturbations in the 001 (Σ_u^+) state.

A 3 × 3 Hamiltonian matrix was constructed for the e parity levels of 001 (Σ_u^+), 03^{1}0 (Π_u), and 03^{3}0 (Φ_u) states.

The vibrational energy of the 03^{1}0 state is smaller than that of the 03^{3}0 states by 8g_{22}, based on a quadratic expression[2] for $G(v_1, v_2^\ell, v_3)$. The 03^{1}0 (Π_u) state was included in the matrix because it interacts with the 03^{3}0 (Φ_u) state through rotational ℓ-type resonance[6] and thus has an indirect effect on the state of interest (001, Σ_u^+). The Hamiltonian matrix for rotational ℓ-type resonance between Π and Φ states was derived by Maki and Lide.[6] After parity transformation and including the Σ_u^+ (e) state, the Hamiltonian matrix of Eq. (1) was obtained for the e levels.[7,8] The matrix elements of the Hamiltonian are provided in Eqs. (2)–(7) in which $x = J(J + 1)$.

$$\mathbf{H} = \begin{pmatrix} E_\Sigma^0\,(001) & -W_{03} & 0 \\ -W_{03} & E_\Phi^0 & W_{31} \\ 0 & W_{31} & E_\Pi^0 + W_{11} \end{pmatrix}. \qquad (1)$$

$$E_\Sigma^0\,(001) = G_{001} + B_{001}x - D_{001}x^2 + H_{001}x^3, \qquad (2)$$

$$E_\Phi^0 = G_\Phi + B_\Phi\,(x - 9) - D_\Phi\,(x - 9)^2, \qquad (3)$$

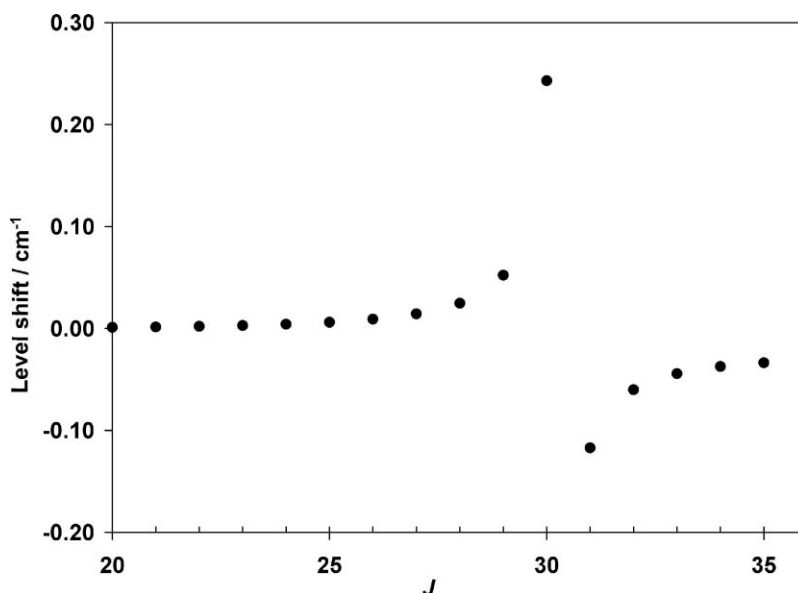$$E_\Pi^0 = (G_\Phi - 8g_{22}) + B_\Pi\,(x - 1) - D_\Pi\,(x - 1)^2, \qquad (4)$$

$$W_{11} = qx + q_Dx^2, \qquad (5)$$

$$W_{31} = \frac{\sqrt{3}}{2}\,(q + q_Dx)\,[(x - 2)\,(x - 6)]^{1/2}, \qquad (6)$$

$$W_{03} = K_{03}\,[x\,(x - 2)\,(x - 6)]^{1/2}. \qquad (7)$$

The rotational energy expressions used for the Φ_u ($\ell = 3$) and Π_u ($\ell = 1$) states in Eqs. (3) and (4) are power series in $[J(J + 1) - \ell^2]$, in which ℓ is the vibrational angular momentum quantum number. The J-dependence of W_{03}, which connects the Σ and Φ states, was determined by applying the $[(J^+)^3]$ operator (in the molecular frame) to the Φ state basis function.

All rotational lines of the 001→000 and 002→001 bands of BeD$_2$ were fitted using the Hamiltonian matrix in Eq. (1) for the 001 levels, while the constants of the 000 and 002 states were fixed to the values reported in Ref. 2. A few more rotational lines of the 001→000 band (up to $J' = 35$) were

FIG. 1. The observed perturbations in the 001 vibrational level of BeD_2.

also assigned and added to the data used in Ref. 2. Rotational constants (B, D) and the ℓ-type doubling constants (q, q_D) of the $03^10(\Pi_u)$ and $03^30(\Phi_u)$ states were fixed to the values estimated by extrapolating the 000, 01^10, 02^00, and 02^20 constants. In order to estimate the $B_{[v]}$ and $D_{[v]}$ values as accurately as possible, expressions with quadratic vibrational dependence were used.[7] The ℓ-type doubling constants $q_{[v]}$ and $q_{D,[v]}$ were estimated using the corresponding constants of the 010 and 020 levels, and the vibrational constant g_{22} was fixed to the value reported in Ref. 3 for BeD_2. A complete list of the spectral line positions used in the fit and the output of our least-squares fitting program is provided in the supplemental material.[9] The least-squares fitting resulted in determination of G_Φ (vibrational energy of the 03^30 state), K_{03} (off-diagonal matrix element between Σ and Φ states), and the unperturbed constants for the 001 (Σ_u^+) state of BeD_2 (Table I). The constants of Table I differ slightly from those reported in Ref. 2

for the 001 (Σ_u^+) state; they are in fact more reliable because the effects of perturbations have been accounted for by the K_{03} constant. The constants of Table I can reproduce all the observed spectral line positions within their experimental uncertainties of ± 0.002 cm^{-1}.

The Σ–Φ interaction constant (K_{03}) was determined to be $2.16(1) \times 10^{-5}$ cm^{-1}. The off-diagonal matrix element W_{03} is zero for $J < 3$ and increases rapidly with J. Near the crossing point of the two states ($J = 30$), W_{03} is about 0.6 cm^{-1}. The vibrational energy of the 03^30 state (G_Φ) was determined to be 1652.61(1) cm^{-1}. Because some rotational constants in our fit were fixed to extrapolated values, the statistical uncertainty of ± 0.01 cm^{-1} for G_Φ in Table I is not realistic. We estimate an absolute accuracy of about ± 0.1 cm^{-1} for the G_Φ constant. The best *ab initio* value for the vibrational energy of the 03^30 state (G_Φ) is 1652.36 cm^{-1} computed by Koput and Peterson[4] which is smaller than the experimental value by 0.25 cm^{-1}.

TABLE I. Unperturbed constants (in cm^{-1}) for the 001 (Σ_u^+) state of BeD_2; the numbers in parentheses are 1σ uncertainties in the last quoted digits. The vibrational energies G_{001} and G_Φ are relative to the ground state vibrational energy (G_{000}).

Constant	001 level	Constant	030 level
G_{001}	1689.6805(3)	G_Φ	1652.61(1)
B_{001}	2.330243(3)	B_Φ	2.38017
$10^5 D_{001}$	2.5732(7)	$10^5 D_\Phi$	2.805
$10^{10} H_{001}$	3.23(4)	g_{22}	2.5276
		B_Π	2.38155
		$10^5 D_\Pi$	2.899
$10^5 K_{03}$ (Σ,Φ)	2.16(1)	$10^2 q$	−2.965
		$10^6 q_D$	1.13

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[9] See supplementary material at http://dx.doi.org/10.1063/1.3533809 for a complete list of line positions and constants.