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Almost-degenerate perturbation theory is used to derive an effective Hamiltonian describing the vibrational states of H_2CO. Eigenvalues have been determined for energies up to 8600 cm^{-1} above the zero-point energy. Both curvilinear and rectilinear representations of the vibrational dynamics are presented and explored. Although differences are observed between the two effective Hamiltonian matrix elements, their eigenvalues generally agree to better than a wave number for the energies studied. Using the Watson Hamiltonian, the mechanism of rotationally induced vibrationally mixing is investigated as a function of K, the projection of the total angular momentum onto the body-fixed a axis. The combination of a-axis Coriolis coupling and Fermi couplings leads to extensive vibrational mixing between the rotational–vibrational states in this energy regime.

I. INTRODUCTION

Several recent experimental and theoretical studies have demonstrated that rotation plays a pronounced role in the intramolecular redistribution of energy,[1-13] rotational lifetimes,[14] and collisional energy transfer.[15] The central outcome of these studies is twofold. First, the idea that rotations and vibrations can be treated as separable problems appears to be an oversimplification that needs more scrutiny. Second, there appears to be ample evidence that rotation can significantly enhance the coupling between the vibrational degrees of freedom. It is therefore of central importance to model realistically highly excited rotational–vibrational states in an effort to understand the mechanism of the rotation–vibration interactions and the consequences of these interactions on molecular dynamics.

We present here a quantum-mechanical study of rotation–vibration coupling in H_2CO. The choice of this particular molecule was motivated by the stimulated emission pumping (SEP) experiment of Dai et al.[1] These workers convincingly argued that rotationally induced vibrational coupling plays a major role in the interpretation of the SEP spectra of the rotational–vibrational states of H_2CO on the ground electronic surface with E_v between 7000–8600 cm^{-1} for even moderate values of the total angular momentum $(J = 16)$.

A first step in understanding rotationally induced vibrational mixing involves solving for the pure vibrational $(J = 0)$ Hamiltonian in the energy regime of the SEP experiments. This is both a challenge and of considerable importance to molecular dynamics and spectroscopy in its own right. This problem is difficult since it includes six coupled anharmonic oscillators. For this reason, a large fraction of this paper is devoted to the numerical solution of this $(J = 0)$ Hamiltonian. There have been several previous quantum-mechanical calculations of the vibrational eigenvalues of H_2CO,[16-18] all of which have employed variational principles. The required large basis sets have limited most of these calculations to lower-energy regimes. Only very recently have variational calculations, using self-consistent-field basis functions, been extended to higher-energy regimes

in order to examine the highly excited vibrational states of interest here.[19]

Our approach to this problem entails using almost-degenerate perturbation theory in order to derive an effective vibrational Hamiltonian, the solution of which allows an easy determination of the eigenvalue spectrum of H_2CO in the energy regime of interest. The perturbative method we use is based on canonical Van Vleck perturbation theory.[20-34] This theory is playing an increasing role in the treatment of electronic degrees of freedom.[23-27] For an excellent discussion see Ref. 24. These ideas have also been applied to the analysis of molecular vibrations.[28-34] The goal of the perturbation theory is to transform canonically the Hamiltonian to a new representation, where the solutions can be obtained using a significantly smaller basis set than is needed to obtain the solutions in the original representation. The information content of the Hamiltonian is the same. This approach allows for great flexibility in choosing the form of the transformed Hamiltonian to suit best the particular characteristics of the system being studied. We note that this approach is not amenable to solving the dynamics of floppy molecules; other methods are recommended here.

The pure vibrational problem is treated perturbatively in both a curvilinear and rectilinear representation. In the former, the normal coordinates are linearly related to the bond stretching and bending coordinates; in the latter, the normal coordinates are linearly related to the Cartesian coordinates. Although the eigenvalues of the effective Hamiltonians for the two representations are in excellent agreement in the energy regime of the SEP experiments, some noticeable differences are found between the matrix elements of the two representations. In particular, we find that the curvilinear representation is providing a better zero-order representation for the out-of-plane bending degree of freedom.

The problem of rotation–vibration interactions in H_2CO is also approached using almost-degenerate perturbation theory. Here we make the approximation that K, the total angular momentum projected onto the body fixed a axis, is a good quantum number. This approximation is a

good one since the interactions between states with different K values have been shown to be small.[1] Nonetheless there are still notable rotational effects. These effects are due to the a-axis Coriolis coupling terms which significantly couple vibrational states, and yet do not couple states with different K quantum numbers. This type of coupling is referred to as rotationally induced vibrational mixing.

An exception to the above statement that a-axis Coriolis coupling does not couple states with different K quantum numbers has recently been shown to arise as a result of the a-axis Coriolis forces modifying the molecular rotational frequencies about the CO axis so that these frequencies are significantly different than that which is expected in the rigid rotor limit for a given value of K.[6] This effect can enhance the coupling of K states due to the molecular asymmetry of the molecule. This mechanism is not considered here.

We find that the a-axis coupling leads to pronounced mixing of the in-plane wag and out-of-plane bend. This rotationally induced vibrational mixing was expected on the basis of extensive spectroscopic research carried out at much lower energies.[35] At the higher energies of interest to this study there are also strong anharmonic couplings between the molecular vibrations. We find that the combination of rotationally induced vibrational mixing and vibrational anharmonic interactions leads to significant mixing between the rotational–vibrational states.

The outline of this paper is as follows. In Sec. II the basic ideas behind the perturbative approach are reviewed. These ideas are then applied to the derivation of a $J = 0$ effective vibrational Hamiltonian in Sec. III. Curvilinear and rectilinear approaches are both investigated. Having solved for the vibrational Hamiltonian we extend the perturbative treatment to include rotation in Sec. IV. The results are summarized in Sec. V.

II. DERIVATION OF THE EFFECTIVE VIBRATIONAL HAMILTONIAN

The perturbative treatment of molecular vibrations has been extensively studied and utilized since the conception of quantum mechanics. The approach used here is similar to that used by Nielsen,[28] although our goals are more modest. Our objective is to transform the Hamiltonian to a representation where the solutions can be obtained using a significantly smaller basis set than is needed to obtain the solutions in the original representation. This modest goal allows for a flexible form of the effective Hamiltonian, which is constructed using one's insight into the possible resonance interactions found in the system. If this is done correctly, one can carry out the perturbative expansions to high order while avoiding the small energy denominators that one associates with the divergence in the perturbative expansion.

The transformation to the effective Hamiltonian is carried out in a superoperator framework.[24,25] Although the algebraic manipulations are very cumbersome, the algebra is carried out very efficiently using FORTRAN codes. The algebraic manipulations are very similar to previous classical and semiclassical perturbative treatments which have applied perturbation theory to very high order using FORTRAN,[36,37] C,[38] and MACSYMA.[39] The canonical Van Vleck

perturbation theory is ideally suited for computational manipulation even though it leads to more cumbersome expressions than other perturbative approaches.[24,26,27] This operator approach has the significant advantage of avoiding storage problems associated with matrix based techniques.

In this paper we will present the basic ideas, as we have applied them specifically to our study of H_2CO. For a more general account of these methods and their application to some model problems, the reader is referred to the work of Sibert.[34,40]

Following Nielson,[28] the Hamiltonian is expanded in the normal coordinates and written as

$$H = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \cdots . \tag{1}$$

Here λ is the perturbation parameter. The zero-order part of the Hamiltonian describes the six harmonic oscillators

$$H^{(0)} = \frac{1}{2} \sum_{j=1}^{6} (p_j^2 + \omega_j^2 q_j^2), \tag{2}$$

$H^{(1)}$ is chosen to contain cubic terms, $H^{(2)}$ contains quartic terms, and so forth. In the next section we will discuss the exact form of the vibrational Hamiltonian for H_2CO.

Our goal is to transform H to a new representation K where the solutions can be obtained using a significantly smaller basis set than is needed to obtain the solutions in the original representation. This is readily accomplished via a succession of canonical transformations. A crucial feature of the present work is that in order to avoid the storage of large matrices we implement the canonical Van Vleck transformations in an operator framework. Primas[25] has developed a canonical form of Van Vleck perturbation theory in a operator framework which takes advantage that such a theory can be completely formulated in the domain of a Lie algebra. Before applying this theory to the study of the vibrations of H_2CO, it is necessary to reexpress the Hamiltonian in terms of the harmonic oscillator raising and lowering operators to give

$$H(\mathbf{a}^\dagger, \mathbf{a}) = \sum_{j=1}^{6} \hbar\omega_j \left(a_j^\dagger a_j + \frac{1}{2} \right) + V_c(\mathbf{a}^\dagger, \mathbf{a}) . \tag{3}$$

Here $V_c(\mathbf{a}^\dagger, \mathbf{a})$ includes all the contributions to H excluding $H^{(0)}$. Although the implementation of this step is quite tedious, it is straightforward and can be readily carried out with the aid of computers.

A. General theory

The transformations to the effective Hamiltonian K (not to be confused with the projection of the angular momentum onto the a axis) are implemented via a series of unitary transformations

$$\exp\{i\lambda^n[S^{(n)},]\} \times \cdots \times \exp\{i\lambda^2[S^{(2)},]\}$$
$$\exp\{i\lambda[S^{(1)},]\}H = K, \tag{4}$$

where $S^{(i)}$ is Hermitian. Rather than calculate the transformed Hamiltonian K order by order using the expressions derived by Shavitt and Redmon,[24] it is computationally easier to implement the transformations

$$\exp\{i\lambda[S^{(1)},]\}H = K_1, \tag{5a}$$
$$\exp\{i\lambda^2[S^{(2)},]\}K_1 = K_2, \tag{5b}$$

$$\exp\{i\lambda^{(n)}[S^{(n)},]\}K_{n-1} = K. \tag{5c}$$

One first calculates K_1, then K_2, and so forth. K_1 is determined by expanding the exponential in Eq. (5a) using the well-known Campbell–Hausdorff formula

$$\exp\{i\lambda [S^{(1)},]\}H = H + i\lambda [S^{(1)},H]$$

$$- \frac{\lambda^2}{2!}[S^{(1)},[S^{(1)},H]] + \cdots , \tag{6}$$

then expanding H and K_1 in powers of λ and equating powers of λ to obtain the standard expressions

$$K_1^{(0)} = H^{(0)}, \tag{7a}$$

$$K_1^{(1)} = H^{(1)} + i[S^{(1)},H^{(0)}], \tag{7b}$$

$$K_1^{(2)} = H^{(2)} + i[S^{(1)},H^{(1)}] - \frac{1}{2!}[S^{(1)},[S^{(1)},H^{(0)}]], \tag{7c}$$

and so forth. For the general case of $H^{(1)}$ expressed in normal form

$$H^{(1)} = \sum_m \sum_n C_{m,n} \prod_{j=1}^6 (a_j^\dagger)^{m_j}(a_j)^{n_j}, \tag{8}$$

a choice of

$$S^{(1)} = \sum_m{}' \sum_n{}' C_{m,n} \frac{\prod_{j=1}^6 (a_j^\dagger)^{m_j}(a_j)^{n_j}}{\sum_{j=1}^6 (m_j - n_j)\hbar\omega_j} \tag{9}$$

leads to

$$K_1^{(1)} = \sum_m{}'' \sum_n{}'' C_{m,n} \prod_{j=1}^6 (a_j^\dagger)^{m_j}(a_j)^{n_j}. \tag{10}$$

The primes and double primes refer to restricted summations, where $\Sigma_m = \Sigma_m'' + \Sigma_m''$. Equivalently, the terms $K_1^{(1)}$ include a subset of the terms in $H^{(1)}$.

Of key importance is the choice of terms to include in $S^{(1)}$. This choice is very flexible; however, a usual choice is that if there are no degeneracies in $H^{(0)}$, then $S^{(1)}$ includes all the terms in $H^{(1)}$, and $K_1^{(1)}$ is zero. If there are degenerate or nearly degenerate states, $K_1^{(1)}$ will include the couplings between these states. We return to the choice of terms to include in $S^{(1)}$ after completing the discussion of the higher-order transformations.

Given a choice for $S^{(1)}$, $K_1^{(i)}$ $(i = 1$ to $n)$ is directly determined from Eq. (7) to the desired order in perturbation. The Hamiltonian K_1, however, only has the desired form through $K_1^{(1)}$. The transformation process is continued by solving for K_2 using Eq. (5b). As before, this is accomplished by expanding K_1 and K_2 in powers of λ to obtain

$$K_2^{(0)} = K_1^{(0)},$$

$$K_2^{(1)} = K_1^{(1)},$$

$$K_2^{(2)} = K_1^{(2)} + i[S^{(2)},K_1^{(0)}], \tag{11}$$

$$K_2^{(3)} = K_1^{(3)} + i[S^{(2)},K_1^{(1)}],$$

.

and so forth. The choice of terms to include in $S^{(2)}$ follows the same considerations as those for $S^{(1)}$, with the key exception that $K_1^{(2)}$ contains diagonal terms, i.e., terms of the form

$$C_{m,m} \prod_{j=1}^6 (a_j^\dagger)^{m_j}(a_j)^{m_j},$$

as well as terms that couple degenerate states. The corresponding terms cannot be included in $S^{(2)}$ and must be included in $K_2^{(2)}$. If the oscillators of Eq. (2) correspond to the normal modes and there are no degeneracies or near degeneracies, then $K_1^{(1)}$ is zero and $K_2^{(2)}$ takes the standard form[28]

$$K_2^{(2)} = \sum_{i=1}^6 \sum_{j=1}^6 \chi_{i,j} (\hat{N}_i + \tfrac{1}{2})(\hat{N}_j + \tfrac{1}{2}), \tag{12}$$

where $\hat{N}_j = a_j^\dagger a_j$ is the number operator, and $\hat{N}_j|n\rangle = N_j|n\rangle$.

The higher-order transformations are carried out in the same manner as the above transformations. At each stage of the transformation the Hamiltonian K_i has the desired form through $K_i^{(i)}$.

B. Form of the effective Hamiltonian

A central feature of the canonical Van Vleck perturbation theory is the flexibility one has in choosing $S^{(i)}$, or equivalently the choice one has in the form of the effective Hamiltonian. Various choices have been discussed previously. There is usually a tradeoff between the ease of solution of the effective Hamiltonian vs the quality of the perturbation expansion. If the desired form of the effective Hamiltonian is such that it only depends on the quantum numbers N_i, the effective Hamiltonian is diagonal, but the perturbation expansion diverges quickly. By choosing a less restricted form for the effective Hamiltonian, one is able to carry out the perturbation expansions to high order before encountering divergences while still finding a new representation in which the solutions are significantly easier to obtain than in the original representation.

In the present work, using our knowledge of the system, we were able to use almost-degenerate perturbation theory, so that the final Hamiltonian matrix is block diagonal within a given symmetry block. This implies that there is an additional approximate constant of motion other than energy. It is

$$N_t = 2(N_1 + N_5) + N_2 + N_3 + N_4 + N_6. \tag{13}$$

This additional constant is a result of the fact that high-frequency CH modes, ω_1 and ω_5, are about 2 times the frequency of the remaining degrees of freedom (cf. Table I). Consequently, one expects a great deal of mixing between states with the same value of N_t, as they may be nearly degenerate and coupled with cubic terms of $H^{(1)}$. Although

TABLE I. Harmonic frequencies ω_i of H_2CO.[a]

Mode	Symmetry	ω_i cm^{-1}	Motion
1	A_1	2937.4	CH symmetric stretch
2	A_1	1777.8	CO stretch
3	A_1	1544.0	HCH bend
4	B_1	1188.3	out-of-plane bend
5	B_2	3012.0	CH asymmetric stretch
6	B_2	1269.4	in-plane wag

[a] Results from Romanowski, Bowman, and Harding (Ref. 18).

states with different values of N_t certainly couple, they mix less strongly due to the energy mismatch between them. We will return to this point below, when specific results are presented. It should be noted that if we had encountered divergences in the perturbative expansions at low order, then we would have had to reconsider our above choice for the form of the effective Hamiltonian, choosing a less restrictive form.

The transformations to an effective Hamiltonian with the constant of motion N_t, is accomplished by constructing $S^{(i)}$ in Eq. (9) so that it includes all the terms of $H^{(i)}$ that couple states with different values of N_t. The remaining terms of $H^{(i)}$, which couple states within the same N_t manifold are included in the effective Hamiltonian of Eq. (10). These terms satisfy

$$\sum_{i=1}^{6} c_i (m_i - n_i) = 0, \tag{14}$$

where $c_i = 2$ for the CH stretching modes ($i = 1$ and 5) and $c_i = 1$ for the remaining lower frequency modes. As an example, in the earlier work of Romanowski et al.[18] it was found that there was a significant resonance interaction between the ν_5 fundamental and the combination state with one quantum in both the ν_3 and ν_6 modes. These states both have $N_t = 2$. One of the terms responsible for the coupling between these states is the term $a_5^\dagger a_3 a_6$. This term satisfies Eq. (14) and is therefore included in the effective Hamiltonian.

To summarize, the transformations yield an effective Hamiltonian which is block diagonal through the desired order of the perturbation parameter. If we neglect the higher-order terms, then the Hamiltonian can be expressed in the form

$$K = K^0 + V, \tag{15}$$

where

$$K^0 = \sum_m C_{m,m} \prod_{j=1}^{6} (a_j^\dagger)^{m_j} (a_j)^{m_j} \tag{16}$$

and

$$V = \sum_m \sum_n C_{m,n} \prod_{j=1}^{6} (a_j^\dagger)^{n_j} (a_j)^{m_j}. \tag{17}$$

The summation in Eq. (17) is subject to the constraint given by Eq. (14), or equivalently one may say that the commutator $[K, \hat{N}_t] = 0$.

Throughout the remainder of this paper we consider the solutions to Hamiltonians with the form of Eq. (15). For H_2CO, we find that this form leads to both of the desired goals: excellent convergence in the perturbative expansions and an effective Hamiltonian whose solution can be found with greatly reduced basis sets. This allows us to investigate energy regimes that the standard variational methods have so far been unable to access.

III. SOLUTIONS TO THE EFFECTIVE VIBRATIONAL HAMILTONIAN

To begin implementing these ideas we must return to our starting point [Eq. (1)] and consider the ($J = 0$) vibrational Hamiltonian. In this paper, two different normal mode representations are contrasted and compared, these

being the rectilinear and curvilinear representations. In the former, the normal coordinates are linear combinations of the Cartesian coordinates, while in the latter, the normal coordinates are linear combinations of the bond stretching and bending extension coordinates. In the limit of small oscillations the two coordinate systems are identical. Sibert et al.[41] have compared and contrasted these two perspectives in their analysis of the 2:1 Fermi resonance in CO_2 between the symmetric stretch and degenerate bend.

We discuss and present results first for the rectilinear representation. An important consideration here will be the form of the potential energy. Results are presented for the eigenvalues of the second-, fourth-, and sixth-order transformed Hamiltonian. These results are also compared to the self-consistent-field (SCF) calculation of Romanowski, Harding, and Bowman (hereafter referred to as RHB).[18] We then present and compare the results of the rectilinear and curvilinear calculations.

A. The rectilinear representation

The Watson Hamiltonian, written in terms of the mass-weighted normal mode extension coordinates q_i, and their conjugate momenta p_i, is

$$H = \frac{1}{2} \sum_{i=1}^{6} (p_i^2 + \omega_i^2 q_i^2) + V(\mathbf{q}) + \frac{1}{2} \sum_{\alpha,\beta} \mu(\mathbf{q})_{\alpha\beta} \pi_\alpha \pi_\beta$$
$$- \frac{\hbar^2}{8} \sum_\alpha \mu(\mathbf{q})_{\alpha\alpha}. \tag{18}$$

For a more complete description of this Hamiltonian the reader is referred to the work of Watson.[42] For the present purposes we briefly describe the key components of Eq. (18). They are the frequency of the ith normal mode ω_i; the components of instantaneous effective inverse moment of inertia tensor, $\mu(\mathbf{q})_{\alpha\beta}$; the "vibrational angular momentum" about the axis α, $\pi_\alpha = \Sigma \zeta_{ij}^{(\alpha)} q_i p_j$; and the anharmonic contribution to the potential energy $V(\mathbf{q})$. The subscripts α and β refer to the x, y, and z components of the Cartesian coordinates. The vibrational angular momentum is a bilinear function of the normal coordinates and momenta. The relevant coefficients $\zeta_{ij}^{(\alpha)}$ depend on the masses and the harmonic force constants.

In the rectilinear representation, the kinetic energy coupling between the normal modes is small in comparison to the potential coupling. A crucial aspect therefore is the representation of the potential and some comments about the representation of the force field are in order. We have used the ab initio, internal coordinate, quartic force of Harding and Ermler[43] as modified by RBH. This force field is expressed in a Simons–Parr–Finlan (SPF) form,[44] which is equivalent to replacing the bond length coordinates R_i by the corresponding SPF coordinate ρ_i, where

$$\rho_i = (R_i - R_{e,i})/R_i = \Delta_i / R_i.$$

This fourth-order expansion is appreciably more accurate than the standard Taylor-series expansion. This is evident in Fig. 1, where we compare the SPF quartic representation of the one-dimension CH stretch potential, with the quartic and sixth-order Taylor-series expansion. This is relevant to the present work, since the operator approach requires that
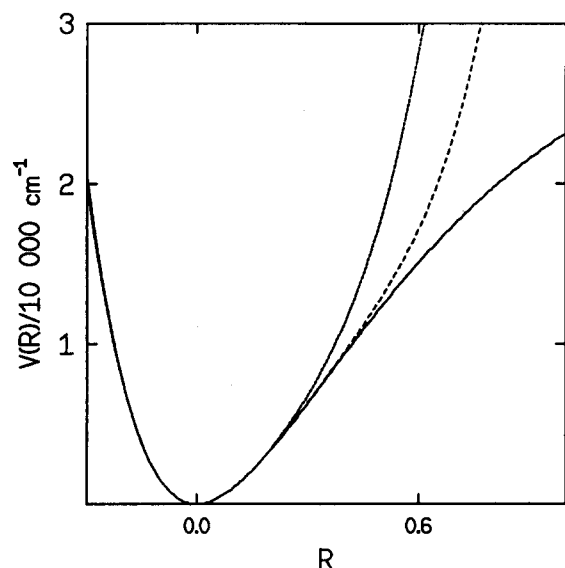
FIG. 1. A comparison of the CH stretch potential of RBH. The solid line is the fourth-order Simons–Parr–Finlan expansion. The (– – –) and (- - -) lines are the fourth- and sixth-order Taylor-series expansions, respectively.

the Hamiltonian be expressed in the normal form of Eqs. (8)–(10), which in turn requires a Taylor-series expansion of the potential. Specifically, the potential must be expanded through order $n + 2$, if the perturbative transformations are carried out through order n.

The Watson Hamiltonian[42] is written in terms of the rectilinear normal coordinates, which are *not* linearly related to the above internal coordinates. For a discussion of this transformation the reader is referred to the work of Hoy, Mills, and Strey.[45] As with the SPF expansion, it is often necessary to transform the normal coordinates to higher order than the initial internal coordinate expansion. This is pertinent here as is evident in Fig. 2. There we display the equipotential contours for the symmetric CH stretch and the out-of-plane bend normal coordinates. Plotted in Fig. 2(a) is the exact normal mode expansion of the SPF quartic force field. Plotted in Figs. 2(b)–2(d) are the equipotential contours for the normal mode force field expanded through fourth, sixth, and eighth order. Due to the "stiffness" of the CH bond relative to that of the out-of-plane bend, the contours are noticeably curved in the normal coordinate repre-
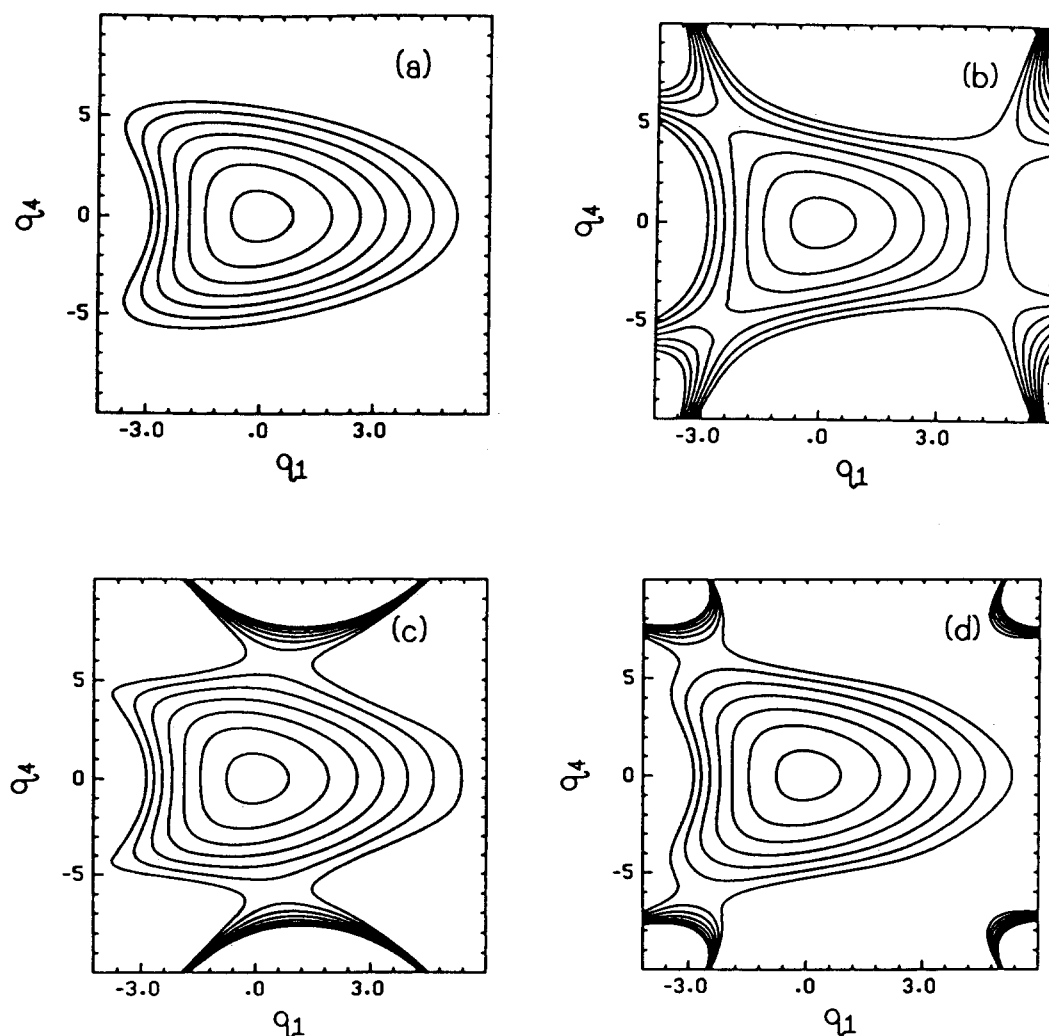

FIG. 2. Equipotential contours for the CH symmetric stretch, q_1, and the out-of-plane bend, q_4, normal coordinates. (a) is the exact result for the fourth-order Simons–Parr–Finlan expansion of RBH, (b)–(d) are the results of truncating the normal mode expansion at fourth, sixth, and eighth order. The equipotential curves are spaced 3000 cm^{-1} apart.

TABLE II. Comparison SCF and perturbative treatments of low-lying vibrational energies (cm^{-1}) for H_2CO.

State	N_t	Sym	$E(SCF)$[a]	$E(2)$[b]	$E(4)$[c]	$E(6)$[d]
4_1	1	B_1	1160.4	1166.4	1166.1	1166.1
6_1	1	B_2	1245.4	1250.2	1250.5	1250.5
3_1	1	A_1	1500.1	1505.2	1505.7	1505.7
2_1	1	A_1	1747.1	1747.4	1747.4	1747.4
4_2	2	A_1	2314.9	2321.9	2323.4	2323.2
$4_1 6_1$	2	A_2	2415.3	2426.2	2426.2	2426.2
6_2	2	A_1	2488.8	2494.6	2497.6	2497.8
$3_1 4_1$	2	B_1	2654.8	2667.4	2667.8	2667.7
$3_1 6_1 + 5_1$	2	B_2	2700.1	2714.5	2727.1	2726.6
1_1	2	A_1	2781.3	2782.5	2780.4	2780.6
$5_1 - 3_1 6_1$	2	B_2	2856.9	2849.5	2845.1	2845.4
$2_1 4_1$	2	B_1	2898.9	2906.3	2905.9	2905.8
3_2	2	A_1	2997.2	3011.0	3009.8	3009.8
$2_1 6_1$	2	B_2	3002.5	3005.4	3001.7	3001.9
$2_1 3_1$	2	A_1	3239.6	3246.1	3245.8	3245.8
4_3	3	B_1	3456.3	3465.6	3471.7	3469.6
2_2	2	A_1	3478.6	3476.1	3476.0	3475.9
$4_2 6_1$	3	B_2	3575.1	3586.8	3590.7	3590.1
$4_1 6_2$	3	B_1	3667.5	3681.6	3684.6	3684.4
6_3	3	B_2	3726.5	3733.0	3742.2	3741.9
$3_1 4_2$	3	A_1	3801.5	3816.9	3821.2	3820.5
$3_1 4_1 6_1 + 4_1 5_1$	3	A_2	3847.8	3877.9	3895.2	3894.5
$3_1 6_2 - 5_1 6_1$	3	A_1	3898.0	3920.4	3947.2	3945.8
$1_1 4_1$	3	B_1	3913.7	3948.1	3937.0	3938.1
$4_1 5_1 - 3_1 4_1 6_1$	3	A_2	3995.2	4006.3	3999.1	3999.4
$1_1 6_1$	3	B_2	4004.4	4031.4	4024.3	4024.7
$2_1 4_2$	3	A_1	4043.4	4054.6	4055.2	4054.8
$3_1 6_2 + 5_1 6_1 + 2_1 6_2$	3	A_1	4083.4	4096.0	4087.6	4088.3
$3_2 6_1 + 3_1 5_1$	3	B_2	4145.8	4185.9	4207.1	4206.0
$3_2 4_1$	3	B_1	4146.1	4168.4	4167.8	4167.5
$2_1 4_1 6_1$	3	A_2	4160.0	4172.5	4167.8	4168.1
$2_1 6_2 - 1_1 3_1$	3	A_1	4229.6	4253.6	4250.4	4250.9
$1_1 3_1 + 2_1 6_2 - 5_1 6_1$	3	A_1	4268.3	4261.5	4258.6	4258.5
$3_2 6_1 - 3_1 5_1 + 2_1 3_1 6_1$	3	B_2	4346.8	4353.0	4341.9	4342.7
$2_1 3_1 4_1$	3	B_1	4385.2	4400.6	4400.1	4400.0
$2_1 3_1 6_1 + 2_1 5_1 + 3_1 5_1$	3	B_2	4459.3	4471.8	4475.2	4475.1
3_3	3	A_1	4499.2	4515.6	4511.1	4511.3
$1_1 2_1$	3	A_1	4528.9	4529.0	4528.7	4528.7
$2_1 5_1 - 2_1 3_1 6_1 - 2_2 6_1$	3	B_2	4581.0	4574.7	4575.3	4575.4
$2_2 4_1$	3	B_1	4621.4	4627.7	4626.7	4626.5
$4_4 - 1_1 4_2$	4	A_1	4623.5	4596.5	4609.7	4609.0
$4_3 6_1$	4	A_2	4718.6	4733.7	4745.2	4743.4
$2_1 3_2$	3	A_1	4729.5	4744.5	4745.2	4742.3
$2_2 6_1 + 2_1 5_1$	3	B_2	4746.0	4.745.0	4737.3	4737.5
$4_2 6_2$	4	A_1	4833.2	4844.3	4855.8	4854.6
$4_1 6_3$	4	A_2	4915.0	4933.6	4941.8	4941.4
$3_1 4_3$	4	B_1	4934.0	4953.7	4965.7	4963.8
$2_2 3_1$	3	A_1	4964.4	4967.8	4966.6	4966.7
$6_4 + 1_1 6_2$	4	A_1	4983.8	4966.9	4984.4	4983.6
$4_2 5_1 + 3_1 4_2 6_1$	4	B_2	4984.2	5019.5	5050.2	5048.5
$4_1 5_1 6_1 - 3_1 4_1 6_2$	4	B_1	5050.6	5092.3	5124.6	5123.2
$1_1 4_2 + 4_4$	4	A_1	5062.5	5101.3	5084.0	5086.1
$5_1 6_2 - 3_1 6_3$	4	B_2	5094.4	5120.3	5166.1	5163.5
$3_1 4_2 6_1 - 4_2 5_1$	4	B_2	5133.8	5151.0	5144.8	5144.4
$1_1 4_1 6_1 + 4_1 6_3$	4	A_2	5153.5	5208.4	5189.9	5191.4
$2_1 4_3$	4	B_1	5175.1	5192.0	5195.9	5194.8
2_3	3	A_1	5200.4	5187.1	5186.4	5186.3
$3_1 5_1 6_1 - 3_2 6_2 + 1_1 6_2 + 5_2 - 6_4$	4	A_1	5312.4	5365.5	5402.5	5399.8
$1_1 3_1 6_1 + 1_1 5_1 + 2_1 6_3 + 3_1 6_3 - 1_1 2_1 6_1$	4	B_2	5411.5	5419.8	5439.3	5438.0
$1_2 - 3_2 6_2 - 5_2$	4	A_1	5492.8	5463.8	5463.0	5462.8
$2_1 3_1 4_2$	4	A_1	5521.5	5542.2	5544.9	5544.2
$3_2 6_2 + 1_2 + 5_2 - 2_1 5_1 6_1 + 2_1 3_1 6_2 + 1_1 3_2$	4	A_1	5540.7	5553.5	5555.6	5556.2
$1_1 5_1 - 1_1 3_1 6_1 - 3_2 5_1 - 3_3 6_1 - 1_2 5_1$	4	B_2	5577.2	5555.6	5534.5	5536.3
$2_1 3_1 6_2 - 1_1 3_2 - 2_1 5_1 6_1 - 3_1 5_1 6_1$	4	A_1	5651.2	5693.3	5698.3	5697.9
$5_2 - 2_1 3_1 6_2 - 3_1 5_1 6_1 - 1_1 3_2$	4	A_1	5680.4	5661.9	5654.9	5655.8

[a] Results from Romanowski, Bowman, and Harding (Ref. 18).
[b] Second-order perturbative result.
[c] Fourth-order perturbative result.
[d] Sixth-order perturbative result.

sentation. Furthermore, low-order expansions do not do a good job of reproducing this curvature.

The eigenvalues of the effective Hamiltonian are given in Table II. Also shown there are the results of a converged vibrational SCF calculation due to RBH. The assignments are those of RBH and are in very good agreement with our assignments. The two important features of Table II, from a computational perspective, are the excellent agreement between the eigenvalues of our fourth- and sixth-order effective Hamiltonians, the greatest change of any eigenvalue being 2.3 cm^{-1}. These results should be distinguished from those due to RBH as those workers truncated the normal mode potential at fourth order, and hence are starting with a different initial Hamiltonian than we are. Even at these low energies, the effects of using the truncated fourth-order potential are apparent.

The similarity between the sixth- and fourth-order results of Table II is an indication that our choice for N_t as a constant of the motion is a good one. The reason for this is made apparent by labeling each eigenvalue of Table II with a value of N_t. Evidently, states with differing values of N_t and which differ by only a few quantum numbers so that coupling matrix elements might be substantial are not degenerate. The constraint that N_t is a constant of the motion is of course not included in the calculation of RBH, nonetheless the state assignments of RBH, shown in Table II, indicate that whenever there is state mixing, it occurs between states with the same values of N_t as defined by Eq. (13).

Before concluding this section we note a fortuitous feature of the perturbation treatment. At low energies the second-order perturbative results agree more closely with the sixth-order perturbative results than they do with the RBH results. This is surprising since the second-order results only include up to the quartic terms in the potential, the same as RBH. A well-known example of this phenomenon is found in the perturbative treatment of the Morse oscillator. There, the second-order perturbative results have the form of Eq. (12), for a one-dimensional problem. This result is identical to the exact expression for the eigenvalues of a Morse potential:

$$E = \hbar\omega\left(n + \frac{1}{2}\right) - \frac{\hbar^2\omega^2}{4D}\left(n + \frac{1}{2}\right)^2. \tag{19}$$

Here, D is the dissociation of the Morse oscillator. This contrasts to truncating the potential at fourth order and solving the Schrödinger equation exactly. This would lead to appreciable differences from the correct result of Eq. (19). We conclude that the perturbation theory fortuitously gives the exact energy levels at second order and this makes it look better than the exact solution of a truncated potential expansion.

B. The curvilinear representation

An alternative approach to solving the vibrational dynamics of H_2CO is to use a Hamiltonian expressed in terms of the bond lengths and angles, rather than their projection onto the equilibrium geometry. In the latter case, which was discussed above, the normal coordinates are linearly related to the Cartesian coordinates, and this greatly facilitates the

embedding of a body-fixed reference frame with the Eckart condition.[46] When we include rotational effects below, we will return to the Watson Hamiltonian. For the $J = 0$ Hamiltonian this is not an issue, and we now describe a general curvilinear coordinate Hamiltonian. The normal coordinates, Q and momenta P are linear functions of the internal coordinates R and their conjugate momenta P_R,

$$R = L Q, \quad P_R = (L^{-1})^\dagger P. \tag{20}$$

The elements of the transformation matrix are constants, and the Hamiltonian,[47] written as a function of the Q's and P's, is

$$H = \sum_{i=1}^{6} \sum_{j=1}^{6} \mathscr{P}_i \mathscr{G}_{ij}(Q) \mathscr{P}_j + V(Q) + V'(Q). \tag{21}$$

Here the $\mathscr{G}_{ij}(Q)$ are linear combinations of the instantaneous Wilson G-matrix elements G_{ij}. Explicitly,

$$\mathscr{G} = L^{-1}G(L^{-1})^\dagger. \tag{22}$$

The G-matrix elements are, in turn, functions of the internal coordinates.[48] The constant contribution to Eq. (22), i.e., $\mathscr{G}$ evaluated at the equilibrium position, is just the unit matrix, in mass weighted coordinates. The potential coupling term $V(Q)$ includes both the harmonic and the anharmonic contributions to the potential coupling. The third term, which is solely a function of the coordinates is

$$V' = \frac{\hbar^2}{8} \sum_{i=1}^{6} \sum_{j=1}^{6} \left[\frac{\partial \mathscr{G}_{ij}}{\partial Q_i} \frac{\partial \ln g}{\partial Q_i} + \mathscr{G}_{ij}\left(\frac{\partial^2 \ln g}{\partial Q_i \partial Q_j} + \frac{1}{4} \frac{\partial \ln g}{\partial Q_i}\frac{\partial \ln g}{\partial Q_j}\right) \right], \tag{23}$$

where g is given by the ratio of the determinants of the moment of intertia tensor, I and $\mathscr{G}$,

$$g = \frac{|I|}{|\mathscr{G}|}.$$

The Hamiltonian is quite complicated when written out in its explicit form. Fortunately, the most complicated part of the kinetic energy V' is usually quite small—its biggest contribution to the energy of H_2CO is an overall shift of approximately 16 cm^{-1} to all the levels.

Computationally, this Hamiltonian is more tractable than if first appears. In order to express Eq. (21) in the form of Eq. (3), one must expand the $\mathscr{G}_{ij}$ elements V and V' in a Taylor series in the normal coordinates. Expanding the potential of RBH is straightforward; this entails expanding the SPF coordinates about the equilibrium position. It is more difficult to expand the remaining terms. The key to doing so is to utilize the relationship between the internal coordinates and the Cartesian coordinates x. This allows one to calculate the G-matrix elements at any given value of the normal coordinates. If we can do this, then finite difference methods can be used to construct the Taylor-series expansion in terms of the normal coordinates.

The first step in the above procedure is to express the internal coordinates explicitly as functions of the Cartesian coordinates. This is essentially just a geometrical problem. For a given structure of the molecule, we take finite differences in the Cartesian coordinates to calculate $\partial R_i / \partial x_j = B_{ij}$, and hence

$$\mathbf{R} = \mathbf{Bx}, \tag{24}$$

for any value of the internal coordinate. Once $\mathbf{B}$ is determined, the G-matrix elements are obtained from

$$G_{ij} = \sum_{k=1}^{12} m_k^{-1} B_{ik} B_{jk}. \tag{25}$$

Here the summation is over the x, y, and z coordinates of the four atoms with masses m_k.

Any arbitrary displacement of the $\mathbf{Q}_i$, can be written as a displacement of the R_i using Eq. (20). Using Eqs. (24) and (25), the G-matrix elements can be constructed at these positions. Again using finite difference methods, the G-matrix elements can be expanded in a Taylor series in the $\mathbf{Q}_i$. As the $\mathbf{L}$ matrix elements only depend on the equilibrium position, it is then an easy step to obtain the $\mathscr{G}_{ij}$-matrix element Taylor-series expansion coefficients. This technique obviates the need to use the analytical expressions derived by Wilson et al.[48] and yet is numerically very accurate. We have found that this approach is very general and that its implementation was substantially easier than including the analytical functional form of the G-matrix elements. Finally, the Taylor-series expansion of g is obtained using the same finite difference technique.

Using these ideas, the Hamiltonian of Eq. (21) was reexpressed in the form of Eq. (3) and subsequently transformed to an effective Hamiltonian K with the same block form as was obtained with the Watson Hamiltonian. Selected eigenvalues are compared to those obtained by the Watson Hamiltonian in Table III. We have not as yet calculated

the sixth-order results in the curvilinear representation, as this requires finding the sixth derivative of all the G-matrix elements; the present results already were in excellent agreement with the rectilinear results.

For the energy regime studied, the eigenvalues have converged quite well by fourth order in both representations. There are, however, some differences. Some insight into these differences can be gleaned by comparing the effective Hamiltonian matrices. Looking at the coupling between the modes 1 and 4, the surface of which is shown in Fig. 2, we see that the matrices in the two representations are substantially different. The fourth-order curvilinear matrix describing the coupling between the states $|n_1, n_4\rangle$ is as follows:

	$|0,6\rangle$	$|1,4\rangle$	$|2,2\rangle$	$|3,0\rangle$
$|0,6\rangle$	6 897.10			
$|1,4\rangle$	144.64	7 349.18		
$|2,2\rangle$	-0.08	124.58	7 759.16	
$|3,0\rangle$	0.00	-0.04	59.90	8 142.40

This is in contrast to the sixth-order rectilinear matrix results

	$|0,6\rangle$	$|1,4\rangle$	$|2,2\rangle$	$|3,0\rangle$
$|0,6\rangle$	7 029.37			
$|1,4\rangle$	-258.22	7 313.96		
$|2,2\rangle$	-0.09	-229.31	7 671.05	
$|3,0\rangle$	0.00	-0.05	-113.58	8 094.35

TABLE III. Comparison of selected rectilinear E_r and curvilinear E_c eigenvalues (cm^{-1}) obtained using almost-degenerate perturbative theory for H_2CO.

State	N_t	Sym	$E_r(4)^a$	$E_r(6)$	$E_c(2)$	$E_c(4)$
4_1	1	B_1	1166.1	1166.1	1166.4	1166.1
6_1	1	B_2	1250.5	1250.5	1250.2	1250.5
3_1	1	A_1	1505.7	1505.7	1505.5	1505.7
2_1	1	A_1	1747.4	1747.4	1747.4	1747.4
4_2	2	A_1	2323.4	2323.2	2325.0	2323.3
$4_1 6_1$	2	A_2	2426.2	2426.2	2426.2	2.426.2
6_2	2	A_1	2497.8	2497.7	2496.3	2497.7
$3_1 4_1$	2	B_1	2667.8	2667.7	2667.4	2667.9
$3_1 6_1 + 5_1$	2	B_2	2727.1	2726.6	2723.6	2726.9
1_1	2	A_1	2780.4	2780.6	2778.8	2780.6
$5_1 - 3_1 6_1$	2	B_2	2845.1	2845.3	2843.1	2845.3
$2_1 4_1$	2	B_1	2905.9	2905.8	2906.3	2905.9
$2_1 6_1$	2	B_2	3001.7	3001.9	3002.8	3001.8
3_2	2	A_1	3009.8	3009.8	3010.2	3009.9
$2_1 3_1$	2	A_1	3245.8	3245.8	3245.9	3245.9
2_2	2	A_1	3475.9	3476.0	3476.1	3476.1
b	6	A_1	8011.3	8008.9	8003.6	8010.3
b	6	A_1	8019.2	8021.5	8012.2	8021.5
b	6	A_1	8029.1	8026.3	8026.0	8028.0
b	6	A_1	8027.5	8027.4	8037.7	8029.1
b	6	A_1	8078.9	8077.2	8063.2	8078.3
b	6	A_1	8115.4	8114.8	8109.2	8114.9
b	6	A_1	8130.7	8128.9	8123.6	8129.3
b	6	A_1	8139.8	8141.6	8132.3	8140.9
b	6	A_1	8220.1	8220.7	8211.4	8220.9
b	6	A_1	8277.3	8278.1	8272.0	8278.2
b	6	A_1	8280.7	8281.4	8282.3	8281.1

[a] $E(N)$ represents N th-order perturbative result.
[b] States have not been assigned, due to the large degree of mixing.

which, we note, are only slightly different than the fourth-order matrix after the additional canonical transformations have been made. The off-diagonal coupling between these states is distinctly more pronounced in the rectilinear calculations; in this respect, the curvilinear representation of the effective Hamiltonian is providing a better zero-order basis. There are two competing factors at work here. One of them is the potential-energy coupling. This is apparent in Fig. 2 which shows the large curvature in the rectilinear potential. The curvature in the corresponding curvilinear representation of the equipotential curves is much less pronounced. The kinetic coupling should also be considered. Although it is larger in the curvilinear representation, this coupling term is smaller than that of the potential coupling in the rectilinear representation with the consequence that the curvilinear representation is providing the better zero-order basis. The differences are more exaggerated between modes 1 and 4 where the curvature is large, than it is between other degrees of freedom. The above results are in agreement with the earlier work of Green et al.[49] who compared curvilinear and rectilinear coupling in trihalomathanes.

The agreement between the curvilinear and rectilinear calculations and the convergence of the perturbation theory is very encouraging. The almost-degenerate perturbation theory has enabled us to investigate the highly excited vibrational states of interest in the SEP experiments of Dai et al.[1] To do so, the effective Hamiltonians had to be transformed to at least fourth order in perturbation theory. Similar results were found by us in an earlier study where effective Hamiltonians were developed that described the stretch–bend couplings in CHD_3.[34]

IV. ROTATIONALLY INDUCED VIBRATIONAL COUPLING IN H_2CO

Rotation–vibration interactions and their central role in intramolecular dynamics and spectroscopy are well recognized. The goal of this section is twofold. The first goal is to calculate eigenvalues of the full rotation–vibration Hamiltonian making the assumption that K is a good quantum number, i.e., we neglect the coupling between states with different K quantum numbers. We argue below that this is a good approximation. We then look at the rotational–vibrational eigenvalues as a function of the K quantum number, which we treat as a perturbation parameter. This highlights the effects of molecular rotation combined with anharmonic coupling.

A. The rotation–vibration Hamiltonian

In this section we will incorporate the largest rotation–vibration couplings into our perturbative treatment presented in Sec. II. In order to include these couplings we use the full Watson Hamiltonian

$$H = \frac{1}{2} \sum_{i=1}^{6} (p_i^2 + \omega_i^2 q_i^2) + V(\mathbf{q}) + \frac{1}{2} \sum_{\alpha,\beta} \mu(\mathbf{q})_{\alpha\beta}$$

$$\times (\Pi_\alpha - \pi_\alpha)(\Pi_\beta - \pi_\beta) - \frac{\hbar^2}{8} \sum_\alpha \mu(\mathbf{q})_{\alpha\alpha}. \quad (26)$$

Here the $\Pi_\alpha \equiv \hbar J_\alpha$ are the body-fixed angular momenta.

The remaining components of this Hamiltonian are the same as in Eq. (18). Following standard methods, this Hamiltonian is divided into three contributions:

$$H = H_v + H_r + H_{vr}. \quad (27)$$

The first contribution H_v is the ($J = 0$) vibrational Hamiltonian, given in Eq. (18). The second contribution H_r is the rigid prolate asymmetric top Hamiltonian. This Hamiltonian, is expressed as a function of the total angular momentum J its projection onto the body-fixed z-axis J_z and the angular momentum raising and lowering operators

$$J^+ = J_x - iJ_y, \quad J^- = J_x + iJ_y, \quad (28)$$

where the plus and minus are exchanged compared to a space-fixed coordinate system.[50] The rotational Hamiltonian is

$$H_r = \left(\frac{\mu_{xx}^0 + \mu_{yy}^0}{4}\right)\hbar^2 J^2 + \left(\frac{\mu_{zz}^0}{2} - \frac{\mu_{xx}^0 + \mu_{yy}^0}{4}\right)\hbar^2 J_z^2$$

$$+ \left(\frac{\mu_{xx}^0 - \mu_{yy}^0}{4}\right)\frac{\hbar^2}{2}(J^+J^+ + J^-J^-). \quad (29)$$

The effective inverse moment of inertia elements evaluated at the equilibrium position are denoted as $\mu_{\alpha\beta}^0$.

The vibrational and rotational Hamiltonians are coupled via H_{vr} which contains both centrifugal and Coriolis coupling terms. The coupling is

$$H_{vr} = \frac{\hbar^2}{2} \sum_{\alpha\beta} \Delta\mu(\mathbf{q})_{\alpha\beta} J_\alpha J_\beta - \hbar \sum_{\alpha\beta} \mu(\mathbf{q})_{\alpha\beta} \pi_\beta J_\alpha, \quad (30)$$

where

$$\Delta\mu(\mathbf{q})_{\alpha\beta} = \mu(\mathbf{q})_{\alpha\beta} - \mu_{\alpha\beta}^0. \quad (31)$$

As an initial step in modeling rotationally induced vibrational coupling we make the approximation that K is a good quantum number. As noted by Dai et al.[1], the largest contribution to the rotational–vibrational coupling is due to a-axis Coriolis coupling. The a axis, which corresponds to the body-fixed z axis, lies along the CO bond when the molecule is in its equilibrium position. The moment of inertia about the a axis is very small as it includes only contributions from the masses of the two hydrogens to lowest order. Consequently, the a-axis Coriolis coupling, which is inversely proportional to the moment of inertia tensor is significantly larger than the b- and c-axis Coriolis coupling terms. In the present work, we include only these a-axis Coriolis coupling terms. These terms are K conserving, i.e., they do not couple states with different K quantum numbers. There are several other terms in the above Hamiltonian which can lead to the breakdown in the goodness of the K quantum number. First, H_2CO is an asymmetric top; however, its asymmetry parameter is $\kappa = -0.96$, hence, the molecular asymmetry is expected to play only a small role in mixing states with different K values. An exception to this is expected for states characterized as having large vibrational angular momentum.[6] Finally, having calculated the magnitudes of the cross terms $J_\alpha J_\beta$, we find that the magnitudes of these terms are very small and to an excellent approximation can be neglected. With these simplifications the rotational and rotational–vibrational contributions to Eq. (26) can be written as

$$H_r + H_{vr} = \left(\frac{\mu_{xx} + \mu_{yy}}{4} \right) \hbar^2 J^2 + \left(\frac{\mu_{zz}}{2} - \frac{\mu_{xx} + \mu_{yy}}{4} \right)$$

$$\times \hbar^2 J_z^2 - \hbar \sum_\alpha \mu_{\alpha z} J_z \pi_\alpha. \tag{32}$$

Although not explicitly shown, the dependence of the effective inverse moment of inertia on the normal coordinates is included by expanding the moment of inertia tensor through second order in the normal coordinates.

B. Results

The eigenvalues of the Watson Hamiltonian were obtained using almost-degenerate perturbation theory as described in Sec. II. The same procedure was followed here with the exception that Eq. (32) was included in the transformations. The cubic terms were included in $H^{(1)}$, the quartic terms in $H^{(2)}$, and so forth. For example, those terms which are quadratic in J_z and linear in the normal coordinates were included in $H^{(1)}$. Both J^2 and J_z commute with the Hamiltonian, so the inclusion of terms which include these operators is straightforward in the algebraic approach; we simply keep track of the functional dependence of J^2 and J_z in the various terms in Eq. (32).

Selected results of this calculation are shown in Fig. 3(a) for states with $N_t = 6$ and $J = 10$. The eigenvalues are plotted as a function of K from $K = 0$ to 9. Only states with B_1 or B_2 vibrational symmetry are shown. The states with A_i ($i = 1,2$) symmetry are not coupled by any of the terms of Eq. (32) to the states with B_i ($i = 1,2$) symmetry. On the other hand, a-axis Coriolis coupling mixes vibrational states with B_1 and B_2 symmetries. The quantum number K was treated as a parameter in this calculation and was allowed to vary continuously in order to highlight the nature of the rotation–vibration couplings. For $K = 0$, the B_1 and B_2 states are uncoupled, but as K increases, so too does the Coriolis coupling and consequently so do the interactions between these two symmetry blocks. This is evident from the mutual repulsions of the states, i.e., the multiple avoided crossings of the eigenvalues shown in Fig. 3(a).

In order to elucidate the mechanism of these avoided crossings which are due to both Fermi couplings, which mix states of the same vibrational symmetry, and Coriolis couplings, we have set all the off-diagonal matrix elements of the effective Hamiltonian that are functions solely of the vibration raising and lowering operators to zero in the effective Hamiltonian. Now states of a given vibrational symmetry are uncoupled for $K = J = 0$. These results are displayed in Fig. 3(b). From the figure it is evident that the vibrational anharmonicites, which lead to the Fermi resonance interactions in the effective Hamiltonian, play a pronounced role in the overall mixing of the rotational–vibrational states. Qualitatively, the mutual repulsions, i.e., the multiple avoided crossings are more significant in the presence of the Fermi couplings.

The two most strongly coupled degrees of freedom in H_2CO are the nearly degenerate (cf. Table I) in-plane CH wag and the out-of-plane CH bend. In a recent paper, Burleigh et al.[6] have studied a simple model system which includes just these two degrees of freedom. The zero-order
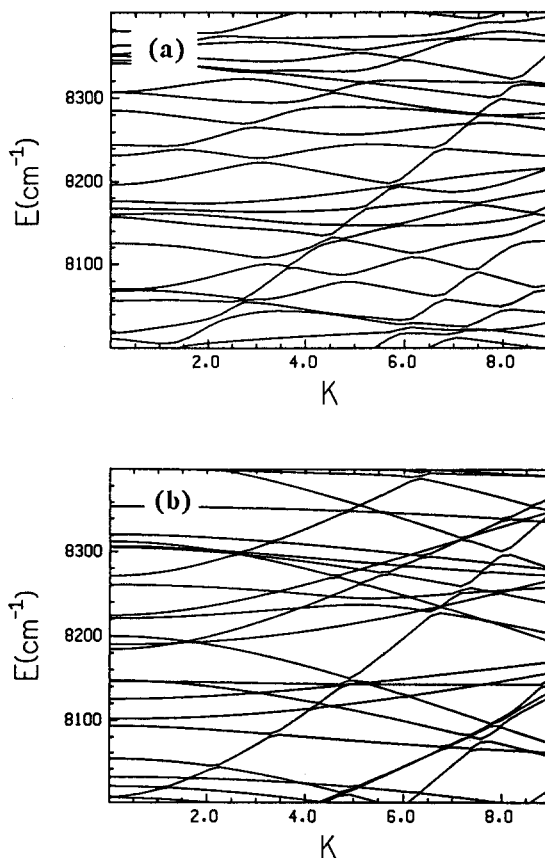

FIG. 3. The vibrational energy levels of B_1 and B_2 symmetry are shown in (a) as a function of K for the full rotational–vibrational Hamiltonian, where only states with the same K quantum number are allowed to couple. In (b) the same set of states are plotted but in the absence of all Fermi resonance interactions in the effective Hamiltonian. Only states with $N_t = 6$ are shown.

Hamiltonian they used to describe this system contains all the terms in the present Hamiltonian, through order $H^{(1)}$, which depend exclusively on these two degrees of freedom. This Hamiltonian written in terms of dimensionless coordinates is

$$H_v^0 = \frac{\omega_4}{2} (p_4^2 + q_4^2) + \frac{\omega_6}{2} (p_6^2 + q_6^2) + cK$$

$$\times \left[\left(\frac{\omega_4}{\omega_6} \right)^{1/2} p_4 q_6 - \left(\frac{\omega_6}{\omega_4} \right)^{1/2} p_6 q_4 \right]. \tag{33}$$

It includes the two harmonic contributions and the first-order a-axis Coriolis coupling term. The Coriolis term is proportional to c ($c = 10.0 \, \text{cm}^{-1}$) which is a function of the masses and the quadratic force field. This Hamiltonian is quadratic in the vibrational coordinates and momenta and hence separable. It can readily be rewritten in terms of its normal modes. To distinquish these normal modes from the standard normal modes we refer to these as the "Coriolis adapted normal modes." Written in these variables the Hamiltonian takes the form

$$H_v^0 = \frac{\lambda_4(K)}{2} (P_4^2 + Q_4^2) + \frac{\lambda_6(K)}{2} (P_6^2 + Q_6^2), \tag{34}$$

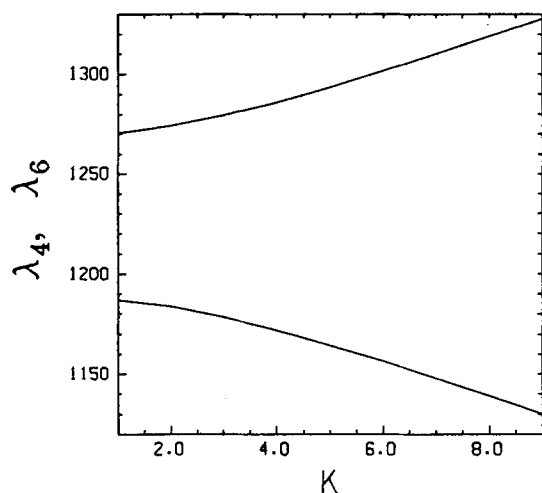where the frequencies λ_i, are functions of K. This functional

FIG. 4. K dependence of normal mode frequencies λ_i (K). The upper curve is for λ_6; the lower curve is for λ_4.

tional dependence is shown in Fig. 4. As K increases, the frequencies become more disparate. For the purpose of the present discussion we note that the eigenvalues of Eq. (33) are given by

$$H_v^0 = \lambda_4(K)(n_4 + \tfrac{1}{2}) + \lambda_6(K)(n_6 + \tfrac{1}{2}). \quad (35)$$

The n_i refer to the quantum numbers of the Coriolis adapted normal modes. Using Eq. (35) and an approximate expression for λ_i (K),[6] it is a straightforward task to compute the slope of the lines in Fig. 3(b). One finds

$$\frac{\partial E}{\partial K} \simeq \frac{c(n_4 - n_6)}{2} \rho(1 + \rho^2)^{-1/2}, \quad (36)$$

where $\rho = 2cK/(\omega_4 - \omega_6)$. The functional K dependence of the curves can be readily understood using Eq. (36): the slopes of the lines in Fig. 3(b) are determined almost entirely by the quantity $(n_4 - n_6)$. The curves with the largest positive slope correspond to states with the most quanta of excitation in the n_6 mode. Some of the curves shown in Fig. 3(b) also appear in Fig. 3(a); whereas, other curves are barely discernible due to the Fermi interactions. Again, the differences are solely a result of the vibrational mixing due to anharmonic terms in the Hamiltonian. The mixing is sufficiently complex that no simple picture of the combined interaction is readily apparent in Fig. 3.

We have obtained nearest-neighbor level spacing statics for the effective Hamiltonian. This work has incorporated the additional constant of the motion N_t which arises from the block diagonal form of the Hamiltonian matrix. We find that as K increases, the distributions show evidence of the mutual repulsions of the levels in so far as they are distinctly unlike those predicted by a Poisson distribution. In none of our calculations, however, did we see a distribution indicative of extensive mixing between the states, i.e., the Wigner surmise.

V. SUMMARY

The vibrations of H_2CO have been investigated using canonical Van Vleck perturbation theory in which the vibrational Hamiltonian was transformed to a block diagonal

form. We find that transforming the Hamiltonian through second order is not adequate to reproduce the eigenvalue spectrum, but that fourth- and sixth-order Hamiltonians give results which are in excellent agreement with each other up to 8600 cm^{-1}. It is interesting to note that a simple, diagonal, second-order spectroscopic Hamiltonian gives excellent agreement with observed eigenvalues.[51] Considering the extensive Fermi couplings that are present we believe that this agreement is fortuitous.

Both rectilinear and curvilinear representations of the dynamics have been investigated. The fourth-order effective Hamiltonians are in excellent agreement, although the curvilinear representation provides a better zeroth-order representation of the system for some of the degrees of freedom.

The role rotation plays in intramolecular redistribution of energy via the mechanism of rotationally induced vibration coupling has also been investigated. Again, canonical Van Vleck perturbation theory has been used to obtain a block diagonal form for the effective Hamiltonian. The a-axis Coriolis coupling is found to play the central role here mixing the out-of-plane bend and in-plane wag motions. The rather simple picture developed to understand this coupling, however, can be considerably complicated by the presence of Fermi resonance interactions.

Much work remains to be done in order to model the SEP spectra of Dai et al.[1] In particular, one needs to calculate the Franck–Condon overlaps between vibrational wave functions for the upper electronic surface used in the SEP experiments and those of the ground electronic surface. This is difficult since the upper surface has such a large amplitude motion for the out-of-plane bend.[52] A curvilinear representation of the dynamics[53] is needed here for quantitative results. Future work will entail a calculation of the eigenvalues and eigenvectors of the full rotational–vibrational Hamiltonian in the curvilinear representation. We also plan to include the b- and c-axis Coriolis contributions as well as the contributions due to the molecular asymmetry.

ACKNOWLEDGMENTS

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