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Calculating intensities using effective Hamiltonians in terms of Coriolis-adapted normal modes

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The calculation of rovibrational transition energies and intensities is often hampered by the fact that vibrational states are strongly coupled by Coriolis terms. Because it invalidates the use of perturbation theory for the purpose of decoupling these states, the coupling makes it difficult to analyze spectra and to extract information from them. One either ignores the problem and hopes that the effect of the coupling is minimal or one is forced to diagonalize effective rovibrational matrices (rather than diagonalizing effective rotational matrices). In this paper we apply a procedure, based on a quantum mechanical canonical transformation for deriving decoupled effective rotational Hamiltonians. In previous papers we have used this technique to compute energy levels. In this paper we show that it can also be applied to determine intensities. The ideas are applied to the ethylene molecule. © 2005 American Institute of Physics. [DOI: 10.1063/1.1831276]

I. INTRODUCTION

Rovibrational spectra are analyzed to determine both the positions and the intensities of spectral lines. Intensities play a key role in interpreting spectra.^{1–4} Used together, experimental intensities and theoretical models enable one, for example, to extract information from remote sensing atmospheric experiments and combustion and astrophysical data.⁵ In addition, intensity information is crucial for understanding spectra taken in the laboratory. Transition intensities are used to make assignments and therefore indirectly provide a means of determining the structure of a molecule, its force constants, etc. From the intensities themselves one can sometimes extract the dipole moment of the molecule.

For semirigid molecules it is very common to analyze both the positions and intensities of spectral transitions by using normal coordinates and perturbation theory.^{2,6,7} If vibrations are of small amplitude normal coordinates are sufficient. If J is not too large and anharmonicity is fairly weak perturbation theory is sufficient. Perturbation theory is used to derive a new Hamiltonian operator, unitarily equivalent to the original Hamiltonian and having smaller off-diagonal matrix elements in the harmonic oscillator basis than those of the original Hamiltonian. Each diagonal matrix element may be considered an effective (rotational) Hamiltonian. Off-diagonal matrix elements are neglected and effective Hamiltonians are diagonalized to obtain rotational levels associated with each vibrational state.³ This approach is successful if it is possible to derive a new Hamiltonian for which the effect of off-diagonal matrix elements on eigenvalues is negligible. In most cases it works well but in some cases setting an

off-diagonal matrix element equal to zero changes the eigenvalues quite a bit. In general, if this is the case, it is due to the fact that the eigenvalues of the two effective Hamiltonians coupled by the off-diagonal matrix element are close. This problem always arises if two or more normal mode frequencies are similar. In this case, it is not possible to obtain an effective rotational Hamiltonian for each vibrational state. Rather, one must compute eigenvalues of an effective rovibrational Hamiltonian matrix. The size of this matrix depends on the number of coupled vibrational states. Often equations for the matrix elements of the effective rovibrational Hamiltonian matrix are not derived, but elements are parametrized and the parameters are fit to experimental results. In a series of papers⁸ we have shown that it is possible to derive decoupled effective rotational Hamiltonians even when Coriolis coupling terms strongly perturb nearly degenerate vibrational states. This is done by writing the Hamiltonian in terms of angular momentum dependent normal coordinates. In previous papers we have studied energy level patterns; in this paper we use a Bogoliubov–Tyablikov (BT) transformation to show that the same ideas can be used to compute intensities.

To compute intensities using the standard approach one transforms the space-fixed components of the dipole moment using the contact transformation that relates the original and the transformed Hamiltonian operator. Intensities of rovibrational transitions are obtained by writing the space-fixed components in terms of molecule-fixed components and expanding the latter in terms of normal coordinates.⁷ If the transformed Hamiltonian is

$$\tilde{H} = e^{iS} H e^{-iS} \quad (1)$$

then the transformed (space-fixed) dipole moment components are

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$$\tilde{\mu}_k = e^{iS} \mu_k e^{-iS}. \quad (2)$$

Intensities are computed from

$$\langle \Psi_f | \mu_k | \Psi_i \rangle = \langle \phi_f | \tilde{\mu}_k | \phi_i \rangle, \quad (3)$$

where

$$\tilde{H} | \phi_i \rangle = E_i | \phi_i \rangle$$

and

$$| \Psi_i \rangle = e^{-iS} | \phi_i \rangle.$$

If off-diagonal elements of \tilde{H} can be neglected then ϕ_i is an eigenfunction of an effective rotational Hamiltonian associated with a single vibrational level. If some off-diagonal elements of \tilde{H} cannot be neglected then ϕ_i is an eigenfunction of an effective rovibrational Hamiltonian associated with all the vibrational levels which are coupled by the off-diagonal elements. If off-diagonal elements of \tilde{H} are important but intensities are computed assuming that ϕ_i is an eigenfunction of an effective rotational Hamiltonian matrix, erroneous results are obtained. It would make analyzing experimental intensities easier if it were possible to compute intensities without diagonalizing an effective rovibrational Hamiltonian matrix. In this paper we show that this is possible.

We apply this approach to ethylene (C_2H_4), an important hydrocarbon present in the atmosphere. It is also of considerable interest in stellar astrophysics because it is formed as a product in chemical reactions of methane in the stratospheres of planets. The equilibrium geometry of ethylene molecule has D_{2h} symmetry and vibrational states with B_{1u} , B_{2u} or B_{3u} symmetry are infrared active; states with A_g , A_{1g} , B_{2g} or B_{3g} symmetry are Raman active.⁹ The rovibrational spectrum of ethylene has been analyzed by a number of research groups.⁹ Ethylene has several vibrational degrees of freedom which are strongly coupled by Coriolis terms and therefore the standard perturbative method of deriving effective rotational Hamiltonians for each vibrational state does not work. In an earlier paper we computed energy levels of *trans-d*₂ ethylene which has lower symmetry and fewer Coriolis coupled pairs.⁸ In the case of ethylene the four normal coordinates Q_4 , Q_7 , Q_{10} and Q_{12} are all pairwise Coriolis coupled.

II. EFFECTIVE HAMILTONIAN FOR ETHYLENE

A. BT transformation for a model Hamiltonian with two normal coordinates

Consider first a model Hamiltonian representing a rigid symmetric top molecule with two normal coordinates strongly coupled by J_z Coriolis terms,

$$H_{vr} = \frac{1}{2} [w_1(P_1^2 + Q_1^2) + w_2(P_2^2 + Q_2^2)] - \hbar^2 \mu_{zz} \zeta_{12}^z J_z \left(\sqrt{\frac{w_2}{w_1}} Q_1 P_2 - \sqrt{\frac{w_1}{w_2}} Q_2 P_1 \right) + H_{rr}, \quad (4)$$

where Q_1 , Q_2 , and P_1 , P_2 are the normal coordinates and their corresponding momenta. The meaning of the other

symbols is described elsewhere.^{7,8a} It is possible to write down exact closed-form equations for the energy levels of this Hamiltonian. The equations are somewhat simpler if, after writing the Hamiltonian in terms of raising and lowering operators

$$B_k^\dagger = \frac{1}{\sqrt{2}} (Q_k - iP_k), \quad B_k = \frac{1}{\sqrt{2}} (Q_k + iP_k), \quad k=1,2 \quad (5)$$

only the Coriolis terms with equal numbers of raising and lowering operators are retained.^{8b} The resulting Hamiltonian is

$$H_{vr} \approx \frac{w_1}{2} (B_1^\dagger B_1 + B_1 B_1^\dagger) + \frac{w_2}{2} (B_2^\dagger B_2 + B_2 B_2^\dagger) - \frac{\hbar^2 \mu_{zz} \zeta_{12}^z}{2i} J_z \left(\sqrt{\frac{w_1}{w_2}} + \sqrt{\frac{w_2}{w_1}} \right) (B_1^\dagger B_2 - B_1 B_2^\dagger) + H_{rr}. \quad (6)$$

To obtain exact energy level equations one introduces new raising and lowering operators defined by

$$\begin{pmatrix} B_1^\dagger \\ B_2^\dagger \\ B_1 \\ B_2 \end{pmatrix} = \begin{pmatrix} U_{11}^* & U_{12}^* & 0 & 0 \\ U_{21}^* & U_{22}^* & 0 & 0 \\ 0 & 0 & U_{11} & U_{12} \\ 0 & 0 & U_{21} & U_{22} \end{pmatrix} \begin{pmatrix} A_1^\dagger \\ A_2^\dagger \\ A_1 \\ A_2 \end{pmatrix}, \quad (7)$$

where the U_{ij} depend on J_z and are given explicitly elsewhere.^{8b} In terms of the new operators the Hamiltonian H_{vr} is

$$H_{vr} = \frac{1}{2} (w_1 + w_2) + 2 \sum_{k=1,2} E_k(J_z) A_k^\dagger A_k + H_{rr} \quad (8)$$

where $E_1(J_z)$ and $E_2(J_z)$ are

$$E_1(J_z) = \frac{1}{2} \left(\frac{w_1 + w_2}{2} \right) + \frac{1}{2} \sqrt{\left(\frac{w_1 - w_2}{2} \right)^2 + \frac{X_1^2(J_z)(w_1 + w_2)^2}{w_1 w_2}},$$

$$E_2(J_z) = \frac{1}{2} \left(\frac{w_1 + w_2}{2} \right) - \frac{1}{2} \sqrt{\left(\frac{w_1 - w_2}{2} \right)^2 + \frac{X_1^2(J_z)(w_1 + w_2)^2}{w_1 w_2}},$$

and

$$X_1(J_z) = \frac{\hbar^2 \mu_{zz} \zeta_{12}^z J_z}{2}.$$

The eigenkets of the middle term in Eq. (8) are denoted $|n_1(J_z)n_2(J_z)\rangle$. The Hamiltonian of Eq. (8) is diagonal in the $|n_1(J_z)n_2(J_z)\rangle |JKM\rangle$ basis, where $|JKM\rangle$ is a symmetric top solution. Note that $|n_1(J_z)n_2(J_z)\rangle |JKM\rangle = |n_1(K)n_2(K)\rangle |JKM\rangle$. The kets $|n_1(K)n_2(K)\rangle$ satisfy the orthogonality relation

$$\langle n_1(K)n_2(K) | n_1'(K)n_2'(K) \rangle = \delta_{n_1 n_1'} \delta_{n_2 n_2'}. \quad (9)$$

If the rigid rotor part of the model Hamiltonian is an asymmetric top Hamiltonian then Eq. (8) remains unchanged but H_{rr} is not diagonal in the $|n_1(J_z)n_2(J_z)JK\rangle$ basis. Off-diagonal matrix elements of the angular momentum raising and lowering operators J_{\pm}^2 in H_{rr} are nonzero. The off-diagonal matrix elements are

$$\begin{aligned} &\langle JK'n_1'(J_z)n_2'(J_z)|J_{\pm}^2|n_1(J_z)n_2(J_z)JK\rangle \\ &= \langle n_1'(K')n_2'(K')|n_1(K)n_2(K)\rangle \langle JK'|J_{\pm}^2|JK\rangle. \end{aligned} \quad (10)$$

The overlap integrals are calculated in the coordinate representation

$$\begin{aligned} &\langle n_1'(K')n_2'(K')|n_1(K)n_2(K)\rangle \\ &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dQ_1 dQ_2 \langle n_1'(K')n_2'(K')|Q_1 Q_2\rangle \\ &\quad \times \langle Q_1 Q_2|n_1(K)n_2(K)\rangle. \end{aligned} \quad (11)$$

If $n_1+n_2 \neq n_1'+n_2'$ the overlap integral vanishes identically. Expressions for the overlap integrals are not complicated. Some examples are

$$\langle 0(K')0(K')|0(K)0(K)\rangle = 1, \quad (12)$$

$$\begin{aligned} &\langle 1(K')0(K')|1(K)0(K)\rangle \\ &= U_{11}^*(K')U_{11}(K) + U_{21}^*(K')U_{21}(K), \end{aligned} \quad (13)$$

$$\begin{aligned} &\langle 0(K')1(K')|0(K)1(K)\rangle \\ &= U_{12}^*(K')U_{12}(K) + U_{22}^*(K')U_{22}(K), \end{aligned} \quad (14)$$

$$\begin{aligned} &\langle 1(K')0(K')|0(K)1(K)\rangle \\ &= U_{11}^*(K')U_{12}(K) + U_{21}^*(K')U_{22}(K), \end{aligned} \quad (15)$$

$$\begin{aligned} &\langle 0(K')1(K')|1(K)0(K)\rangle \\ &= U_{12}^*(K')U_{11}(K) + U_{22}^*(K')U_{21}(K), \end{aligned} \quad (16)$$

and others are presented elsewhere.^{8b}

B. Ethylene Hamiltonian

No molecule has only two normal coordinates. How can we therefore apply the model to analyze the spectra of a real molecule? It is common to use perturbation theory to study the spectra of semirigid molecules. To do this the Hamiltonian operator is transformed so that in the original harmonic oscillator/rigid rotor basis blocks of the Hamiltonian matrix that correspond to different vibrational basis functions are weakly coupled. If a term in the Hamiltonian strongly couples two zeroth-order states it is best not to transform the Hamiltonian to decrease coupling due to this term. This term then appears in its original form in the final transformed Hamiltonian. For a molecule with $3N-6$ normal coordinates in which k coordinates (Q_1, Q_2, \dots, Q_k), are strongly coupled by Coriolis terms, one would proceed as follows: (1) use standard perturbation theory to derive an effective Hamiltonian labeled by quantum numbers $n_{k+1}, n_{k+2}, \dots, n_{3N-6}$ for each of the weakly coupled zeroth-order states; (2) compute eigenvalues of the effective Hamiltonians containing the strongly coupled terms. There is an effective

Hamiltonian for each set of quantum numbers $n_{k+1}, n_{k+2}, \dots, n_{3N-6}$ which depends on $Q_1, Q_2, \dots, Q_k, P_1, P_2, \dots, P_k$, and angular momentum operators. We use the BT transformation method of the preceding section to compute eigenvalues of each of these effective Hamiltonians. Ethylene has four vibrational modes, Q_7, Q_{10}, Q_4 and Q_{12} , that are pairwise strongly coupled by Coriolis terms. Dropping a constant, the effective Hamiltonian for $n_{k+1}=n_{k+2}=\dots=n_{3N-6}=0$ is

$$\begin{aligned} H_{7,10,4,12} = &\left(\sum_{i=7,10,4,12} H_{ii} \right) + H_{7-10} + H_{4-10} + H_{10-12} \\ &+ H_{7-12} + H_{7-4} + H_{4-12} + H_{rr}, \end{aligned} \quad (17)$$

where

$$\begin{aligned} H_{ii} = &\frac{\hbar^2}{2hc} \{ (\mu_{xx}^i)_{\text{eff}} J_x^2 + (\mu_{yy}^i)_{\text{eff}} J_y^2 + (\mu_{zz}^i)_{\text{eff}} J_z^2 \} - \{ \Delta_i^j (J^2)^2 \\ &+ \Delta_{JK}^i J^2 J_z^2 + \Delta_K^i J_z^4 + \frac{1}{2} [\delta_J^i J^2 + \delta_K^i J_z^2, J_+^2 + J_-^2]_+ \}, \end{aligned}$$

$$\begin{aligned} H_{7-10} = &-i \xi_{7-10}^z J_z (B_7^\dagger B_{10} - B_7 B_{10}^\dagger) \\ &+ \eta_{7-10}^{xy} (J_x J_y + J_y J_x) (B_7^\dagger B_{10} + B_7 B_{10}^\dagger), \end{aligned}$$

$$\begin{aligned} H_{4-10} = &-i \xi_{4-10}^x J_x (B_4^\dagger B_{10} - B_4 B_{10}^\dagger) \\ &+ \eta_{4-10}^{yz} (J_y J_z + J_z J_y) (B_4^\dagger B_{10} + B_4 B_{10}^\dagger), \end{aligned}$$

$$H_{10-12} = i \xi_{10-12}^y J_y (B_{10}^\dagger B_{12} - B_{10} B_{12}^\dagger),$$

$$H_{7-12} = i \xi_{7-12}^x J_x (B_7^\dagger B_{12} - B_7 B_{12}^\dagger),$$

$$H_{7-4} = \eta_{7-4}^{xz} (J_x J_z + J_z J_x) (B_4^\dagger B_7 + B_4 B_7^\dagger),$$

and

$$H_{4-12} = i \xi_{4-12}^z J_z (B_4^\dagger B_{12} - B_4 B_{12}^\dagger),$$

with

$$\xi_{ij}^z = \frac{\hbar^2 \mu_{zz}}{2hc} \left(\sqrt{\frac{w_i}{w_j}} + \sqrt{\frac{w_j}{w_i}} \right) \zeta_{ij}^z,$$

and likewise for ξ_{ij}^x and ξ_{ij}^y . $[A, B]_+$ is the symmetrized product $AB + BA$. The rotational constants in H_{ii} depend on the raising and lowering operators associated with the strongly coupled modes,

$$\mu^i = \mu_0 + \sum_{j=7,10,4,12} \alpha_i^j \left(\frac{B_j^\dagger B_j + B_j B_j^\dagger}{2} \right). \quad (18)$$

We compute energy levels of $H_{7,10,4,12}$ by introducing new raising and lowering operators that decouple the pairs Q_7, Q_{10} and Q_4, Q_{12} . To define these operators we rewrite

$$H_{7,10,4,12} = H_0 + H_r, \quad (19)$$

where

$$H_0 = \left(\sum_{i=7,10,4,12} H_{ii} \right) + H_{7-10}^z + H_{4-12} + H_{rr}^{ST}(J_\alpha, J_\beta, J_\gamma),$$

$$\begin{aligned} H_r = &H_{4-10} + H_{10-12} + H_{7-12} + H_{7-4} + H_{7-10}^r \\ &+ [H_{rr} - H_{rr}^{ST}(J_\alpha, J_\beta, J_\gamma)], \end{aligned}$$

$$H_{7-10}^z = -i\xi_{7-10}^z J_z (B_7^\dagger B_{10} - B_7 B_{10}^\dagger),$$

and

$$H_{7-10}^r = \eta_{7-10}^{xy} (J_x J_y + J_y J_x) (B_7^\dagger B_{10} + B_7 B_{10}^\dagger).$$

In the above equation, H_{rr}^{ST} is the symmetric top portion of the rigid rotor Hamiltonian. In terms of the old raising and lowering operators H_0 is given by

$$\begin{aligned} H_0 = & \sum_{k=7,10,4,12} \frac{w_k}{2} (B_k^\dagger B_k + B_k B_k^\dagger) \\ & - i\xi_{7,10}^z J_z \left(\sqrt{\frac{w_7}{w_{10}}} + \sqrt{\frac{w_{10}}{w_7}} \right) (B_7^\dagger B_{10} - B_7 B_{10}^\dagger) \\ & + i\xi_{4,12}^z J_z \left(\sqrt{\frac{w_4}{w_{12}}} + \sqrt{\frac{w_{12}}{w_4}} \right) (B_4^\dagger B_{12} - B_4 B_{12}^\dagger) \\ & + H_{rr}^{ST}(J_\alpha, J_\beta, J_\gamma). \end{aligned} \quad (20)$$

In terms of the new raising and lowering operators H_0 can be rewritten as

$$\begin{aligned} H_0 = & \frac{1}{2}(w_7 + w_{10}) + 2 \sum_{k=7,10} E_k(J_z) A_k^\dagger A_k + \frac{1}{2}(w_4 + w_{12}) \\ & + 2 \sum_{k=4,12} E_k(J_z) A_k^\dagger A_k + H_{rr}^{ST}(J_\alpha, J_\beta, J_\gamma), \end{aligned} \quad (21)$$

where

$$\begin{aligned} E_7(J_z) = & \frac{1}{2} \left(\frac{w_7 + w_{10}}{2} \right) \\ & + \frac{1}{2} \sqrt{\left(\frac{w_7 - w_{10}}{2} \right)^2 + \frac{X_1^2(J_z)(w_7 + w_{10})^2}{w_{10}w_7}}, \\ E_{10}(J_z) = & \frac{1}{2} \left(\frac{w_7 + w_{10}}{2} \right) \\ & - \frac{1}{2} \sqrt{\left(\frac{w_7 - w_{10}}{2} \right)^2 + \frac{X_1^2(J_z)(w_7 + w_{10})^2}{w_{10}w_7}}, \\ E_4(J_z) = & \frac{1}{2} \left(\frac{w_4 + w_{12}}{2} \right) \\ & + \frac{1}{2} \sqrt{\left(\frac{w_4 - w_{12}}{2} \right)^2 + \frac{X_2^2(J_z)(w_4 + w_{12})^2}{w_4w_{12}}}, \end{aligned}$$

and

$$\begin{aligned} E_{12}(J_z) = & \frac{1}{2} \left(\frac{w_4 + w_{12}}{2} \right) \\ & - \frac{1}{2} \sqrt{\left(\frac{w_4 - w_{12}}{2} \right)^2 + \frac{X_2^2(J_z)(w_4 + w_{12})^2}{w_4w_{12}}}, \end{aligned}$$

with

$$X_1(J_z) = \frac{\hbar^2 \mu_{zz} \xi_{7,10}^z J_z}{2},$$

and

TABLE I. Energy levels.

$n_{10}n_7n_4n_{12}K_{-1}K_1$	Diagonal element	Block diagonal approx.	Variational energies
1,0,0,0,1,15		3774.26	3774.24
1,0,0,0,1,14	3799.18	3793.36	3794.14
1,0,0,0,3,13		3820.14	3820.89
1,0,0,0,3,12	3831.91	3822.00	3822.94
1,0,0,0,5,11		3883.96	3884.67
1,0,0,0,5,10	3883.28	3883.95	3884.68
1,0,0,0,7,9		3979.66	3980.29
1,0,0,0,7,8	3979.29	3979.66	3980.29
1,0,0,0,9,7		4107.37	4107.88
1,0,0,0,9,6	4107.13	4107.37	4107.88
1,0,0,0,11,5		4266.80	4267.18
1,0,0,0,11,4	4266.66	4266.80	4267.18
1,0,0,0,13,3		4457.74	4457.05
1,0,0,0,13,2	4457.66	4457.74	4457.96
1,0,0,0,15,1		4679.96	4679.99
1,0,0,0,15,0	4679.95	4679.96	4679.99
0,0,1,0,1,15		3281.31	3281.10
0,0,1,0,1,14	3293.87	3300.15	3299.37
0,0,1,0,3,13		3327.59	3326.84
0,0,1,0,3,12	3327.59	3329.28	3328.37
0,0,1,0,5,11		3392.88	3392.15
0,0,1,0,5,10	3390.35	3392.89	3392.17
0,0,1,0,7,9		3490.69	3489.94
0,0,1,0,7,8	3474.92	3490.69	3489.94
0,0,1,0,9,7		3620.94	3620.94
0,0,1,0,9,6	3620.73	3620.94	3620.94
0,0,1,0,11,5		3783.23	3782.96
0,0,1,0,11,4	3783.10	3783.23	3782.96
0,0,1,0,13,3		3977.22	3977.04
0,0,1,0,13,2	3977.16	3977.22	3977.04
0,0,1,0,15,1		4202.59	4202.54
0,0,1,0,15,0	4202.57	4202.59	4202.54
0,0,0,1,1,15		3357.38	3357.85
0,0,0,1,1,14	3381.49	3375.90	3377.95
0,0,0,1,3,13		3401.68	3403.74
0,0,0,1,3,12	3400.78	3403.51	3406.05
0,0,0,1,5,11		3463.13	3465.20
0,0,0,1,5,10	3457.89	3463.12	3465.20
0,0,0,1,7,9		3555.30	3557.59
0,0,0,1,7,8	3554.94	3555.30	3557.59
0,0,0,1,9,7		3678.34	3679.74
0,0,0,1,9,6	3678.12	3678.34	3679.74
0,0,0,1,11,5		3832.05	3833.24
0,0,0,1,11,4	3831.91	3832.05	3833.24
0,0,0,1,13,3		4016.25	4017.01
0,0,0,1,13,2	4016.17	4016.25	4017.01
0,0,0,1,15,1		4230.78	4230.83
0,0,0,1,15,0	4230.77	4230.78	4230.83
0,1,0,0,1,15		3157.41	3156.92
0,1,0,0,1,14	3170.28	3176.21	3174.21
0,1,0,0,3,13		3201.62	3199.67
0,1,0,0,3,12	3200.69	3203.62	3201.20
0,1,0,0,5,11		3262.27	3260.35
0,1,0,0,5,10	3261.57	3262.27	3260.35
0,1,0,0,7,9		3353.34	3351.58
0,1,0,0,7,8	3352.96	3353.34	3351.58
0,1,0,0,9,7		3475.16	3473.56
0,1,0,0,9,6	3474.92	3475.16	3473.56
0,1,0,0,11,5		3627.62	3626.31
0,1,0,0,11,4	3627.47	3627.62	3626.31
0,1,0,0,13,3		3810.66	3809.72
0,1,0,0,13,2	3810.59	3810.66	3809.72
0,1,0,0,15,1		4024.20	4023.36
0,1,0,0,15,0	4024.18	4024.20	4023.85

$$X_2(J_z) = \frac{\hbar^2 \mu_{zz} \zeta_{4,12}^z J_z}{2}.$$

For ethylene we have used parameter values derived by fitting the effective Hamiltonian to experimental spectra.¹⁰ We have computed energy levels of $H_{7,10,4,12}$ in three different ways. These results are presented in Table I. It is straightforward to calculate eigenvalues of $H_{7,10,4,12}$, written in terms of the B raising and lowering operators [Eq. (20)] by using a basis of products of eigenfunctions of $B_i^\dagger B_i$ and rigid rotor functions. We denote this matrix \mathbf{H}_B . We have verified that we obtain the same eigenvalues from $H_{7,10,4,12}$ written in terms of the A raising and lowering operators [Eq. (21)] by using a basis of products of eigenfunctions of $A_i^\dagger A_i$ and rigid rotor functions. We denote this matrix \mathbf{H}_A . Note that although it is much harder to compute matrix elements of \mathbf{H}_A (doing so requires, for example, using the overlap integrals), \mathbf{H}_A is more nearly block diagonal (with blocks labeled by eigenvalues of $A_i^\dagger A_i$). The exact eigenvalues are given in the last column of Table I. Zeroth-order energy level labels are in the first column. The second column contains the diagonal matrix elements of \mathbf{H}_A . For low values of $K=K_{-1}$ the diagonal matrix elements are clearly poor approximations for the energy levels. The quality of the results in the second column can be drastically improved by diagonalizing blocks $\langle JK n_7(J_z) n_{10}(J_z) n_4(J_z) n_{12}(J_z) | H_{7,10,4,12} | n_{12}(J_z) n_4(J_z) n_{10}(J_z) n_7(J_z) JK' \rangle$. The size of this block is only $2J+1$. These results are shown in the third column. For several reasons^{8a} the approximate energy levels are essentially the same as accurate numerical values when K_{-1} is close to J (despite the fact that the Coriolis term in the original Hamiltonian is largest when K is largest) and are less accurate for smaller values of K_{-1} .

III. CALCULATION OF INTENSITIES

Intensities of rovibrational transitions depend on the absolute squares of matrix elements of components of the space-fixed dipole moment operator $\hat{\mu}^7$,

$$I \propto \sum_{W=X,Y,Z} |\langle \psi_i | \hat{\mu}_W | \psi_j \rangle|^2 \quad (22)$$

where ψ_i and ψ_j are eigenfunctions of the Hamiltonian. Because ψ_i and ψ_j are written in terms of normal coordinates

and Euler angles that specify the orientation of the molecule-fixed frame, the space-fixed components of the dipole are replaced by

$$\hat{\mu}_W = \sum_{\alpha} \lambda_{W\alpha} \hat{\mu}_{\alpha} \quad W=X,Y,Z \quad (23)$$

where $\hat{\mu}_{\alpha}$ ($\alpha=x,y,z$) are molecule-fixed components and $\lambda_{\alpha W}$ are direction cosines. The components $\hat{\mu}_{\alpha}$ depend on normal coordinates.

To compute intensities we use *ab initio* molecule-fixed dipole moment components. The effective Hamiltonian we work with, $H_{7,10,4,12}$, is obtained from the Watson Hamiltonian by contact transformation. Let us denote its eigenfunctions ϕ_i , i.e.,

$$H_{7,10,4,12} \phi_i = E_i \phi_i. \quad (24)$$

Because $H_{7,10,4,12}$ is transformed and $\hat{\mu}_{\alpha}$ is not, it would not, in general, be correct to compute intensities from $\langle \phi_i | \hat{\mu}_{\alpha} | \phi_i \rangle$ matrix elements. $H_{7,10,4,12}$ is related to the full Hamiltonian by

$$H_{7,10,4,12} = e^{iS} \hat{H} e^{-iS} \quad (25)$$

and $|\phi_i\rangle$ is related to $|\psi_i\rangle$ by

$$|\phi_i\rangle = e^{iS} |\psi_i\rangle. \quad (26)$$

The matrix element we need to calculate is

$$\langle \psi_i | \hat{\mu}_W | \psi_j \rangle = \langle \phi_i | \hat{\mu}_W | \phi_j \rangle, \quad (27)$$

where $\hat{\mu}_{\alpha} = e^{iS} \hat{\mu}_{\alpha} e^{-iS}$. Due to the fact that S contains angular momentum operators and $\lambda_{\alpha W}$ depend on the Euler angles it is important to use the symmetrized form

$$\begin{aligned} \langle \phi_i | \hat{\mu}_W | \phi_j \rangle &= \frac{1}{2} \langle \phi_i | \sum_{\alpha} \lambda_{W\alpha} e^{iS} \hat{\mu}_{\alpha} e^{-iS} | \phi_j \rangle \\ &+ \frac{1}{2} \langle \phi_i | \sum_{\alpha} e^{iS} \hat{\mu}_{\alpha} e^{-iS} \lambda_{W\alpha} | \phi_j \rangle. \end{aligned} \quad (28)$$

We expand $\hat{\mu}_{\alpha}$ and truncate after the linear term,

$$\hat{\mu}_{\alpha} = \mu_{\alpha}^e + \sum_{k=1}^{3N-6} \frac{\partial \mu_{\alpha}}{\partial Q_k} \hat{Q}_k. \quad (29)$$

TABLE II. Parameters used for calculating energy levels and dipole matrix elements for ethylene.

	Ground state	$n_7=1$	$n_{10}=1$	$n_4=1$	$n_{12}=1$
E_v	0.0	948.770 952	825.926 68	1025.5897	1442.4750
A	4.864 606 4	4.865 810 8	4.876 479	4.838 890	4.858 81
B	1.001 054 5	1.001 327 3	1.000 556	0.998 353	1.001 64
C	0.828 042 4	0.829 420 0	0.826 493 7	0.828 154 8	0.826 50
$\Delta_J \times 10^6$	1.465 12	1.446 34	1.386 44	1.545 78	1.465 1
$\Delta_{JK} \times 10^6$	10.2309	10.2622	11.5929	9.0278	10.2309
$\Delta_K \times 10^6$	86.3983	100.9411	73.0141	77.3396	86.398
$\delta_J \times 10^6$	0.283 55	0.269 11	0.243 38	0.321 38	0.283 6
$\delta_K \times 10^6$	10.0341	9.6034	7.813	12.3665	10.034
$\xi_{7,10}^x = -4.426 13$	$\xi_{4,10}^x = 1.794 37$	$\xi_{4,12}^x = -5.2324$	$\xi_{7,12}^x = 1.7392$	$\xi_{10,12}^x = -0.137 64$	$\eta_{7,10}^{xy} = -0.000 109$
$\eta_{4,10}^{yz} = 0.011 821$	$\eta_{4,7}^{yz} = -0.007 363$				

$\hat{\mu}_\alpha = e^{iS} \hat{\mu}_\alpha e^{-iS}$ can be written as a sum of terms, $\sum_{mn} \mu_{mn}^\alpha$, each of order $\kappa^{m+2n} r^m J^n e a_0$, where $\kappa = (m_e/m_n)^{1/4}$ is the Born-Oppenheimer expansion parameter.^{4,7} Because we retain only the first term in this series

$$e^{iS} \hat{\mu}_\alpha e^{-iS} \approx \hat{\mu}_\alpha. \quad (30)$$

Setting $Q_j = 0$, $j = k + 1, \dots, 3N - 6$ for the normal coordinates that are not strongly coupled and writing the strongly coupled normal coordinates in terms of the $\{A_i, A_i^\dagger\}$ we obtain

$$\hat{\mu}_\alpha \approx \mu_e^\alpha + \sum_{i=7,10,4,12} L_i^\alpha(J_z) A_i + \sum_{i=7,10,4,12} L_i^{\dagger\alpha}(J_z) A_i^\dagger, \quad (31)$$

where

$$L_i^\alpha = \frac{1}{\sqrt{2}} [\mu_7^\alpha U_{1i} + \mu_{10}^\alpha U_{2i}], \quad i = 7, 10$$

and

$$\begin{aligned} \mathbf{T}_i^\dagger \hat{\mu}_W \mathbf{T}_j &= \sum_{K n_4 n_7 n_{10} n_{12}} (T^t)_{i, K n_4 n_7 n_{10} n_{12}} \sum_\alpha \frac{1}{2} \langle JK | \lambda_{\alpha W} | JK' \rangle \langle n_4(K) n_7(K) n_{10}(K) n_{12}(K) | \hat{\mu}_\alpha(K') | n_4'(K') n_7'(K') \\ &\times n_{10}'(K') n_{12}'(K') \rangle T_{JK' n_4' n_7' n_{10}' n_{12}', j} + \sum_{K n_4 n_7 n_{10} n_{12}} (T^t)_{i, K n_4 n_7 n_{10} n_{12}} \sum_\alpha \frac{1}{2} \langle JK | \lambda_{\alpha W} | JK' \rangle \\ &\times \langle n_4(K) n_7(K) n_{10}(K) n_{12}(K) | \hat{\mu}_\alpha(K) | n_4'(K') n_7'(K') n_{10}'(K') n_{12}'(K') \rangle T_{JK' n_4' n_7' n_{10}' n_{12}', j}. \end{aligned} \quad (35)$$

$\hat{\mu}_\alpha$ is a function of K because in Eq. (31) the L_i^α and $L_i^{\dagger\alpha}$ depend on J_z . Note that to obtain this equation we have replaced

$$|n_4(J_z) n_7(J_z) n_{10}(J_z) n_{12}(J_z) JK\rangle$$

with

$$|n_4(K) n_7(K) n_{10}(K) n_{12}(K) JK\rangle.$$

The matrix elements $\langle JK | \lambda_{\alpha Z} | JK' \rangle$ are calculated using the Wigner-Eckart theorem.

To compute the matrix elements

$$\begin{aligned} \langle n_4(K) n_7(K) n_{10}(K) n_{12}(K) | \hat{\mu}_\alpha(K) | n_4'(K') n_7'(K') n_{10}'(K') \\ \times n_{12}'(K') \rangle \end{aligned}$$

we replace $\hat{\mu}_\alpha(K)$ with

$$\begin{aligned} L_7^\alpha(K) A_7 + L_4^\alpha(K) A_4 + L_{10}^\alpha(K) A_{10} + L_{12}^\alpha(K) A_{12} + L_7^{\dagger\alpha}(K) A_7 \\ + L_4^{\dagger\alpha}(K) A_4 + L_{10}^{\dagger\alpha}(K) A_{10} + L_{12}^{\dagger\alpha}(K) A_{12} \end{aligned}$$

and act with the A raising and lowering operators on $|n_4' n_7' n_{10}' n_{12}'\rangle$. To do this one must evaluate overlap integrals. For example, the A_7 matrix element is

$$L_i^\alpha = \frac{1}{\sqrt{2}} [\mu_4^\alpha U_{3i} + \mu_{12}^\alpha U_{4i}], \quad i = 4, 12.$$

We now need to compute $\langle \phi_i | \hat{\mu}_W | \phi_{i'} \rangle$ matrix elements. We know $|\phi_i\rangle$ in the $\{|n_7(K) n_{10}(K) n_4(K) n_{12}(K) JK\rangle\}$ basis. In this basis the eigenvalue problem is

$$\mathbf{H}_{7,10,4,12} \mathbf{T} = \mathbf{T} \mathbf{E} \quad (32)$$

and

$$\langle \phi_i | \hat{\mu}_W | \phi_j \rangle = \mathbf{T}_i^\dagger \hat{\mu}_W \mathbf{T}_j, \quad (33)$$

where $\hat{\mu}_W$ is the matrix representing the W th dipole moment component in the

$$\{|n_7(K) n_{10}(K) n_4(K) n_{12}(K) JK\rangle\}$$

basis and \mathbf{T}_j is the j th column of \mathbf{T} . Using Eqs. (28) and (30),

$$\mathbf{T}_i^\dagger \hat{\mu}_W \mathbf{T}_j = \mathbf{T}_i^\dagger \sum_\alpha \frac{1}{2} \lambda_{\alpha W} \hat{\mu}_\alpha \mathbf{T}_j + \mathbf{T}_i^\dagger \sum_\alpha \frac{1}{2} \hat{\mu}_\alpha \lambda_{\alpha W} \mathbf{T}_j. \quad (34)$$

Exposing the basis function labels yields

$$\begin{aligned} \langle n_4(K) n_7(K) n_{10}(K) n_{12}(K) | A_7 | n_4'(K') \\ \times n_7'(K') n_{10}'(K') n_{12}'(K') \rangle \\ = \langle n_7(K) | (n_7' - 1)(K') \rangle \langle n_4(K) | n_4'(K') \rangle \\ \times \langle n_{10}(K) | n_{10}'(K') \rangle \langle n_{12}(K) | n_{12}'(K') \rangle \sqrt{n_7'}. \end{aligned} \quad (36)$$

We have computed dipole matrix elements using the Hamiltonian discussed in the preceding section, Hamiltonian parameters taken from the literature, and a dipole moment function calculated using CADPAC.¹¹ See Tables II and III for Hamiltonian and dipole parameters. The equilibrium dipole moment and dipole moment (normal coordinate) derivatives were computed using density functional theory, a 6311G** basis, and the BLYP functional. Our computed dipole matrix elements are presented in Table IV. In the last column we give matrix elements computed using either the basis of

TABLE III. Dipole moment derivatives of the ethylene molecule.

ν	$\partial \mu_x / \partial Q$	$\partial \mu_y / \partial Q$	$\partial \mu_z / \partial Q$
ν_{10}	0	-0.1125	0
ν_7	1.4813	0	0
ν_4	0	0	0
ν_{12}	0	0	0.4176

TABLE IV. Ethylene dipole moment matrix elements for different values of J .

Final state	Initial state	With BT effective rot Hamiltonian	Exact	Final state	Initial state	With BT effective rot Hamiltonian	Exact
1,0,0,0,2,1,1	0,0,0,0,1,1,0	0.0174	0.0180	0,1,0,0,5,4,1	0,0,0,0,4,4,0	0.0508	0.0511
1,0,0,0,2,1,2	0,0,0,0,1,1,1	0.0232	0.0235	0,1,0,0,5,4,2	0,0,0,0,4,4,1	0.3368	0.3370
1,0,0,0,2,0,2	0,0,0,0,1,0,1	0.0174	0.0180	0,1,0,0,5,3,2	0,0,0,0,4,3,1	0.1925	0.1928
1,0,0,0,3,2,1	0,0,0,0,2,2,0	0.0124	0.0128	0,1,0,0,5,3,3	0,0,0,0,4,3,2	0.1068	0.1071
1,0,0,0,3,2,2	0,0,0,0,2,2,1	0.0200	0.0207	0,1,0,0,5,2,3	0,0,0,0,4,2,2	0.0812	0.0813
1,0,0,0,3,1,2	0,0,0,0,2,1,1	0.0224	0.0226	0,1,0,0,5,2,4	0,0,0,0,4,2,3	0.0242	0.0247
1,0,0,0,3,1,3	0,0,0,0,2,1,2	0.0200	0.0207	0,1,0,0,5,1,4	0,0,0,0,4,1,3	0.0209	0.0213
1,0,0,0,3,0,3	0,0,0,0,2,0,2	0.0124	0.0128	0,1,0,0,5,1,5	0,0,0,0,4,1,4	0.0159	0.0162
1,0,0,0,4,3,1	0,0,0,0,3,3,0	0.0097	0.0100	0,1,0,0,5,0,5	0,0,0,0,4,0,4	0.0083	0.0089
1,0,0,0,4,3,2	0,0,0,0,3,3,1	0.0166	0.0172	0,1,0,0,6,5,1	0,0,0,0,5,5,0	0.0421	0.0422
1,0,0,0,4,2,2	0,0,0,0,3,2,1	0.0207	0.0211	0,1,0,0,6,5,2	0,0,0,0,5,5,1	0.1609	0.1609
1,0,0,0,4,2,3	0,0,0,0,3,2,2	0.0221	0.0224	0,1,0,0,6,4,2	0,0,0,0,5,4,1	0.0924	0.0920
1,0,0,0,4,1,3	0,0,0,0,3,2,2	0.0207	0.0211	0,1,0,0,6,4,3	0,0,0,0,5,4,2	0.0353	0.0358
1,0,0,0,4,1,4	0,0,0,0,3,1,3	0.0165	0.0172	0,1,0,0,6,3,3	0,0,0,0,5,3,2	0.0246	0.0247
1,0,0,0,4,0,4	0,0,0,0,3,0,3	0.0097	0.0100	0,1,0,0,6,2,4	0,0,0,0,5,2,3	0.0126	0.0130
1,0,0,0,5,4,1	0,0,0,0,4,4,0	0.0079	0.0080	0,1,0,0,6,2,5	0,0,0,0,5,2,4	0.0221	0.0225
1,0,0,0,5,4,2	0,0,0,0,4,4,1	0.0140	0.0147	0,1,0,0,6,1,6	0,0,0,0,5,1,5	0.0181	0.0184
1,0,0,0,5,3,2	0,0,0,0,4,3,1	0.0185	0.0194	0,1,0,0,6,0,6	0,0,0,0,5,0,5	0.0071	0.0076
1,0,0,0,5,3,3	0,0,0,0,4,3,2	0.0217	0.0222	0,0,0,1,2,1,1	0,0,0,0,1,1,0	0.1258	0.1262
1,0,0,0,5,2,3	0,0,0,0,4,2,2	0.0219	0.0221	0,0,0,1,2,1,2	0,0,0,0,1,1,1	0.1240	0.1244
1,0,0,0,5,2,4	0,0,0,0,4,2,3	0.0217	0.0222	0,0,0,1,2,0,2	0,0,0,0,1,0,1	0.0421	0.0425
1,0,0,0,5,1,4	0,0,0,0,4,1,3	0.0185	0.0193	0,0,0,1,3,2,1	0,0,0,0,2,2,0	0.1051	0.1058
1,0,0,0,5,1,5	0,0,0,0,4,1,4	0.0141	0.0147	0,0,0,1,3,2,2	0,0,0,0,2,2,1	0.0731	0.0735
1,0,0,0,5,0,5	0,0,0,0,4,0,4	0.0079	0.0079	0,0,0,1,3,1,2	0,0,0,0,2,1,1	0.0850	0.0850
1,0,0,0,6,5,1	0,0,0,0,5,5,0	0.0066	0.0067	0,0,0,1,3,1,3	0,0,0,0,2,1,2	0.0431	0.0435
1,0,0,0,6,5,2	0,0,0,0,5,5,1	0.0122	0.0123	0,0,0,1,3,0,3	0,0,0,0,2,0,2	0.0080	0.0083
1,0,0,0,6,4,2	0,0,0,0,5,4,1	0.0164	0.0173	0,0,0,1,4,3,1	0,0,0,0,3,3,0	0.0958	0.0961
1,0,0,0,6,4,3	0,0,0,0,5,4,2	0.0195	0.0202	0,0,0,1,4,3,2	0,0,0,0,3,3,1	0.0720	0.0733
1,0,0,0,6,3,3	0,0,0,0,5,3,2	0.0213	0.0220	0,0,0,1,4,2,2	0,0,0,0,3,2,1	0.0560	0.0565
1,0,0,0,6,3,4	0,0,0,0,5,3,3	0.0218	0.0218	0,0,0,1,4,2,3	0,0,0,0,3,2,2	0.0710	0.0713
1,0,0,0,6,2,4	0,0,0,0,5,2,3	0.0213	0.0219	0,0,0,1,4,1,3	0,0,0,0,3,1,2	0.0422	0.0428
1,0,0,0,6,2,5	0,0,0,0,5,2,4	0.0195	0.0202	0,0,0,1,4,1,4	0,0,0,0,3,1,3	0.0130	0.0132
1,0,0,0,6,1,5	0,0,0,0,5,1,4	0.0164	0.0170	0,0,0,1,4,0,4	0,0,0,0,3,0,3	0.0039	0.0041
1,0,0,0,6,1,6	0,0,0,0,5,1,5	0.0122	0.0123	0,0,0,1,5,4,2	0,0,0,0,4,4,1	0.0727	0.0731
1,0,0,0,6,0,6	0,0,0,0,5,0,5	0.0067	0.0067	0,0,0,1,5,3,2	0,0,0,0,4,3,1	0.0580	0.0587
0,1,0,0,2,1,1	0,0,0,0,1,1,0	0.2719	0.2721	0,0,0,1,5,3,3	0,0,0,0,4,3,2	0.0490	0.0495
0,1,0,0,2,1,2	0,0,0,0,1,1,1	0.1546	0.1548	0,0,0,1,5,2,3	0,0,0,0,4,2,2	0.0650	0.0652
0,1,0,0,2,0,2	0,0,0,0,1,0,1	0.2461	0.2462	0,0,0,1,5,2,4	0,0,0,0,4,2,3	0.0413	0.0420
0,1,0,0,3,2,1	0,0,0,0,2,2,0	0.3475	0.3479	0,0,0,1,5,1,4	0,0,0,0,4,1,3	0.0170	0.0171
0,1,0,0,3,2,2	0,0,0,0,2,2,1	0.1582	0.1584	0,0,0,1,5,1,5	0,0,0,0,4,1,4	0.0073	0.0076
0,1,0,0,3,1,2	0,0,0,0,2,1,1	0.1059	0.1063	0,0,0,1,5,0,5	0,0,0,0,4,0,4	0.0021	0.0023
0,1,0,0,3,1,3	0,0,0,0,2,1,2	0.0252	0.0253	0,0,0,1,6,4,2	0,0,0,0,5,4,1	0.0602	0.0607
0,1,0,0,3,0,3	0,0,0,0,2,0,2	0.0100	0.0103	0,0,0,1,6,4,3	0,0,0,0,5,4,2	0.0474	0.0482
0,1,0,0,4,3,1	0,0,0,0,3,3,0	0.4431	0.4434	0,0,0,1,6,3,3	0,0,0,0,5,3,2	0.0380	0.0386
0,1,0,0,4,3,2	0,0,0,0,3,3,1	0.2407	0.2409	0,0,0,1,6,2,4	0,0,0,0,5,2,3	0.0006	0.0006
0,1,0,0,4,2,2	0,0,0,0,3,2,1	0.1218	0.1221	0,0,0,1,6,2,5	0,0,0,0,5,2,4	0.0001	0.0001
0,1,0,0,4,2,3	0,0,0,0,3,2,2	0.0886	0.0889	0,0,0,1,6,1,5	0,0,0,0,5,1,4	0.0100	0.0105
0,1,0,0,4,1,3	0,0,0,0,3,1,2	0.0248	0.0250	0,0,0,1,6,1,6	0,0,0,0,5,1,5	0.0043	0.0046
0,1,0,0,4,1,4	0,0,0,0,3,1,3	0.0160	0.0163	0,0,0,1,6,0,6	0,0,0,0,5,0,5	0.0014	0.0015
0,1,0,0,4,0,4	0,0,0,0,3,0,3	0.0085	0.0087				

eigenfunctions of $A_i^\dagger A_i$ or the basis of eigenfunctions of $B_i^\dagger B_i$ (the same numbers are obtained with both basis sets).

In the first two columns we give labels for the initial and final states. States are labeled by the BT basis functions with the largest coefficients. We give dipole matrix elements for transitions between $(n_7 n_{10} n_4 n_{12}) = (0000)$ and $(n'_7 n'_{10} n'_4 n'_{12}) = \{(1000), (0100), \text{ and } (0001)\}$. The A raising and lowering operators enable us to determine energy levels and wave functions of H_0 in Eq. (20) without doing calculations. H_r is too important to be neglected but if we neglect off-diagonal matrix elements of $H_0 + H_r$ in the basis of products of eigenfunctions of $A_i^\dagger A_i$ we obtain effective rotational

Hamiltonians. Eigenfunctions of these effective Hamiltonians should be good approximations for the ϕ_i functions. These effective Hamiltonians are not diagonal in the symmetric top basis because of terms in H_{4-10} , H_{10-12} , H_{7-12} , H_{7-4} , H_{7-10}^r , and $(H_{rr} - H_{rr}^{ST})$ that couple basis functions with different values of K . If $H_0 + H_r$ matrix elements off diagonal in the basis of products of eigenfunctions of $A_i^\dagger A_i$ are set to zero the matrix \mathbf{T} in Eq. (32) is block diagonal. To calculate dipole matrix elements in this fashion it is only necessary to diagonalise matrices of size $2J+1$. Dipole matrix elements computed in this manner are in the third column of Table IV. The results obtained from the effective

rotational Hamiltonians (third column) and the exact results (fourth column) agree very well. As it is difficult to determine experimental intensities accurately, the effective Hamiltonian method should certainly be good enough to model experimental results. Note that very poor results would be obtained by neglecting off-diagonal matrix elements in a basis of products of eigenfunctions of $B_i^\dagger B_i$.

IV. CONCLUSION

Effective rotational Hamiltonians are very useful in spectroscopy. They enable spectroscopists to analyze and fit spectra by diagonalizing a matrix of size $2J+1$. The size of the matrix representing the full rovibrational Hamiltonian is $2J+1 \times N_v$, where N_v is the number of vibrational states, which is much larger. Traditional effective Hamiltonians are derived by transforming the original Hamiltonian to remove terms that couple zeroth-order vibrational states. If two such states are nearly degenerate perturbation theory fails and it is not possible to derive effective rotational Hamiltonians.

To compute intensities one must evaluate dipole matrix elements in the basis of the eigenfunctions of the Hamiltonian. If there are no nearly degenerate zeroth-order vibrational states the effective Hamiltonians derived from perturbation theory are sufficient and their eigenfunctions can be used to compute dipole matrix elements and hence intensities. If nearly degenerate zeroth-order vibrational states invalidate the perturbative method for obtaining effective Hamiltonians then, until now, spectroscopists have had two options: (1) ignore the coupling between the effective rotational Hamiltonians and hope that it does not have a big effect on intensities or (2) diagonalise an effective rovibrational Hamiltonian.

In this paper we have shown that it is possible to use decoupled effective rotational Hamiltonians even if zeroth-order vibrational states are nearly degenerate. This is done by introducing new angular momentum dependent normal coordinates. We show that dipole moment matrix elements computed by neglecting coupling between the new effective rotational Hamiltonians are very accurate. This indicates that it should be possible to use these ideas to analyze and under-

stand intensity distributions in molecules with nearly degenerate vibrational levels strongly coupled by Coriolis terms.

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