

# A Breakdown of the Watson-Type Hamiltonian for Some Asymmetric-Top Molecules: The Case of the Spin-Multiplet State

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A breakdown of the standard Watson-type rotational Hamiltonian was suggested for a molecule with  $H_2XYZ$  structure [Š. Urban and K. M. T. Yamada, *J. Mol. Spectrosc.* **160**, 279–288 (1993)]. This breakdown is due to a near-resonant interaction between the ground state rotational levels and rotational levels in an excited vibrational state. This interaction has been observed in the excited electronic state of  $H_2CCC^-$  ( $^2A_1$  state) by high-resolution autodetachment spectroscopy. The centrifugal distortion coupling term and nonvanishing matrix elements for electronic spin doublet and triplet states are described using Hund's case (*b*) basis sets. The results are used to interpret the centrifugal distortion couplings between the  $\nu_6$  and  $\nu_9$  modes and the vibrational ground states in  $H_2CCC^-$ . Centrifugal distortion coupling constants  $C_6^{ac} = 1.0723(2) \times 10^{-4}$  and  $C_9^{ab} = -1.5397(5) \times 10^{-5}$  were obtained for this system. © 1996 Academic Press, Inc.

## INTRODUCTION

The Watson-type Hamiltonian (*1*) is commonly used to model the rotational levels of the vibrational ground state of polyatomic molecules. However, Yamada (*2*) found that the validity of the Watson-type Hamiltonian breaks down when it is applied to the interaction between the vibrational ground state and  $\nu_5$  of HNCN. The breakdown that Yamada discovered can be understood as a nonnegligible centrifugal distortion coupling between the rotational levels of vibrationally excited states and nearby rotational levels of the vibrational ground state. Although the vibrationally excited states reside far from vibrational ground levels in many cases, the energies of vibrationally excited states can be compared to the ground vibrational state rotational levels for molecules that have small rotational moments of inertia. An entire class of such molecules includes those with an  $H_2XYZ$ -type structure. Urban and Yamada (*3*) have demonstrated that the effective rotational Hamiltonian in its standard power-series expansion converges only within a limited range of rotational quantum numbers for such molecules. They demonstrated the effects of the centrifugal distortion coupling contributions for some rotational constants for  $H_2CCO$  and  $H_2CNC$  and predicted that the divergence of this power series occurs at  $K > 20$ . Unfortunately, molecules with this amount of rotational excitation (e.g.,  $4000\text{ cm}^{-1}$ ) are difficult to prepare in sufficient concentration for spectroscopic detection.

An exception to this trend is propadienylidene,  $H_2CCC$ . The lowest energy  $H_2CCC$  vibrational mode is much lower than that for either  $H_2CCO$  or  $H_2CNC$ , and a recent study with high-resolution autodetachment spectroscopy revealed that the centrifugal distortion coupling occurs between  $\nu' =$

0 and a nearby CCC out-of-plane bending mode ( $\nu_6$ ) and between  $\nu' = 0$  and CCC in-plane bending mode ( $\nu_9$ ) in the excited electronic state ( $^2A_1$  state) of  $H_2CCC^-$  (*4, 5*). This observation motivated us to rederive the centrifugal distortion coupling term for use with spin-multiplet states. In this paper, the conditions that lead to the breakdown of the standard Watson-type Hamiltonian are reviewed, and the centrifugal distortion coupling term is used to account for the breakdown discussed for spin-multiplet states. Nonvanishing matrix elements are obtained for doublet and triplet states of a  $C_{2v}$  molecule. The results are used to interpret the autodetachment spectrum of  $H_2CCC^-$ .

## THEORY

The effective centrifugal distortion operator can be derived from a rotation–vibration Hamiltonian expanded in normal vibrational coordinates by using a standard perturbation treatment. This is usually carried out in the harmonic oscillator ( $H_{20}$ ) basis (*1, 6*) and includes quartic, sextic, and higher-order terms. In the notation used in the following discussion, the first subscript indicates the order of the vibrational operator and the second subscript indicates the order of the rotational operator. In this perturbation approach, the quartic centrifugal distortion operator  $H_{04}$  is obtained from  $H_{12}$ ,

$$\hat{H}_{12} = - \sum_s q_s \omega_s \sum_{\alpha, \beta} C_s^{\alpha\beta} \hat{J}_\alpha \hat{J}_\beta. \quad [1]$$

Here  $s$  is the normal mode and  $\alpha$  and  $\beta$  represent two Cartesian coordinates ( $x$ ,  $y$ , or  $z$ ). The dimensionless parameter,  $C_s^{\alpha\beta}$ , is given by

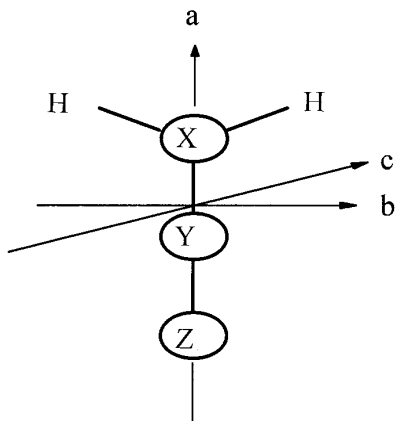


FIG. 1. Molecular structure of  $H_2XYZ$  and the molecule-fixed axes.

$$C_s^{\alpha\beta} = [4\pi^2\hbar/(\omega_s c)]^{3/2} a_s^{\alpha\beta} / (2I_{\alpha\beta}), \quad [2]$$

where the  $a_s^{\alpha\beta}$  are the partial derivatives of the components of the reciprocal inertia tensor,  $\mu_s^{\alpha\beta}$ . In a similar manner, the terms of  $H_{06}$  are generated using the  $H_{12}$ ,  $H_{21}$ ,  $H_{02}$ , and  $H_{30}$  operators with fourth-order perturbation theory. This process continues, as the terms of  $H_{0n}$  are calculated using  $(n-2)$ -order perturbation theory. The resulting effective rotational Hamiltonian in terms of the angular momentum operators,  $\hat{J}$ ,  $\hat{J}_z$ ,  $\hat{J}_+$ , and  $\hat{J}_-$ , takes the form

$$\begin{aligned} H_{\text{rot}}^V &= B_{200}^V \hat{J}^2 + B_{020}^V \hat{J}_z^2 + D_{400}^V \hat{J}^4 + D_{220}^V \hat{J}^2 \hat{J}_z^2 \\ &+ D_{040}^V \hat{J}_z^4 + H_{600}^V \hat{J}^6 + H_{420}^V \hat{J}^4 \hat{J}_z^2 + H_{240}^V \hat{J}^2 \hat{J}_z^4 \\ &+ H_{060}^V \hat{J}_z^6 + \dots \\ &= \frac{1}{2} \sum_{i,j,k} X_{2i,2j,2k}^V [\hat{J}^{2i} \hat{J}_z^{2j}, (\hat{J}_+^{2k} + \hat{J}_-^{2k})]_+, \end{aligned} \quad [3]$$

where  $[\hat{A}, \hat{B}]_+$  represents the anticommutator of  $\hat{A}$  and  $\hat{B}$ ,  $\hat{A}\hat{B} + \hat{B}\hat{A}$ .

### General Expression

In this section we derive the nonvanishing matrix elements for the centrifugal distortion operator shown in Eq. [1]. We follow Mulliken's definition for the symmetry operations in planar  $C_{2v}$  molecules (7), and the symmetries of the normal vibrations are the same as those given in Table 1 of Ref. (3). The angular momentum components  $\hat{J}_x$ ,  $\hat{J}_y$ , and  $\hat{J}_z$  correspond to the irreducible representations  $B_1$ ,  $B_2$ , and  $A_2$ , respectively. The totally symmetric components of the  $H_{12}$  operator for the lowest vibrational states with  $B_1$  and  $B_2$  character ( $n = 5, 6$  and  $m = 7-9$ ) can be calculated using

$$\begin{aligned} \hat{H}_{12}^{(L)} &= - \sum_n \omega_n q_n C_n^{yz} [\hat{J}_y, \hat{J}_z]_+ \\ &- \sum_m \omega_m q_m C_m^{xz} [\hat{J}_x, \hat{J}_z]_+, \end{aligned} \quad [4]$$

where modes  $n$  and  $m$  have  $B_1$  and  $B_2$  character, respectively. To a first approximation, the first term in Eq. [4] vanishes for a planar molecule. However, this term is retained as it is required to explain the observed interaction in  $H_2CCC^-$ . If we use the  $I^r$  representation (8) for the molecule-fixed coordinate ( $x \rightarrow b$ ,  $y \rightarrow c$ , and  $z \rightarrow a$ ), as shown in Fig. 1, then Eq. [4] can be written in terms of  $a$ ,  $b$  and  $c$ ,

$$\begin{aligned} \hat{H}_{12}^{(L)} &= - \sum_n \omega_n q_n C_n^{ca} [\hat{J}_c, \hat{J}_a]_+ - \sum_m \omega_m q_m C_m^{ba} [\hat{J}_b, \hat{J}_a]_+ \\ &= - \sum_n \frac{1}{2i} \omega_n q_n C_n^{ca} [(\hat{J}_+ - \hat{J}_-), \hat{J}_a]_+ \\ &- \sum_m \frac{1}{2} \omega_m q_m C_m^{ba} [(\hat{J}_+ + \hat{J}_-), \hat{J}_a]_+ \\ &= \sum_n H_{12}^n + \sum_m H_{12}^m, \end{aligned} \quad [5]$$

where

$$\hat{J}_{\pm} = \hat{J}_b \pm i\hat{J}_c. \quad [6]$$

The parity-conserving basis function with the symmetric-ortho basis set for Hund's case (a) is given by

$$\begin{aligned} |L \Lambda\rangle |S \Sigma\rangle |J M \Omega\rangle^{\pm} &= [|L \Lambda\rangle |S \Sigma\rangle |J M \Omega\rangle \\ &\pm |L - \Lambda\rangle |S - \Sigma\rangle |J M - \Omega\rangle] / \sqrt{2}, \end{aligned} \quad [7]$$

where  $L$ ,  $S$ , and  $J$  indicate the quantum numbers for electron orbital angular momentum, electron spin angular momentum, and total angular momentum, respectively. The angular momentum components projected onto the molecule  $a$ -axis are denoted by  $\Lambda$ ,  $\Sigma$ , and  $K$ . The sum of these three quantum numbers is  $\Omega$  ( $\Omega = \Lambda + \Sigma + K$ ). The projection of total angular momentum,  $J$ , onto the space-fixed axis is given by  $M$ . Thus, the nonvanishing matrix elements for the interaction term  $H_{12}^L$  in Hund's case (a) description can be written as

$$\begin{aligned} \langle {}^p L \Lambda; S \Sigma; J M \Omega \pm 1 | H_{12}^n | J M \Omega; S \Sigma; L \Lambda {}^p \rangle \\ = \pm \frac{1}{2i} \omega_n q_n C_n^{ca} (2\Omega \pm 1) [J(J+1) - \Omega(\Omega \pm 1)]^{1/2} \end{aligned} \quad [8]$$

$$\begin{aligned} \langle {}^p L \Lambda; S \Sigma; J M \Omega \pm 1 | H_{12}^m | J M \Omega; S \Sigma; L \Lambda {}^{p'} \rangle \\ = - \frac{1}{2} \omega_m q_m C_m^{ba} (2\Omega \pm 1) [J(J+1) - \Omega(\Omega \pm 1)]^{1/2}, \end{aligned} \quad [9]$$

where  $p$  indicates the parity sign given in Eq. [7] and can be either + or -. The sign of  $p$  is always opposite to that of  $p'$ . If the electronic states are the singlet states, and the orbital angular momentum is negligible, the interaction terms of Eqs. [8] and [9] simplify to

$$\begin{aligned} \langle {}^p J M K \pm 1 | H_{12}^n | J M K {}^p \rangle &= \pm \frac{1}{2i} \omega_n q_n C_n^{ca} (2K \pm 1) \\ &\times [J(J+1) - K(K \pm 1)]^{1/2} \quad [10] \end{aligned}$$

and

$$\begin{aligned} \langle {}^p J M K \pm 1 | H_{12}^m | J M K {}^p \rangle &= -\frac{1}{2} \omega_m q_m C_m^{ba} (2K \pm 1) \\ &\times [J(J+1) - K(K \pm 1)]^{1/2}. \quad [11] \end{aligned}$$

### Description for the Multiplet States

With these results, we can now derive the centrifugal distortion coupling term for Hund's coupling case (b). In order to evaluate the interaction term in the Hund's coupling case (b) basis set,  $|\nu\rangle|\Lambda\rangle|NK SJ M\rangle$ , it is necessary first to derive the interaction term under Hund's case (a), and then

transform the basis set into Hund's case (b) coordinates, in order to obtain the nonzero matrix elements for Hund's case (b) representation. Brown and Howard (9) showed that the basis sets in Hund's (a) and (b) coupling cases are related as

$$\begin{aligned} |\nu\rangle|\Lambda\rangle|N K S J M\rangle &= \sum_{\Sigma, \Omega} (-)^{N-S+\Omega} [2N+1]^{1/2} \\ &\times \begin{pmatrix} J & S & N \\ \Omega & -\Sigma & -K \end{pmatrix} |J M \Omega; S \Sigma; L \Lambda\rangle |\nu\rangle. \quad [12] \end{aligned}$$

The description for Hund's case (b) is obtained by transforming the basis sets given in Eq. [12] using the Hamiltonian in Eq. [5].

The nonvanishing matrix elements for the centrifugal distortion coupling term for the multiplet states can be derived in a manner similar to that for the doublet and triplet states. These elements are as follows:

*Doublets: S = 1/2, N = J + 1/2*

$$\begin{aligned} \langle {}^p N K \pm 1 S J M; \Lambda | H_{12}^n | \Lambda; N K S J M {}^p \rangle &= \pm \frac{1}{2i} C_n^{ca} q_n \omega_n \left( \frac{N-1}{N} \right) [2K \pm 1] [N(N+1) - K(K \pm 1)]^{1/2} \\ \langle {}^p N K \pm 1 S J M; \Lambda | H_{12}^m | \Lambda; N K S J M {}^p \rangle &= -\frac{1}{2} C_m^{ba} q_m \omega_m \left( \frac{N-1}{N} \right) [2K \pm 1] [N(N+1) - K(K \pm 1)]^{1/2} \end{aligned} \quad [13]$$

*Doublets: S = 1/2, N = J - 1/2*

$$\begin{aligned} \langle {}^p N K \pm 1 S J M; \Lambda | H_{12}^n | \Lambda; N K S J M {}^p \rangle &= \pm \frac{1}{2i} C_n^{ca} q_n \omega_n \left( \frac{N+2}{N+1} \right) [2K \pm 1] [N(N+1) - K(K \pm 1)]^{1/2} \\ \langle {}^p N K \pm 1 S J M; \Lambda | H_{12}^m | \Lambda; N K S J M {}^p \rangle &= -\frac{1}{2} C_m^{ba} q_m \omega_m \left( \frac{N+2}{N+1} \right) [2K \pm 1] [N(N+1) - K(K \pm 1)]^{1/2} \end{aligned} \quad [14]$$

*Triples: S = 1, N = J + 1*

$$\begin{aligned} \langle {}^p N K \pm 1 S J M; \Lambda | H_{12}^n | \Lambda; N K S J M {}^p \rangle &= \pm \frac{1}{2i} C_n^{ca} q_n \omega_n \left( \frac{(2N-3)(N-1)}{(2N-1)N} \right) [2K \pm 1] [N(N+1) - K(K \pm 1)]^{1/2} \\ \langle {}^p N K \pm 1 S J M; \Lambda | H_{12}^m | \Lambda; N K S J M {}^p \rangle &= -\frac{1}{2} C_m^{ba} q_m \omega_m \left( \frac{(2N-3)(N-1)}{(2N-1)N} \right) [2K \pm 1] [N(N+1) - K(K \pm 1)]^{1/2} \end{aligned} \quad [15]$$

*Triples: S = 1, N = J*

$$\begin{aligned} \langle {}^p N K \pm 1 S J M; \Lambda | H_{12}^n | \Lambda; N K S J M {}^p \rangle &= \pm \frac{1}{2i} C_n^{ca} q_n \omega_n \left( \frac{N^2 + N - 3}{(N+1)N} \right) [2K \pm 1] [N(N+1) - K(K \pm 1)]^{1/2} \\ \langle {}^p N K \pm 1 S J M; \Lambda | H_{12}^m | \Lambda; N K S J M {}^p \rangle &= -\frac{1}{2} C_m^{ba} q_m \omega_m \left( \frac{N^2 + N - 3}{(N+1)N} \right) [2K \pm 1] [N(N+1) - K(K \pm 1)]^{1/2} \end{aligned} \quad [16]$$

Triplets:  $S = 1, N = J - 1$

$$\begin{aligned} \langle {}^p N K \pm 1 S J M; \Lambda | H_{12}^n | \Lambda; N K S J M^p \rangle &= \pm \frac{1}{2i} C_n^{ca} q_n \omega_n \left( \frac{(2N+5)(N+2)}{(2N+3)(N+1)} \right) [2K \pm 1] [N(N+1) - K(K \pm 1)]^{1/2} \\ \langle {}^p N K \pm 1 S J M; \Lambda | H_{12}^m | \Lambda; N K S J M^p \rangle &= -\frac{1}{2} C_m^{ba} q_m \omega_m \left( \frac{(2N+5)(N+2)}{(2N+3)(N+1)} \right) [2K \pm 1] [N(N+1) - K(K \pm 1)]^{1/2}. \end{aligned} \quad [17]$$

In Eqs. [13]–[17], we have used the relationship

$$|\nu\rangle|\Lambda\rangle|N K S J M^\pm\rangle = [|\nu\rangle|\Lambda\rangle|N K S J M\rangle \pm |\nu\rangle|-\Lambda\rangle|N - K S J M\rangle]/\sqrt{2}. \quad [18]$$

### Expression in Hund's Case (a)

In the previous section the matrix elements have been derived in Hund's case (b) by starting from Hund's case (a) basis sets and the Hamiltonian. That is, to obtain a matrix element given by  $\langle b|a\rangle\langle a|H_a|a\rangle\langle a|b\rangle$ , where  $H_a$  is the Hamiltonian in Hund's case (a) description,  $|a\rangle$  and  $|b\rangle$  are basis sets in Hund's cases (a) and (b), respectively. The matrix elements can also be derived in Hund's case (a) by starting from both the Hamiltonian and basis sets in Hund's case (b), and then converting them to a Hund's case (a) description by using Eq. [12], i.e.,  $\langle a|b\rangle\langle b|H_b|b\rangle\langle b|a\rangle$ .

The Hund's case (b) Hamiltonian can be expressed simply as

$$\begin{aligned} \hat{H}_{12}^{(L)} &= -\sum_n \frac{1}{2i} \omega_n q_n C_n^{ca} [(\hat{N}_+ - \hat{N}_-), \hat{N}_a]_+ \\ &\quad - \sum_m \frac{1}{2} \omega_m q_m C_m^{ba} [(\hat{N}_+ + \hat{N}_-), \hat{N}_a]_+ \end{aligned} \quad [19]$$

by replacing  $\hat{J}_+$ ,  $\hat{J}_-$ , and  $\hat{J}_a$  in Eq. [5] by  $\hat{N}_+$ ,  $\hat{N}_-$ , and  $\hat{N}_a$ , respectively. Since the Hund's (b) basis sets have a relation given by Eq. [12], by using Hund's (a) basis sets on the Hamiltonian, Eq. [19], the centrifugal distortion coupling term in Hund's case (a) description is obtained. Since  $N$  is no longer a good quantum number, the resulting expression exhibits a very complicated form (10). Thus, we adopt the simpler form shown in Eqs. [13]–[17] for the analysis of centrifugal distortion coupling in  $\text{H}_2\text{CCC}^-$ .

### APPLICATION TO $\text{H}_2\text{CCC}^-$

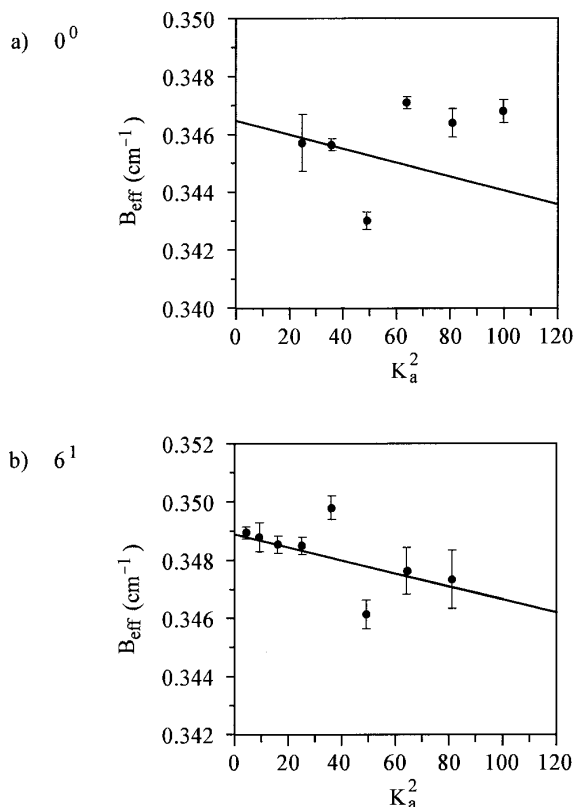
Urban and Yamada (3) have shown that the energy term of the centrifugal distortion formula given in Eq. [4] in its standard power series expansion converges only within a limited range of rotational quantum number  $K$ . The convergence criteria can be estimated using the parameter  $\eta$  given by

$$\eta = \left( \frac{2B_{020}}{\omega_s + B_{020}} \right)^2. \quad [20]$$

The convergence condition is given by  $K^2\eta \ll 1$ . This condition thus will be violated when the rotational quantum number  $K$  is sufficiently large. For example, the criterion is violated for  $K > 20$  in diazomethane and ketene, where the critical parameter  $\eta$  is  $1.653 \times 10^{-3}$  and  $1.604 \times 10^{-3}$ , respectively. In the case of the  ${}^2A_1$  state of  $\text{H}_2\text{CCC}^-$ , we find  $B_{020} = 9.16409(4) \text{ cm}^{-1}$  and  $\omega_6 = 221.447(2) \text{ cm}^{-1}$  for mode  $\nu_6$ , and estimated  $B_{020} = 9.16 \text{ cm}^{-1}$  and  $\omega_9 = 276.69(5) \text{ cm}^{-1}$  for mode  $\nu_9$ . The critical values of the  $i$ th mode,  $\eta_i$ , are found to be  $\eta_6 = 6.3165(2) \times 10^{-3}$  and  $\eta_9 = 4.107(1) \times 10^{-3}$ , respectively. Therefore, the convergence condition  $K^2\eta \ll 1$  will be violated when  $K$  is as low as 10 for both modes. Centrifugal distortion coupling is much more readily observable.

As expected, we find a breakdown of Watson's  $S$ -reduced Hamiltonian in the excited state ( ${}^2A_1$  state) of  $\text{CCCH}_2^-$ . The effective rotational constants,  $[B + C]/2$ , for each  $K_a$ -stack are plotted as a function of  $K_a^2$  in Fig. 2. There is an anomaly observed around  $K'_a = 7$ –10 in the  $v' = 0$  state (see Fig. 2a). A similar rotational constant anomaly was observed in the nearby vibrational state,  $6^1$  level, around  $K'_a = 6, 7$  (see Fig. 2b). Thus, we ascribe the anomaly observed at  $v' = 0$ ,  $K'_a = 7$ –8 to the centrifugal distortion coupling between  $6^1$  and  $0^0$ , and the anomaly observed at  $v' = 0$ ,  $K'_a = 9$ –10 to the same coupling between  $9^1$  and  $0^0$ . Although the  $9^1$  level was not observed directly, we were able to reproduce energy levels by utilizing the Coriolis interaction analysis between  $6^1$  and  $9^1$ . The  $H_{12}^n$  terms shown in Eqs. [13] and [14] were included in the  $6^1$  and  $0^0$  interaction,  $H_{12}^m$  terms were used for the interaction between  $9^1$  and  $0^0$ , and the molecular constants were then obtained using a nonlinear least-squares fitting procedure (4, 5). It should be noted that the interaction term is purely imaginary for the  $\nu_6$  mode, as shown in Eqs. [13] and [14]. These imaginary terms can be handled as real terms by taking advantage of the phase relation of the vibrational eigenfunction. By choosing the phase of the  $6^1$  level as  $i$  and that of the  $0^0$  level as  $+1$ , the matrix elements are always real numbers.

Incorporating the above interaction term, as well as a Coriolis interaction term, into Watson's  $S$ -reduced rotational Hamiltonian in a Hund's case (b) description, the eigenvalue



**FIG. 2.** Dependence of the effective rotational constants;  $B_{\text{eff}} = [B + C]/2$  for each  $K_a$  is plotted as a function of the quantum number  $K_a^2$  for (a)  $0^0$  and (b)  $6^1$  of the  ${}^2A_1$  state of  $\text{H}_2\text{CCC}^-$ . The solid lines indicate a deperturbed value obtained by introducing a centrifugal distortion coupling interaction term. Panel (a) shows the clear discontinuity at  $K_a = 7-10$ . A discontinuity can also be seen at  $K_a = 6$  and  $7$  in (b).

is obtained by direct diagonalization of a secular equation which includes three vibronic levels  $0^0$ ,  $6^1$ , and  $9^1$  given as

$$\begin{vmatrix} F_0 - E & H_{\text{CD}}^{0,6} & H_{\text{CD}}^{0,9} \\ H_{\text{CD}}^{6,0} & F_6 + G_6 - E & H_{\text{cor}}^{6,9} \\ H_{\text{CD}}^{9,0} & H_{\text{cor}}^{9,6} & F_9 + G_9 - E \end{vmatrix} = 0. \quad [21]$$

Here,  $F_i$  and  $G_i$  are the rotational energy terms and the vibrational energy terms for the  $i$ th mode,  $H_{\text{CD}}^{ij}$  is the centrifugal distortion term between the  $i$ th and the  $j$ th modes (Eqs. [13] and [14]), and  $E$  is the eigenvalue. The anomalous data indicate that the interaction term should be applied in the  $K'_a = 6-10$  levels of  $v' = 0$ ,  $K'_a = 6-7$  levels of  $6^1$ , and  $K'_a = 8-9$  levels of  $9^1$ . In addition, the  $6^1$  and the  $9^1$  levels are strongly coupled by type (a) Coriolis coupling. Therefore, we included three interactions and obtained the eigenvalues of all levels simultaneously by using the direct diagonalization method (4, 5). From this analysis we obtain the centrifugal distortion coupling coefficients  $C_6^{ac} = 1.0723(2) \times 10^{-4}$  and  $C_9^{ab} = 1.5397(5) \times 10^{-5}$ , but the signs of these two constants are not determinable from this

analysis. Based on these centrifugal distortion coupling constants, the deperturbed values of  $B_{200}$  and  $D_{220}$  were obtained. These values were used to obtain the solid lines shown in Fig. 2.

This  ${}^2A_1$  excited state of  $\text{H}_2\text{CCC}^-$  is best characterized as a dipole-bound state (DBS), where the electron is bound by approximately 20 meV (4) in a very diffuse ( $\sim 25 \text{ \AA}$ ) orbital at the positive end of the nuclear dipole. Consequently, the geometric structure of the DBS is quite similar to that of the ground state neutral propadienyldiene. Thus, we expect that the anomaly observed for the DBS should also be detectable in neutral  $\text{H}_2\text{CCC}$ . There have been several reported microwave studies of the rotational constants in neutral  $\text{H}_2\text{CCC}$  (11). However, none have reported centrifugal distortion coupling. This is due to the fact that the  $K_a$  levels examined in those studies are still well below those required to observe this effect.

As shown earlier, the interaction term  $H_{12}^n$  vanishes for planar molecules. Since the  ${}^2A_1$  state of  $\text{H}_2\text{CCC}^-$  has a structure similar to that of neutral  $\text{H}_2\text{CCC}$ , which is planar, we assume that it is a planar structure as well. Therefore, we should not expect to observe centrifugal distortion interaction in  $\nu_6$  mode. However, because the  $\nu_6$  mode experiences strong mixing with the  $\nu_9$  mode through a Coriolis interaction, we are able to observe centrifugal distortion due to the mixed components of the  $\nu_9$  mode.

The centrifugal distortion effect on the spin-rotation interactions is given by

$$H_{12}^{(S)} = - \sum_n \omega_n q_n C_n^{xz} [\hat{S}_x, \hat{N}_z]. \quad [22]$$

This term can mix the states in the same manner. However, this interaction does not primarily contribute to the observed shifts in effective  $B$  values, because it does not produce the energy correction proportional to  $N[N+1]$ . Thus, we have neglected this higher-order interaction in the present analysis.

## CONCLUSION

Centrifugal distortion coupling has been addressed in light of spin-multiplet states. The coupling term was described in Hund's case (b) for electronic spin doublet and triplet states. The result obtained for the doublet case was applied to the autodetachment spectrum of  $\text{H}_2\text{CCC}^-$ . The centrifugal distortion couplings between (1) the out-of-plane bending mode  $\nu_6$  and the vibrational ground state and (2) the in-plane bending mode  $\nu_9$  and the vibrational ground state were analyzed utilizing the interaction-term rederived spin-multiplet states in this work, and the coupling coefficients  $C_6^{ac}$  and  $C_9^{ab}$  were found to be  $1.0723(2) \times 10^{-4}$  and  $-1.5397(5) \times 10^{-5}$ , respectively.

## ACKNOWLEDGMENTS

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