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Higher excited vibrational states of polyatomic molecules

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The overtone bands in the vibrational specturm of methane can be accounted for on the same footing as the fundamentals by use of a simple vibrational Hamiltonian and the application of conventional symmetry considerations and radiative selection rules. This approach gives a rough map of all stretch vibrational states up to ~24 000 cm^{-1}, by fitting the states of the appropriate symmetry to the observed overtone spectrum. All vibrational states are described in terms of anharmonic symmetrized internal coordinate (SIC) states which are very close to the eigenstates of the Hamiltonian. The one-quantum SIC states are identical to the normal modes while some multiquantum SICs present features analogous to the "local modes" conventionally used in the interpretation of overtone spectra. The discrete structure of the vibrational state–space obtained from this treatment is in conflict with the symmetryless quasicontinuous structure of state–space postulated to explain IR multiphoton absorption in polyatomic molecules. At the same time, it suggests that this process might take place mainly through an equidistant ladder of states, as is found in molecules with several identical bonds.

I. INTRODUCTION

Our main source of experimental information regarding higher vibrational states in polyatomic molecules is, at present, the study of overtone spectra particularly those involving several quanta (5–8) of C–H stretching vibrations. Such spectra consist of a series of Lorentzian bands whose frequencies follow the Birge–Sponer relationship $\omega \simeq Av - Bv^2$, as in diatomics, even in molecules containing several C–H bonds. This observation has led to the "local mode" interpretation of higher vibrational states.[1,2] That is, the spectra are understood to represent the excitation of a single CH bond in the whole molecule, rather than the vibration of all CH's with a definite phase among them as in the "normal mode" fundamentals. These local mode states, however, are thought to decay[3] into a quasicontinuum of "background" vibrational states at time scales of a few tens of femtosecond as their Lorentzian line shapes indicate.

Several theoretical papers have appeared in support of this empirical idea for the description of higher excited vibrational states: the proper partitioning of the quantum mechanical molecular Hamiltonian[4] readily gives local mode states, while classical trajectory calculations[5] indicate that some high-energy vibrations of coupled anharmonic oscillators are localized on only one oscillator. However, although near dissociation we may expect energy to be localized on only one bond, the spectroscopically accessible vibrational bound states are not easily reconciled with the classical picture of local modes as a single vibrating CH: this picture is certainly not applicable to the fundamental vibrations and first overtones, which are generally regarded as "delocalized" normal modes. At the same time, for the higher overtones, for which this picture is usually invoked, it presents a counter-intuitive breakdown of molecular symmetry, especially with respect to the radiative interaction: it is well known that all bound vibrational eigenstates have to transform like the irreducible representations of the point group of the molecule and that the overtone-active states must belong to

the same irreducible representation as the dipole operator. In molecules of high symmetry, therefore, motion of a single CH would require excitation by light also of eigenstates that do not possess the right symmetry.

Clearly, these problems could be solved if the description of the overtone spectrum were cast, as an extension of the theory of the fundamentals, within the context of a quantum mechanical molecular Hamiltonian and the application of molecular symmetry considerations and radiative selection rules. Within this traditional theoretical basis, the information available in overtone spectra could be used in constructing a more complete model for the structure of higher excited vibrational states which, in turn, could provide an insight into other phenomena involving such states, as, for example, the process of multiphoton absorption recently observed also in CH-containing molecules.[6] In using this traditional approach to obtain a global picture for the (bound) vibrational state space, we would like to emphasize that all the considerations that apply to the fundamentals (such as wave function symmetry, radiative selection rules) are quite applicable to the higher-excited vibrational states. One may call the most anharmonic eigenstates local modes, but that does not imply that energy becomes localized on one particular bond (destroying the molecular symmetry) or that a nonstationary local state is prepared upon excitation of an overtone. Of course in H_2O or in dihalomethanes, where vibrational states of both possible symmetries carry oscillator strength, it may be claimed that the state prepared in overtone spectroscopy is a superposition of eigenstates such that only one bond vibrates. Such a claim, however, cannot be made in molecules of higher symmetry, as, for example, in benzene, in which only one of the eigenstates of higher anharmonicity (of symmetry E_{1u}) out of a total of four ($A_{1g}, B_{1u} E_{1u}, E_{2g}$) carries oscillator strength at a given vibrational level v. The importance of symmetry in the description of higher-excited vibrational states has been recognized for some time in the literature: several authors have pointed out that all bound vibrational states must be properly symmetrized[2,7] and that the radiative selection rules determine the appearance of the overtone spectrum.[8] In particular, dipole selection rules and bond-dipole separability bring out the most anharmonic eigen-

states and give the spectrum a local mode appearance,[2] while other types of excitation (e.g., a Franck–Condon transition) may have access to more harmonic eigenstates of the proper symmetry giving rise to normal mode-like spectra.[8]

In this paper, we rely on a simple assumption regarding the Hamiltonian that applies to the higher-excited states of C–H containing molecules: we assume the Hamiltonian derivable from the harmonic analysis of the fundamentals is still valid if it is simply modified by the inclusion of the diagonal anharmonicity of the C–H stretches. This idea has been extensively used in the literature in connection with the overtone spectrum of H_2O,[9] benzene,[2] and other small molecules.[10] To describe the higher-excited vibrational structure, we use symmetrized internal coordinate states appropriate for anharmonic stretches, analogous to the symmetrized states used in the theory of fundamental vibrational modes. For the sake of concreteness, we examine the case of methane one of the few molecules for which extensive spectroscopy has been performed both on its fundamentals[11] and on its higher overtones,[12] and for which symmetry considerations greatly facilitate its theoretical treatment.

The paper is organized as follows: in Sec. II, we construct a map of the vibrational states of methane, by introducing and solving the vibrational Hamiltonian. In order to make contact with the available overtone spectra, we examine the states that have predominantly C–H stretch character, as well as the states that involve a single "bend" quantum in addition to their stretch character. In Sec. III, we compare this vibrational map to the observed overtone spectra and discuss the interactions which could give rise to the different band profiles. Finally, in Sec. IV, we summarize our conclusions on the vibrational state structure that can be deduced from overtone spectra and examine the implications of such a structure on other radiative processes, such as IR multiphoton absorption.

II. THE VIBRATIONAL MAP OF METHANE

The vibrational Hamiltonian of a molecule can be written in matrix notation, within the harmonic approximation as

$$H = \tfrac{1}{2}(\mathbf{P}^+ \cdot \mathbf{G} \cdot \mathbf{P} + \mathbf{Q}^+ \cdot \mathbf{F} \cdot \mathbf{Q}) , \qquad (1)$$

where $\mathbf{Q}$ and $\mathbf{P}$ are $3N$-6-dimensional column vectors composed of the displacements and conjugate momenta, respectively, of the molecular vibrational modes, while $\mathbf{F}$ and $\mathbf{G}$ are the $(3N$-6$)\times(3N$-6$)$ Wilson matrices[13] that depend on the force field and the geometry of the molecule. N is the number of atoms in the molecule. The harmonic Hamiltonian [Eq. (1)] is diagonal if $\mathbf{Q}$ and $\mathbf{P}$ are expressed in the normal mode basis. However, due to the anharmonic terms in the molecular force field, the representation of the true Hamiltonian in the normal mode basis is not diagonal and becomes progressively worse at higher quantum levels as the anharmonic contributions become progressively larger. To describe the higher-excited vibrational states, we adopt a simple model for the anharmonic potential, which accounts for

the main features of molecular anharmonicity. We assume that the individual bond stretches are Morse potentials, while all other anharmonic terms are set equal to zero. Indeed, in simple, hydrogen-containing molecules, force fields derived either from *ab initio* calculations[14] or from the spectra of the fundamentals and first overtone bands[15] indicate that the anharmonic part of the potential presents the smallest cross terms if it is represented in terms of internal (valence) molecular coordinates, and that the largest anharmonicity, by far, is associated with the bond stretching vibration. The choice of a Morse potential arises from the fact that its eigenvalues follow the Birge–Sponer relationship and can thus be expected to provide a good fit for the first ten to 12 overtones. Within this model, the structure of the molecular eigenstates can be viewed as arising from the interplay of the bond-stretching anharmonicity, which tends to localize all vibrational quanta on the same bond, and the delocalizing interactions of the $\mathbf{F}$ and $\mathbf{G}$ matrices which spread the excitation evenly throughout all equivalent bonds of the molecule.

This simple potential cannot be expected to describe very accurately the vibrational-rotational structures of each excited vibrational state, as the more sophisticated Hamiltonians that have been optimized for individual spectral bands. It can, however, give a rough map of all highly excited vibrational states of a molecule, which can be scaled by fitting the states of the appropriate symmetry to the observed overtone spectrum using *a single parameter* beyond the harmonic approximation, i.e., the Morse anharmonicity. The low resolution with which high overtone spectra are available at present, precludes the use of multiparameter potentials. Such a model has been successfully applied to the overtone spectrum of H_2O[9] by numerically diagonalizing the Hamiltonian matrix, which in turn was calculated analytically from the well-known properties of the Morse oscillators. For molecules of spectroscopic or photochemical interest, however, this procedure would necessitate prohibitively large numerical calculations. For example, in a molecule with only four stretches, the $v = 6$ level involves the diagonalization of a 210×210 matrix, while simultaneous considerations of the (harmonic) bending modes increases the matrix size to 1500×1500.[16]

For this reason, in this paper, we treat the Hamiltonian by operator techniques which can translate most diagonalization procedures into simple algebraic manipulations of the operators composing the Hamiltonian, thus permitting the application of the method to much larger molecules. In this treatment, after the (algebraic) diagonalization of the anharmonicity and the stretch–bend interaction, the transformed Hamiltonian of methane involves only the four CH stretches with their mutual interactions, and has matrix elements only between states with the same number of stretch quanta. Each quantum level of the transformed Hamiltonian, therefore, may be treated separately through methods analogous to those commonly used in normal mode analysis. That is, by using basis states which transform like the irreducible representations of T_d, the point group of methane, the Hamiltonian matrix can be broken

up into small blocks along the diagonal, each involving only states of the same symmetry and the same number of stretch quanta. Calculation of the vibrational map of methane (i.e., of the eigenstates, their energies, and symmetries), then, reduces to the solution of these partial individual blocks.

A. Transformation of the Hamiltonian

The molecular vibrational Hamiltonian can be written in internal coordinates as the sum of the individual stretch and bend Hamiltonians, together with their mutual interactions

$$H = \sum_i H^i_{str} + \sum_{i>j} H^{ij}_{str-str} + H_{bend} + H_{str-bend} \ . \tag{2}$$

The Hamiltonian of each individual stretch H^i_{str} is that of a Morse oscillator, while all other partial Hamiltonian in Eq. (2) are obtained directly from the **F** and **G** matrices.[13] In particular, for the case of methane, taking into account the symmetry of the molecule, the stretch–stretch interaction Hamiltonian can be written as

$$H_{SS} = F_{SS} \sum_{i>j} q_i q_j + \frac{\cos \alpha}{m_C} \sum_{i>j} p_i p_j \ , \tag{3}$$

where $\cos \alpha = \cos 109°28' = -1/3$ and m_C is the mass of the carbon atom, while the stretch–bend Hamiltonian is

$$H_{SB} = \frac{\sqrt{3}}{2} \left(F_{SB} \sum_{i=1}^{4} q_i q^u_i - \frac{8}{3 dm_C} \sum_{i=1}^{4} p_i p^u_i \right), \tag{4}$$

where d is the equilibrium distance of the CH bond and q^u_i and p^u_i refer to the bending mode that directly couples to the stretch of the ith bond. That is, q^u_i is the displacement operator for the "umbrella" deformation of the three CH bonds that exclude bond i, as can be seen by symmetry. It should be noted that although the four stretches are mutually orthogonal, the four umbrella modes are *not*: they span a three-dimensional space, since

$$\sum_{i=1}^{4} q^u_i = \sum_{i=1}^{4} p^u_i = 0 \tag{5}$$

and this gives rise to the normalization factor $\sqrt{3}/2$. Equation (5) reflects the redundant nature of the six angular coordinates of CH_4, since it is not possible to have a totally symmetric bending vibration in which all HCH angles simultaneously increase. The pure bend Hamiltonian of CH_4 can be written as

$$H_B = \frac{3}{4} \sum_{i=1}^{4} \left[\frac{(p^u_i)^2}{2\mu_u} + \frac{\mu_u \Omega^2_u}{2} (q^u_i)^2 \right] + \sum_{i=1}^{2} \left[\frac{p^{B'}_i}{2\mu_{B'}} + \frac{\mu_{B'} \Omega^2_{B'}}{2} (q^{B'}_i) \right], \tag{6}$$

where μ and Ω denote the reduced mass and frequency, respectively, of the corresponding bending mode. This Hamiltonian spans five linearly independent bending modes, three among which are represented by the four nonorthogonal umbrella bends and correspond to the F_2 bending normal modes. The subscript B' denotes the two other bends which correspond to the E-symmetry bending normal modes of methane. Since the E modes do not interact with any other vibrations within the approximation adopted for the Hamiltonian, they will not be considered any further.

The Morse potential of each individual stretch is expanded in a power series and truncated at the quartic term, so that each H^i_{str} can be written as

$$H^i_{str} = \frac{1}{2} \frac{p^2_i}{\mu} + \tfrac{1}{2}\mu\omega^2 q^2_i + \beta' q^3_i + \delta' q^4_i \ , \tag{7}$$

where μ is the reduced mass of the CH stretch, and ω is its (harmonic) frequency, while the cubic and quartic coefficients follow:

$$\delta' = \frac{7}{6} \frac{\beta'^2}{\mu\omega^2} \ . \tag{8}$$

The anharmonicity of the Morse oscillator is related to these coefficients by

$$\epsilon = \frac{3\hbar^2}{2\mu^2\omega^2} \left(\frac{5\beta'^2}{2\mu\omega^2} - \delta' \right) = \frac{2}{\mu} \left(\frac{\hbar\beta'}{\mu\omega^2} \right)^2 \ . \tag{9}$$

Treatment of Eq. (3) by perturbation theory up to second order in β' and first order in δ' gives exactly the same eigenvalues as the full Morse Hamiltonian, while the wave functions of eigenstates far from the dissociation limit in the two types of Hamiltonian are quite similar. Thus, for modeling the first 10 to 12 levels of the CH stretching vibration (which is usually described by a Morse Hamiltonian with approximately 25 bound states), the perturbational solution is practically equivalent to the exact.

We can write the Hamiltonian in second quantization, by using the correspondence (with $\hbar = 1$)

$$p = i \left(\frac{m\omega}{2} \right)^{1/2} (b^+ - b) \ , \tag{10a}$$

$$q = \left(\frac{1}{2m\omega} \right)^{1/2} (b^+ + b) \ . \tag{10b}$$

For the bond-stretching vibrations, the creation/annihilation operators follow Bose commutation relations:

$$[b_i, b_j] = 0; \quad [b^+_i, b^+_j] = 0; \quad [b_i, b^+_j] = \delta_{ij} \ , \tag{11}$$

while for the umbrella bending modes, we have, instead of Eq. (11c),

$$[B_i, B^+_i] = 1 \ , \tag{12a}$$

$$[B_i, B^+_j] = 1/3, \quad \text{for } i \neq j \ , \tag{12b}$$

because of the nonorthogonality of the four bending motions. The vibrational Hamiltonian [Eq. (2)] can then be written as

$$H_S = \sum_{i=1}^{4} \omega b^+_i b_i + \beta(b^+_i + b_i)^3 + \delta(b^+_i + b_i)^4 \ , \tag{13a}$$

$$H_{SS} = \sum_{i>j} \gamma(b^+_i b_j + b^+_j b_i) + \eta(b^+_i b^+_j + b_i b_j) \ , \tag{13b}$$

$$H_B = \tfrac{3}{4}\Omega \sum_{i=1}^{4} B^+_i B_i \ , \tag{13c}$$

$$H_{SB} = \frac{\sqrt{3}}{2}\Omega \sum_{i=1}^{4} [g(b^+_i B_i + b_i B^+_i) + h(b^+_i B^+ + b_i B)] \ , \tag{13d}$$

where the new constants are related to the old, according to

$$\beta = \beta' \left(\frac{1}{2\mu\omega} \right)^{3/2} \cdot \delta = \delta' \left(\frac{1}{2\mu\omega} \right)^2 \ ,$$

$$\gamma = \left(\frac{F_{SS}}{2\mu\omega} - \frac{\omega}{6}\frac{m_H}{m_C + m_H}\right) \; ; \quad \eta = \left(\frac{F_{SS}}{2\mu\omega} + \frac{\omega}{6}\frac{m_H}{m_C + m_H}\right) \; ,$$

$$g = \left(\frac{F_{SB}}{2d}M^{1/2} - \frac{4M^{1/2}}{3dm_C}\right) \; ; \quad h = \left(\frac{F_{SB}}{2dM^{1/2}} + \frac{4M^{1/2}}{3dm_C}\right) \; ,$$

with

$$M = \frac{\Omega\omega}{\left(\frac{2}{m_H} + \frac{16}{2m_C}\right)\left(\frac{1}{m_H} + \frac{4}{3m_C}\right)}$$

and

$$\mu = \frac{m_H m_C}{m_H + m_C} \; .$$

We treat the Hamiltonian [Eq. (13)] by diagonalizing each time the largest interaction term. Thus, by diagonalizing successively (1) the stretch anharmonicity of each bond; (2) the stretch–bend interaction; and (3) the two-quantum stretch–stretch interaction, we obtain (see the Appendix)

$$H = \sum_{i=1}^{4}[\bar{\omega}(N_i)N_i - \epsilon N_i] + Z_1\sum_{i>j}N_i N_j \qquad (14a)$$

$$+ \sum_{i\neq j}b_i^{\dagger}b_j\,\bar{\gamma}(N_i, N_j) + Z_2\sum_{i\neq j}b_i^{\dagger}b_i^{\dagger}b_j b_j \qquad (14b)$$

$$+ \frac{3}{4}\sum_{i=1}^{4}\bar{\Omega}(N_i)B_i^{\dagger}B_i \; . \qquad (14c)$$

In this transformed Hamiltonian, the stretches and bends are decoupled, while the stretch anharmonicity is incorporated in the structure of the stretch basis states. The Hamiltonian has thus the appearance of four inter-acting anharmonic stretches, the interaction consisting of the propagation of a stretch quantum throughout the molecules. At this point, it is advantageous to consider explicitly the basis states of the Hamiltonian [Eq. (14a)] and use the symmetry properties of the molecule in the determination of its eigenstates.

B. The symmetrized internal coordinates

The eigenstates of the zeroth-order Hamiltonian of Eq. (14a) can be written in the occupation number representation as kets of the form $|0020\rangle$ to denote, for example, the state that involves two quanta of excitation in the third CH stretch (internal coordinate) and zero everywhere else. This state is, of course, degenerate, with three other states that involve a double excitation but because of the anharmonicity ϵ, it is *not* degenerate with any other configuration of two stretch quanta, such as states of the form $|1100\rangle$. The two subspaces into which the two-quantum state–space is separated because of the anharmonicity may each be spanned by a set of symmetrized internal coordinate (SIC) basis states, which transform like the irreducible representations of the point group of CH_4 (T_d). Thus, the four orthonormal SIC states that span the subspace of the form $|2000\rangle$ (or, in general, $|v000\rangle$) belong to two symmetry species: A_1 and F_2

$$|2000; A_1\rangle = \tfrac{1}{2}(|2000\rangle + |0200\rangle + |0020\rangle + |0002\rangle) \; , \qquad (15a)$$

$$|2000; F_2\rangle = \begin{cases} \tfrac{1}{2}(|2000\rangle + |0200\rangle - |0020\rangle - |0002\rangle) & (15b) \\[4pt] \tfrac{1}{2}(|2000\rangle - |0200\rangle + |0020\rangle - |0002\rangle) & (15c) \\[4pt] \tfrac{1}{2}(|2000\rangle - |0200\rangle - |0020\rangle + |0002\rangle) \; , & (15d) \end{cases}$$

while the six SIC states that span the subspace of the form $|1100\rangle$ belong to A_1, E, and F_2. For example,

$$\frac{1}{\sqrt{6}}(|1100\rangle + |1010\rangle + |1001\rangle + |0110\rangle + |0101\rangle + |0011\rangle)$$
$$\rightarrow |1100; A_1\rangle \; , \qquad (16a)$$

$$\tfrac{1}{2}(|1010\rangle - |1001\rangle - |0110\rangle + |1010\rangle) \rightarrow |1100; E\rangle \; , \qquad (16b)$$

$$\frac{1}{\sqrt{2}}(|1100\rangle - |0011\rangle) \rightarrow |1100; F_2\rangle \; , \qquad (16c)$$

plus the index permutations that give the remaining states of symmetries E and F_2.

The SIC states of the level $v = 1$ [having the form of Eq. (15), but with $2 \rightarrow 1$] diagonalize exactly the molecular vibrational Hamiltonian, and constitute therefore the correct eigenstates for that level. They correspond, of course, to the ν_1 and ν_3 normal modes of the molecule. The A_1 normal mode is split in energy from the three F_2 because of the term $\bar{\gamma}$ in Eq. (14b), which represents the delocalization of a single stretch quantum. The SIC states corresponding to more than one vibrational quantum do not diagonalize exactly the stretch Hamiltonian but cause it to separate into small blocks along the main diagonal, since the Hamiltonian can have matrix elements only between SIC basis states of the same symmetry *and* of the same total number of vibrational quanta. However, because the anharmonicity (which is already incorporated in the SIC states) is generally larger than the delocalizing interactions of Eq. (14b), these blocks are close to being diagonal, especially at high quantum levels, so that the SIC's converge very fast to the true eigenstates of the Hamiltonian. In fact, SIC states of the form $|v000\rangle$ for $v > 5$ have an amplitude contribution of >0.98 to the highest-anharmonicity eigenstates of the corresponding symmetry, and can therefore be considered as good approximations to those states.

We note that, except for the case $v = 1$, SIC states cannot be described classically in any simple way. For example, for states of the form $|v000; F_2\rangle$ with $v = 1$, the classical phase difference between any two CH stretches can be obtained as 0 or π by evaluating a correlation function of the form $\langle q_1 q_2\rangle$. Such states can, therefore, be interpreted classically as representing the oscillation of all CH stretches with a definite phase relationship among them. However, for $v > 1$, the correlation function gives $\langle q_i q_j\rangle = 0$, indicating that the oscillation phase difference is undefined, yet the wave functions of these states consist of a superposition of four excited bond–stretches with well-defined (phased) coefficients. Thus, these states do not correspond to a classical correlated motion of all the CH's yet they do not represent a simple localization of the energy on only one CH. Another particularity of such states arises from the fact that at high quantum levels, the molecular eigenstates that are approximated by SIC states of the form $|v000; A_1\rangle$ and $|v000; F_2\rangle$ are very close in energy.

This implies that in any superposition of these four SIC states, the relative phase of the wave functions does not evolve in time, and as a consequence, a state that corresponds to an excitation initially localized on a particular bond, does not propagate in the molecule. In order to establish a common language with the existing literature in overtone spectroscopy, SIC states like $|v000; F_2\rangle$ will be called local mode excitations, even though the classical concept of the local modes suppresses their symmetry features which (as discussed in Secs. III and IV) are essential for the understanding of their radiative interactions.

It is straightforward to also construct SIC states involving stretch–bend combinations. As an example, we consider states involving one quantum of umbrella-type deformation in addition to v stretching quanta on a single bond, as these types of combinations states appear in the overtone spectrum by borrowing intensity from local mode-type states $|v000; F_2\rangle$. We shall denote by $|i,j\rangle$ the state in which the ith stretch and jth umbrella are excited (by v and 1 quanta, respectively). By application of group theory, then we obtain the corresponding SIC as

$$|i,i; A_1\rangle = \tfrac{1}{2}\{|1,1\rangle + |2,2\rangle + |3,3\rangle + |4,4\rangle\}, \tag{17a}$$

$$|i,i; F_2\rangle = \tfrac{1}{2}\{|1,1\rangle + |2,2\rangle - |3,3\rangle - |4,4\rangle\}, \tag{17b}$$

$$|i,j; E\rangle = \frac{\sqrt{3}}{\sqrt{2}}\{|1,3\rangle + |1,4\rangle - |2,3\rangle + |2,4\rangle + |3,1\rangle$$
$$- |3,2\rangle - |4,1\rangle + |4,2\rangle\}, \tag{17c}$$

$$|i,j; F_1\rangle = \frac{\sqrt{3}}{4\sqrt{2}}\{|1,3\rangle - |1,4\rangle - |2,3\rangle$$
$$+ |2,4\rangle - |3,1\rangle + |3,2\rangle + |4,1\rangle - |4,2\rangle\}, \tag{17d}$$

$$|i,j; F_2\rangle = \tfrac{1}{2}\{|1,2\rangle + |2,1\rangle - |3,4\rangle - |4,3\rangle\}, \tag{17e}$$

plus the states that may be obtained by permutting the indices in the symmetry species E, F_1, and F_2. For the level $v = 0$, there is one triply degenerate pure bending state of symmetry F_2

$$\frac{\sqrt{3}}{4}\{|1\rangle + |2\rangle - |3\rangle - |4\rangle\}, \tag{18a}$$

$$\frac{\sqrt{3}}{4}\{|1\rangle - |2\rangle + |3\rangle - |4\rangle\}, \tag{18b}$$

$$\frac{\sqrt{3}}{4}\{|1\rangle - |2\rangle - |3\rangle + |4\rangle\}, \tag{18c}$$

which corresponds to the three components of the ν_4 fundamental transforming like x, y, z, respectively.

C. The vibrational eigenstate of methane

We have explicitly calculated the "pure stretch" state up to 15 000 cm^{-1} and the stretch–umbrella combinations up to 8000 cm^{-1} (see Tables I and II), by using the SIC basis and the Hamiltonian of Eq. (14). We have used literature values[15] for most constants, and have treated only the stretch frequency and anharmonicity as adjustable parameters, giving the best fit with the available low-resolution overtone spectrum of methane.[12] The values used are $\omega = 3123.5$ cm^{-1}, $\epsilon = 59.5$ cm^{-1}, $\gamma = -30.5$ cm^{-1}, $\Omega = 1325.0$ cm^{-1}, $g = -54.5$ cm^{-1}, with η and h related to γ and g as in Eq. (13).

For each type of vibrations (e.g., the pure stretch states), we note that for a given total number (v) of stretch quanta, the individual eigenstates are spread over a frequency range that depends essentially on the anharmonicity. For $v = 5$, that spread is already of the order of 1200 cm^{-1}, but the distribution of states within that frequency range is not uniform. At the low frequency end of the range, the eigenstates are clustered (within a few tens of wave numbers) around the energies of their parent "unsymmetrized" states $|n_1, n_2, n_3, n_4\rangle$. In fact, within each v manifold, the lowest energy states are always two local modes of energies near $E = v\omega - v(v+1)\epsilon$, symmetrized as $|v000; A_1\rangle$ and $|v000; F_2\rangle$. With increasing v, these two states become almost degenerate, while their separation from the next lowest eigenstates of the same total v, increases proportionately to v. At the high energy end of the v manifold, on the other hand, the clusters tend to merge due to the relatively large value of the interaction between geminal C–H stretches. They consist of states in which the v quanta are distributed essentially uniformly throughout the four bonds. The energy of the highest state is generally slightly lower than $v\nu_3$, both because of the anharmonicity ϵ (for $v > 5$) and because of the stretch–stretch interaction γ. (See Fig. 1).

Since the energies of stretch states are determined essentially by the anharmonicity, their density is never uniform but displays large gaps coincident essentially with the spacings of four independent anharmonic oscillators. Of course, if bends and stretch–bend combinations are simultaneously considered, together with their rotational levels, the gaps disappear and the state distribution is essentially uniform. It is commonly asserted[17] that the region above three or four vibrational quanta has to be considered as a quasicontinuum whose density of states increases rapidly with energy, and in which individual modes can not be distinguished, since in such a dense manifold even weak interactions will mix all states with each other. Within our simple Hamiltonian [Eq. (2)], however, these interactions, if they exist, are not taken into account and individual states retain their identity in the quasicontinuum. Spectroscopic analysis of the higher-excited vibrational states should give evidence on the nature of the interactions that produce the quasicontinuum, and they may thus be included in the Hamiltonian.

III. THE OVERTONE SPECTRUM OF METHANE

The states that are active in the one-photon spectroscopy of methane are of symmetry F_2. Figure 2 presents a comparison of the frequencies and intensities for the F_2 states calculated by our model, to the observed low resolution overtone spectrum. For the band near 6000 cm^{-1} (labeled $2\nu_3$ in the literature), the pure vibrational term has been measured[18] to be 6004.65 cm^{-1}, as compared to 6006 in our calculations, while the band near 9050 (usually labeled $3\nu_3$) has been found to have three origins[19] (probably resulting from Fermi resonances) at 9047, 9049, and 9018 cm^{-1}, as compared to 9034 cm^{-1} in our calculations. Rotational-vibrational analysis has not been carried out for any other band, as most bands appear as unresolved envelopes 100–200 cm^{-1} wide.

TABLE I. The stretch-only vibrations.

v	Symmetry	Energy	Parentage (largest contributions)
1	A_1	2 918	$\mid 1000;\ A_1\rangle$
	F_2	3 019	$\mid 1000;\ F_2\rangle$
2	A_1	5 793	$0.75\mid 2000;\ A_1\rangle - 0.66\mid 1100;\ A_1\rangle$
		5 960	$0.75\mid 1100;\ A_1\rangle + 0.66\mid 2000;\ A_1\rangle$
	E	6 039	$\mid 1100;\ E\rangle$
	F_2	5 851	$0.94\mid 2000;\ F_2\rangle + 0.33\mid 1100;\ F_2\rangle$
		6 006	$0.94\mid 1100;\ F_2\rangle - 0.33\mid 2000;\ F_2\rangle$
3	A_1	8 584	$0.87\mid 3000;\ A_1\rangle + 0.46\mid 2100;\ A_1\rangle$
		8 734	$0.73\mid 2100;\ A_1\rangle + 0.49\mid 1110;\ A_1\rangle - 0.48\mid 3000;\ A_1\rangle$
		8 979	$0.86\mid 1100;\ A_1\rangle - 0.51\mid 2100;\ A_1\rangle$
	E	8 846	$\mid 2100;\ E\rangle$
	F_1	8 937	$\mid 2100;\ F_1\rangle$
	F_2	8 601	$0.96\mid 3000;\ F_2\rangle$
		8 802	$0.90\mid 2100;\ F_2^+\rangle + 0.29\mid 1110;\ F_2\rangle$
		8 904	$0.96\mid 2100;\ F_2^-\rangle$
		9 034	$0.95\mid 1110;\ F_2\rangle - 0.31\mid 2100;\ F_2^+\rangle$
4	A_1	11 238	$0.97\mid 4000;\ A_1\rangle$
		11 493	$0.72\mid 3100;\ A_1\rangle + 0.49\mid 2110;\ A_1\rangle + 0.41\mid 2200;\ A_1\rangle$
		11 700	$0.64\mid 3100;\ A_1\rangle - 0.62\mid 2100;\ A_1\rangle - 0.36\mid 2200,\ A_1\rangle$
		11 799	$0.83\mid 2200;\ A_1\rangle - 0.46\mid 2110;\ A_1\rangle - 0.29\mid 1111;\ A_1\rangle$
		12 035	$0.91\mid 1111;\ A_1\rangle - 0.39\mid 2110;\ A_1\rangle$
	E	11 578	$0.85\mid 3100;\ E\rangle - 0.45\mid 2200;\ E\rangle + 0.26\mid 2110;\ E\rangle$
		11 784	$0.88\mid 2200;\ E\rangle + 0.47\mid 3100;\ E\rangle$
		11 958	$0.97\mid 2110;\ E\rangle$
	F_1	11 645	$0.99\mid 3100;\ F_1\rangle$
		11 941	$0.99\mid 2110;\ F_1\rangle$
	F_2	11 240	$0.97\mid 4000;\ F_2\rangle$
		11 539	$0.68\mid 3100;\ F_2^+\rangle + 0.49\mid 3100;\ F_2^-\rangle + 0.36\mid 2200;\ F_2\rangle + 0.33\mid 2110;\ F_2^-\rangle$
		11 616	$0.81\mid 3100;\ F_2^-\rangle - 0.46\mid 3100;\ F_2^+\rangle - 0.30\mid 2200;\ F_2\rangle$
		11 756	$0.69\mid 2200;\ F_2\rangle - 0.55\mid 3100;\ F_2^+\rangle + 0.46\mid 2110;\ F_2^-\rangle$
		11 839	$0.73\mid 2110;\ F_2\rangle - 0.54\mid 2200;\ F_2\rangle + 0.37\mid 2110;\ F_2^+\rangle$
		11 883	$0.90\mid 2110;\ F_2^+\rangle - 0.39\mid 2110;\ F_2^-\rangle$
5	A_1	13 759	$0.98\mid 5000;\ A_1\rangle$
		14 169	$0.86\mid 4100;\ A_1\rangle + 0.32\mid 3200;\ A_1\rangle + 0.30\mid 3110;\ A_1\rangle$
		14 379	$0.61\mid 3200;\ A_1\rangle + 0.47\mid 2210;\ A_1\rangle - 0.45\mid 4100;\ A_1\rangle$
		14 527	$0.71\mid 3200;\ A_1\rangle - 0.47\mid 3100;\ A_1\rangle - 0.38\mid 2111;\ A_1\rangle - 0.36\mid 2210;\ A_1\rangle$
		14 690	$0.74\mid 3110;\ A_1\rangle - 0.56\mid 2210;\ A_1\rangle - 0.35\mid 2111;\ A_1\rangle$
		14 810	$0.82\mid 2110;\ A_1\rangle - 0.55\mid 2210;\ A_1\rangle$
	E	14 260	$0.94\mid 4100;\ E\rangle + 0.32\mid 3200;\ E\rangle$
		14 434	$0.90\mid 3200;\ E\rangle - 0.34\mid 4100;\ E\rangle + 0.23\mid 2210;\ E\rangle$
		14 640	$0.93\mid 3110;\ E\rangle - 0.25\mid 2210;\ E\rangle + 0.24\mid 3200;\ E\rangle$
		14 795	$0.94\mid 2210;\ E\rangle + 0.30\mid 3110;\ E\rangle$
	F_1	14 265	$0.97\mid 4100;\ F_1\rangle + 0.20\mid 3200;\ F_1\rangle$
		14 565	$0.93\mid 3200;\ F_1\rangle - 0.28\mid 3110;\ F_1\rangle - 0.23\mid 4100;\ F_1\rangle$
		14 648	$0.90\mid 3110;\ F_1\rangle + 0.30\mid 3200;\ F_1\rangle - 0.29\mid 2210;\ E_1\rangle$
		14 831	$0.96\mid 2210;\ F_1\rangle + 0.29\mid 3110;\ F_1\rangle$
	F_2	13 760	$0.98\mid 5000;\ F_2\rangle$
		14 211	$0.83\mid 4100;\ F_2^-\rangle + 0.38\mid 4100;\ F_2^+\rangle + 0.23\mid 3110;\ F_2^-\rangle$
		14 225	$0.81\mid 4100;\ F_2^+\rangle - 0.46\mid 4100;\ F_2^+\rangle - 0.30\mid 3200;\ F_2^+\rangle$
		14 422	$0.80\mid 3200;\ F_2^+\rangle - 0.42\mid 4100;\ F_2^+\rangle - 0.32\mid 2210;\ F_2^+\rangle + 0.26\mid 3110;\ F_2^-\rangle$
		14 534	$0.74\mid 3200;\ F_2^-\rangle + 0.42\mid 3110;\ F_2^+\rangle + 0.38\mid 3110;\ F_2^-\rangle - 0.27\mid 4100;\ F_2^-\rangle$
		14 564	$0.56\mid 3110;\ F_2^-\rangle + 0.48\mid 2210;\ F_2^-\rangle - 0.40\mid 3110;\ F_2^+\rangle - 0.39\mid 3200;\ F_2^+\rangle$
		14 618	$0.63\mid 3110;\ F_2^+\rangle - 0.62\mid 3200;\ F_2^-\rangle - 0.30\mid 3110;\ F_2^-\rangle$
		14 744	$0.67\mid 2201;\ F_2^+\rangle + 0.57\mid 3110;\ F_2^-\rangle - 0.34\mid 2210;\ F_2^-\rangle$
		14 801	$0.75\mid 2210;\ F_2^-\rangle + 0.50\mid 2210;\ F_2^+\rangle + 0.38\mid 3110;\ F_2^-\rangle$
		14 940	$0.94\mid 2111;\ F_2\rangle + 0.29\mid 2210;\ F_2^+\rangle$

Our calculated frequencies fall within 10–30 cm^{-1} from the band centers. Thus, the agreement between the observed and calculated frequencies indicates that our model gives a reasonable vibrational map for methane up to 24 000 cm^{-1}. It should be noted that Fermi resonance between stretches and bends has been neglected, and thus features involving two bend quanta (e.g., the band at 5600 cm^{-1}) are not accounted for. The calculated intensities were obtained by assuming as a first approximation that the transition dipole can be written as the sum of the individual bond dipoles.[2] Within this approximation, only SICs of the form

TABLE II. Stretch–bend combinations.

v_{str}	Symmetry	Energy	Parentage
0	F_2	1310	$\lvert 0, i;\ F_2)$
1	A_1	4326	$\lvert i, i;\ A_1)$
	E	4326	$\lvert i, j;\ E)$
	F_1	4327	$\lvert i, j;\ F_1)$
	F_2	4225	$0.71\ \lvert i, i;\ F_2) + 0.70\ \lvert i, j;\ F_2)$
		4327	$-0.70\ \lvert i, i;\ F_2) + 0.71\ \lvert i, j;\ F_2)$
2	A_1	7159	$0.94\ \lvert ii, i;\ A_1) + 0.33\ \lvert ij, i;\ A_1)$
		7313	$-0.33 \qquad\qquad +0.94$
	E	7159	$0.94\ \lvert ii, i;\ E) + 0.33\ \lvert ij, i;\ E)$
		7313	$-0.33 \qquad\qquad +0.94$
	F_1	7160	$0.94\ \lvert ii, j;\ F_1) - 0.24\ \lvert ij, i;\ F_1) - 0.24\ \lvert ij, k;\ F_1)$
		7313	$0.33 \qquad\qquad +0.67 \qquad\qquad -0.67$
		7346	$0 \qquad\qquad +0.71 \qquad\qquad -0.71$

			$\lvert ii, i;\ F_2)$	$\lvert ii, j;\ F_2)$	$\lvert ij, i;\ F_2^+)$	$\lvert ij, i;\ F_2^-)$	$\lvert ij, k;\ F_2)$
	F_2	7114	0.55	0.53	0.37	0.37	0.37
		7155	0.65	−0.66	−0.01	0.25	−0.26
		7252	0.45	0.45	−0.44	−0.45	−0.44
		7318	0.26	−0.26	0.01	−0.66	0.66
		7347	0	0	0.82	−0.40	−0.41

$\lvert v000;\ F_2\rangle$ carry oscillator strength, and the overtone spectrum consists of only those states that have a projection onto $\lvert v000;\ F_2\rangle$. The electrical anharmonicity was taken into account phenomenologically by normalizing the intensity of the most anharmonic eigenstate at each v level to the observed intensity. The general pat-
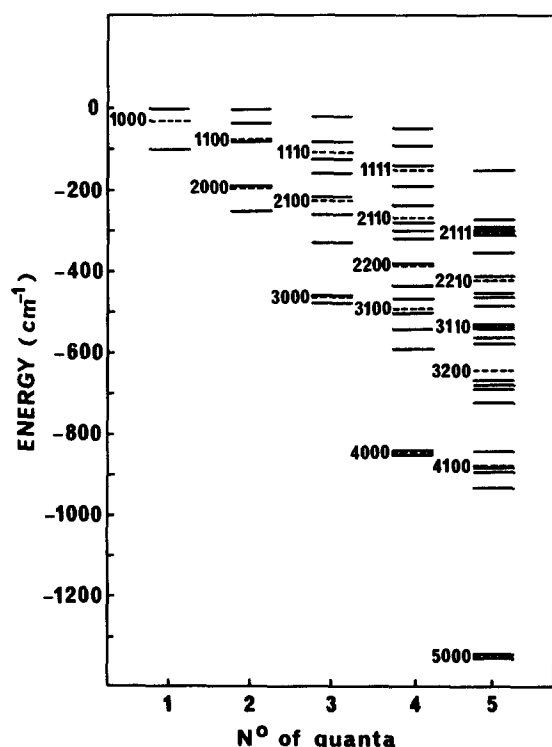

FIG. 1. Energies of stretch vibrational states in methane (————), relative to the multiples of the energy of the ν_3 fundamental. Dotted lines (- - -) are states obtainable by fitting overtone spectrum to four *independent* anharmonic oscillators; four digit numbers designate the respective vibrational quantum configurations.
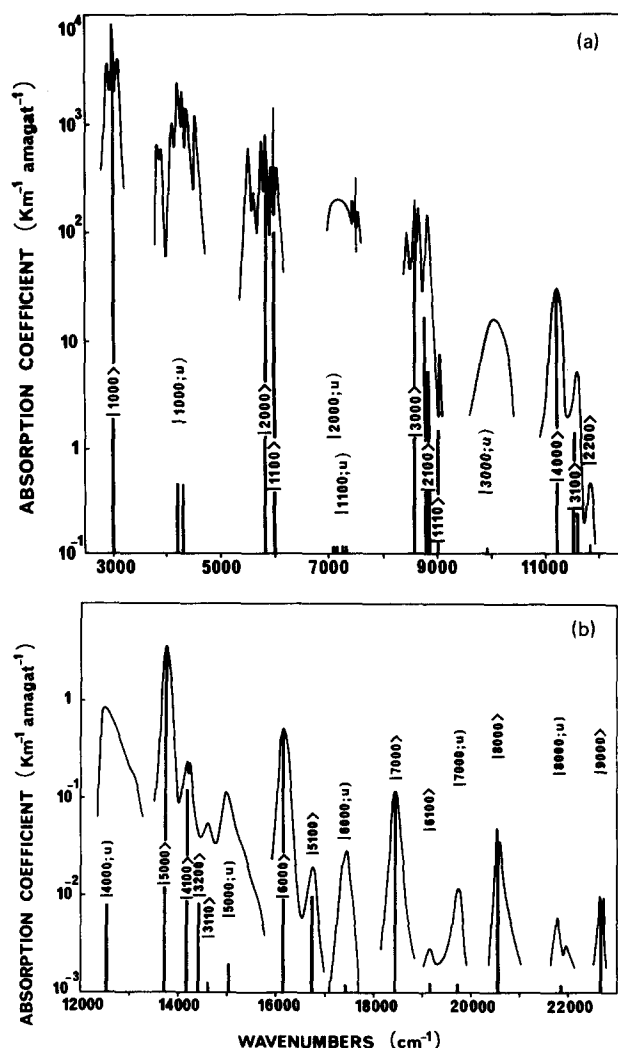

FIG. 2. Calculated positions and intensities of overtone active states in methane. Experimental spectrum taken from Ref. 12. Four digit number in kets designate the configuration of stretch quanta in corresponding SIC, u indicates excitation of "umbrella" deformation.

tern of calculated intensities for the stretch-only states, is quite similar to the observed spectrum, thus supporting our assumption. However, there is a quantitative discrepancy between the observed and calculated intensities especially for the stretch–bend combinations, which can be attributed to two sources: (1) additional interactions (such as the vibration-rotation interactions discussed below) may redistribute the oscillator strength among the states, and (2) the assumption of a bond-separable transition dipole may be of limited validity, so that the relative intensities observed may result from small cross terms in the dipole of two stretches or a stretch and an umbrella bend.

Further information concerning the structure of the higher-excited vibrational states of methane can be obtained by analyzing the overtone band shapes. Rotational structure is resolved and easily identifiable in only four bands: the only "pure stretch" states among these are "$2\nu_3$" and "$3\nu_3$." All other states appear as broad bands on which no regular rotational structure can be discerned. In the lower energy overtones, the band envelope gives hints of underlying structure, but with increasing energy envelopes become progressively smoother, retaining, however, irregular shapes.[12] Furthermore, the band at 16150 cm^{-1}, corresponding to the stretch state $|6000\rangle$, has been shown to consist of individual resolvable lines.[20] All this evidence indicates that in methane the relatively wide (100–200 cm^{-1}) overtone bands constitute simply congested vibrational-rotational spectra. These spectra are inhomogeneous in the sense that, under collisionless conditions, different parts of the spectrum are caused by different molecules, since each molecule is found initially in a definite state can therefore effect transitions only to those final states which satisfy the angular-momentum selection rules.

The calculation of detailed vibrational-rotational band profiles is not at present possible, given our poor knowledge of the spectral parameters of the higher excited vibrational states. However, as in the case of the fundamentals, spectral congestion in the overtones can be expected to arise principally from strong vibration-rotation interactions between nearby vibrational states. These interactions cause a splitting of the individual symmetry-allowed rotational lines, while at the same time they redistribute spectral intensity, causing the appearance of otherwise symmetry-forbidden vibrational rotational transitions. Detailed theories of vibrational-rotational interactions in methane have been developed to account for the very high resolution spectra obtained for the fundamentals.[11] Thus, as in our calculation of vibrational states, we can assume that the vibrational-rotational interactions that can be deduced from the spectra of the fundamentals are operative in the higher excited vibrational states, modified, of course, for the inclusion of anharmonicity in the C–H stretch potential.

We can gain some qualitative insight into the effect of vibrational-rotational interactions by examining the case of the Coriolis interactions. Within our model, Coriolis coefficients between any two higher-excited stretch states can easily be calculated from the known coeffi-

cients of the $v=1$ symmetry coordinates[21] $\zeta_3 = 0.1$, $\zeta_4 = 0.4$, and $\zeta_{34} = 3\sqrt{6}/10$. For harmonic vibrations, the operator for the vibrational angular momentum along the x axis can be written in second quantization as

$$\pi^x = \pi_3^x + \pi_4^x + \pi_{34}^x = i\zeta_3^x(a_y a_z^+ - a_z a_y^+) + i\zeta_4^x(A_y A_z^+ - A_z A_y^+)$$
$$+ i\zeta_{34}^x [C(a_y A_z^+ - a_y^+ A_z + a_z^+ - a_z A_y^+)$$
$$+ S(a_y^+ A_z^+ - a_y A_z - a_z^+ A_y^+ + a_z A_y)] , \qquad (19)$$

where $a_x^+/a_x(A_x^+/A_x)$ are creation/annihilation operators corresponding to the x component of the triply degenerate stretch (bend) symmetry coordinate, while

$$C = \tfrac{1}{2}\{(\Omega/\omega)^{1/2} + (\omega/\Omega)^{1/2}\}, \quad S = \tfrac{1}{2}\{(\Omega/\omega)^{1/2} - (\omega/\Omega)^{1/2}\}$$

with ω, (Ω) being the corresponding frequencies of the stretch (bend) modes. The vibrational angular momentum operator for anharmonic and interacting stretches and bends can be obtained by writing the symmetrized vibrational operators in terms of individual stretch and umbrella operators [according to Eqs. (15) and (18)] and subsequently applying the unitary transformation used in diagonalizing the Hamiltonian (see the Appendix). Thus, looking at the quantum-conserving stretch-only part of the vibrational angular momentum operator, after the application of the unitary transformation, we have

$$\pi_{\text{Str}}^x = \frac{i}{2}[-(\tilde{Z}_3 b_3^+ - \tilde{Z}_4 b_4^+)(b_1 - b_2) + (\tilde{Z}_1 b_1^+ - \tilde{Z}_2 b_2^+)(b_3 - b_4)$$
$$-(\tilde{G}_3 b_3^+ - \tilde{G}_4 b_4^+)(b_1 G_1 - b_2 G_2) + (\tilde{G}_1 b_1^+ - \tilde{G}_2 b_2^+)(b_3 G_3 - b_4 G_4)$$
$$+ \zeta_4(H_3 b_3^+ - H_4 b_4^+)(b_1 H_1 - b_2 H_2) - \zeta_4(H_1 b_1^+ - H_2 b_2^+)(b_1 H_1 - b_2 H_2)],$$
$$(20)$$

where

$$H_i = \frac{h}{\omega + \Omega - 2\epsilon N_i}, \quad G_i = \frac{g}{\omega - \Omega - 2\epsilon N_i}, \quad \tilde{G}_i = C\zeta_{34} + \zeta_4 G_i ,$$

and $\tilde{Z}_i = \zeta_3 + C\zeta_{34} G_i$. The matrix elements of the operator (20) are the Coriolis coefficients between the corresponding two states.

In general, the Coriolis interaction causes large line splittings and significant intensity redistributions, if it occurs between closely-lying states. We would thus expect it to be largest between states of the same "unsymmetrized" stretch parentage, and to cause a spread of the spectral intensity of the F_2 vibrational state to states of other symmetries, producing thus a "forest" of vibrational-rotational lines centered around the frequency of the unsymmetrized stretch state. For the band at 6006 cm^{-1}, the Coriolis coefficient with the E-symmetry state at 6039 cm^{-1} is obtained from Eq. (20) to be 0.02, in accordance with the fact that this band is uncongested. The diagonal Coriolis coefficient is calculated as $\zeta_{6005}^{6005} = 0.030$ as compared to 0.034, the measured value.[18] Similarly, for the uncongested band at 9047 cm^{-1}, the Coriolis interaction with the A_1 state of the same local parentage at 8979 cm^{-1} is disallowed by symmetry. At higher quantum levels, however, uncongested bands cannot be expected to arise easily since intensity redistributions among states of the same local parentage can occur even when such

states do not interact directly, if their energies become almost degenerate. In particular, the states corresponding to the local modes $|v000; F_2\rangle$ and $|v000; A_1\rangle$ both have a Coriolis interaction with $|v-1, 1, 0, 0; F_1\rangle$. The splitting caused by this interaction decreases with v, because of the energy difference (due to anharmonicity) within each pair of interacting states. However, since both quasidegenerate local mode states interact with the same F_1 state, the second-order interaction redistributes the spectral intensity essentially equally between them, and the rotational levels of both can be expected to contribute to the overtone spectrum.

IV. DISCUSSION

In hydrocarbons and up to the energies for which the C–H stretches can be described as simple anharmonic oscillators, the vibrational eigenstate are best expressed as linear combinations of a few symmetrized internal coordinate states, which involve a given number of vibrational quanta on each bond and transform like the irreducible representations of the point group of the molecule. Of special interest are the eigenstates of highest anharmonicity as they can be studied by overtone spectroscopy. Such states are well-approximated by SIC states carrying several quanta on only one bond and their energies are grouped around that of their parent unsymmetrized state $|v000\rangle$. They are thus often referred to as local modes. It should be noted, however, that such states are symmetrized quantum states and do not correspond to a simple classical energy localization on one bond. The low anharmonicity eigenstates on the other hand are linear combinations of several SIC, corresponding to a uniform distribution of the excitation on all four bonds.

Consideration of all the vibrational eigenstates at high energies, together with their rotational levels gives a high, essentially uniform density of states. Vibration-rotation interactions can mix individual states with separations up to $100-200$ cm^{-1}, mixing at the same time their symmetries. A direct implication of this interaction is that overtone bands are to a large extent inhomogeneous congested vibrational-rotational spectra, so that fast intramolecular relaxation processes need not be invoked to account for the observed band profiles.

In benzene, the higher overtones ($v = 5$ to 8) have been fitted to smooth Lorentzians and have been interpreted as homogeneous line shapes arising from the relaxation of the local mode doorway state $|s\rangle = |v00000\rangle$ into the manifold of background states, and primarily into the local-mode combinations of the form $|m\rangle = |v-1, 1, 0000\rangle$. The main success of the relaxation theory[3] has been the justification of the narrowing of the overtone bands of C_6H_6 with increasing v, and the broadening upon deuteration. This effect has been attributed to the energy difference between $|s\rangle$ and $|m\rangle$ which increases with v but decreases upon deuteration. The weak point of the theory, however, is that it calculates the observed linewidth of $\Gamma_s \sim 100$ cm^{-1} by postulating a linewidth for the m states of $\Gamma_m \sim 500$ to 1100 cm^{-1} and attributes the latter to a relaxation of the form $|v-1, 1, 0000\rangle - |v-2, 1, 1, 000\rangle$ or to "rapid dephasing due to the hopping of the single quantum among the five degenerate states."

Clearly, neither mechanism of intermediate relaxation can account for such a large Γ_m. The first mechanism (which is simply an iteration the relaxation $|s\rangle \to |m\rangle$) would require a width for the $v-2, 1, 1, 000\rangle$ states which is even larger than Γ_m, while the second mechanism would give no width at all to Γ_m: delocalization of a single quantum simply causes a splitting of the m states of different symmetries rather than a broadening due to dephasing. Furthermore, in all molecules in which local-mode combination bands have been observed in the overtone spectrum, their widths have been of the order of $\Gamma_m \sim 100-200$ cm^{-1} and not $500-1100$ cm^{-1}.

In view of our interpretation of the methane band shapes, however, it is reasonable to expect that in benzene too, the observed overtone profiles are inhomogeneous arising from spectrally congested vibrational-rotational bands rather than reflect the occurrence of intramolecular relaxation. In fact, given that in larger molecules rotational lines are much more closely spaced ($B_0 = 0.19$ cm^{-1} for benzene and $B_0 = 5.24$ cm^{-1} for methane), vibrational-rotational interactions would cause spectral congestion much more easily. Although it is not possible at present to calculate detailed band profiles, several effects may be envisaged which could give a large number of vibrational-roational lines inside a centrally-peaked, Lorentzian-like envelope. One such contribution in C_6H_6 could be the Coriolis interaction between the overtone-active $|v00000; E_{1u}\rangle$ state and the nearby states that have projections onto the five different $|v-1, 1, 0000; E_{1u}\rangle$ SICs. As the Coriolis splittings of the overtone-active transitions decrease with v due to increasing spacing of the interacting levels, the inhomogeneous envelope will appear narrower as v increases.

The idea of a compact quasicontinuum of states, in which symmetries are scrambled so that radiative selection rules are relaxed above the third or fourth quantum level, has been extensively invoked to account for the occurrence of IR multiphoton absorption (MPA) by the vibrational modes polyatomic molecules.[17] The relatively sharp nature of the observed overtone spectra, however, tells us otherwise: it indicates that the vibrational state space *is not compact* and can participate in a radiative process only within the regions that can fulfill the selection rules regarding the origin and symmetry of its states. Môre specifically, the selection rules of one-photon overtone spectroscopy in methane dictate that to a first approximation a state may carry oscillator strength only to the extent that it can project onto the most anharmonic stretch state of v quanta and symmetry F_2, i.e., $|v000; F_2\rangle$. The appearance of the overtone spectrum thus shows that this rule still holds in the quasicontinuum and that it is satisfied only in the neighborhood of $|v000; F_2\rangle$. The agreement of our calculations with the low resolution overtone spectrum of methane indicates that the mixing of $|v000\rangle$ with other stretch states is accounted for to a large extent by simply including anharmonicity to the Hamiltonian derived from the spectroscopy of the fundamental vibration. Such a Hamiltonian can mix only nearby states of the appropriate symmetries through vibration-vibration and vibration-rotation interactions, producing thus a dense

but highly structured forest of states. The structured nature of the quasicontinuous region is corroborated by the discrete vibrational spectra of very large molecules in which the quasicontinuum is already populated at room temperature,[22] by the experimental preparation of highly excited molecular ions, which even near dissociation are found to be in spectroscopically sharp vibrational states,[23] and by the occurrence of MPA in NH_3 and other small molecules[24] in which the quasicontinuum is certainly sparse and the states that constitute it retain their characteristics.

Thus, for the understanding of radiative processes involving higher-excited vibrational states such as MPA, the usual assumption of a region of state-space with uniform density and no symmetry is not sufficient and spectroscopic information has to be taken into account. Clearly, overtone spectra cannot be used directly as maps of the vibrational state space available for the multiphoton absorption since the states directly observable in such spectra are almost certainly *not* involved in MPA resonant with $v = 1$: Overtones appear only for very anharmonic states, which constitute just the "tip of the iceberg" of the vibrational state-space, while the symmetry selection rules for one-photon spectroscopy are generally different from those of MPA. As in overtone spectroscopy, however, we should expect that for the process of MPA (whether it is considered to occur stepwise through real intermediate states or as a nonlinear absorption process involving intermediate state near-resonance enhancement) the conventional spectroscopic requirements of symmetry, transition-dipole matrix elements and resonance have to be met at every step. Thus, if MPA could occur in methane resonant with its IR-active stretch at 3019 cm^{-1}, the transition-dipole requirement would restrict the state-space available to MPA mainly to those states that have a strong stretch component, while the resonance requirement would favor states for which the stretch quanta are uniformly distributed throughout the four bonds. Finally, the symmetry requirement dictates that the states that participate in the second step (two-photon absorption) have symmetries $(F_2)^2 = A_1 + E + F_2$, in the third step $(F_2)^3 = A_1 + E_1 + F_1 + F_2$ and so on. In view of these requirements, we would expect that the vibrational-rotational levels that participate in MPA have the character of the stretch states at 6039 (E), 6006 (F_2), and/or 5960 (A_1) for the second photon, the states at 9034 (F_2), 8979 (A_1), 8937 (F_1), and 8846 (E) for the third photon, etc. It should be noted that at the level $v = 2$, the state at 6006, which is active in one-photon (overtone) spectroscopy, displays an uncongested spectrum while the Coriolis interactions of the other two states (which are overtone-inactive) with their neighbors are small (for the E state) or disallowed by symmetry (for the A_1 state), indicating that they probably have very sparse vibrational-rotational levels. Thus, if MPA can occur in methane, it probably displays a very strong dependence on the rotational quantum number J, as very few vibrational-rotational levels would be in a position to fulfill the resonance and angular momentum requirements.

Clearly, the same considerations apply in molecules

like cyclopropane and ethyl chloride, in which MPA is now well-documented.[6] It should be noted that in these molecules, we would expect resonance and angular momentum requirements to be fulfilled relatively easily since both molecules have several CH bonds, while the congested appearance of their overtones as low as $v = 2$ indicates that their vibrational-rotational state structure is very dense.

The conclusions of this model regarding the full state map of anharmonic C–H stretching vibrations and, in particular, the characteristics of vibrational states inaccessible to overtone spectroscopy must, of course, be tested experimentally through nonlinear IR spectroscopy. Two-photon absorption experiments in CH_4 are now in progress in our laboratory, in order to investigate as a first step two-quantum states of symmetries A_1, E, and F_2, by using two tunable IR sources.[25] The information available in the two-beam n-photon spectroscopy of the vibrational state having the appropriate symmetry is complementary to that of the overtone spectrum. Such experiments will thus help to better characterize the vibrational and rotational Hamiltonian applicable to high-energy states, give us an insight into the nature of the quasicontinuum and the molecular interactions that produce it, and contribute thus to the elucidation of the MPA process.

ACKNOWLEDGMENTS

APPENDIX: PARTIAL DIAGONALIZATION OF THE HAMILTONIAN

In expressing Eq. (13) in terms of Bose creation/annihilation operators, we implicitly took the harmonic stretching and bending modes as our zeroth order basis. In this basis, the largest interaction terms especially for levels of high quantum numbers are the anharmonic intrabond interactions of Eq. (13a). We may diagonalize each individual bond Hamiltonian H_S^i separately, by a technique introduced by Coulter[26] which diagonalizes iteratively the interaction between nondegenerate states up to the desired order by use of a unitary transformation. This technique is very similar to the contact transformation used extensively in the treatment of rotation-vibration interactions.

By use of a unitary transformation e^{iK} described in Ref. 26, we transform the Hamiltonian [Eq. (13)]

$$\tilde{H} = e^{iK} H e^{-iK} = \tilde{H}_S + \tilde{H}_{SS} + \tilde{H}_B + \tilde{H}_{SB} , \qquad (A1)$$

such that the transformed Hamiltonian of each individual stretch $\tilde{H}_S$, is diagonal up to second order in β and first order in δ. The transformed stretch-stretch Hamiltonian $\tilde{H}_{SS}$ has terms that involve the overall creation or annihilation of 4, 3, 2, 1, or 0 stretch quanta. The terms that correspond to a change of ± 4, ± 3, or ± 1 quanta are of the order of at most 1 cm^{-1}, while they link states that differ by at least 3000 cm^{-1}. Thus, at quantum levels below $v = 10$, these terms may be safely neglected. The same is true for the terms involving ± 2 quanta that are not proportional to η. The quantum conserving

terms, on the other hand, must be retained, as they link states that may be degenerate. The transformed Hamiltonian may then be written as

$$H = \left\{ \omega - \epsilon + 72\left(\frac{\beta}{\omega}\right)^2 \left(\frac{\eta+\gamma}{2}\right) \right\} \sum_{i=1}^{4} N_i - \epsilon \sum_{i=1}^{4} N_i^2$$

$$+ 72\left(\frac{\beta}{\omega}\right)^2 (\eta+\gamma) \sum_{\substack{i=1 \\ i>i}}^{4} N_i N_j \tag{A2a}$$

$$+ \gamma \sum_{i\neq j} b_i^* b_j + \eta \sum_{\substack{i=1 \\ i>j}}^{4} (b_i^* b_j^* + b_i b_j) \tag{A2b}$$

$$+ 8\left(\frac{\beta}{\omega}\right)^2 (2\eta - \gamma) \sum_{i\neq j} b_i^* b_j (N_i + N_j + 1)$$

$$+ 2\left(\frac{\beta}{\omega}\right)^2 (5\gamma - 6\eta) \sum_{i\neq j} b_i^* b_i^* b_j b_j \tag{A2c}$$

$$+ \frac{3}{4} \Omega \sum_{i=1}^{4} B_i^* B_i \tag{A2d}$$

$$+ \frac{\sqrt{3}}{2} \left\{ g \sum_{i=1}^{4} (b_i^* B_i + B_i^* b_i) + h \sum_{i=1}^{4} (b_i^* B_i^* + b_i B_i) \right\}, \tag{A2e}$$

where $\epsilon \equiv (30\beta^2/\omega) - 6\delta$ is the Morse anharmonicity of the stretch oscillators, while $N_i \cong b_i^* b_i$. We have also approximated $H_{SB} \rightarrow \tilde{H}_{SB}$.

We choose as the new basis for the transformed Hamiltonian the set of all eigenstates of the anharmonic stretches [Eq. (A2a)] and the harmonic bends [Eq. (A2d)]. In this basis, the stretch–bend interaction [Eq. (A2e)] constitutes the largest off-diagonal term. In the treatment of the fundamental, it links states that are separated by at least $\Delta = \omega - 2\epsilon - \Omega \simeq 1700$ cm^{-1} through interactions of the order of 50 cm^{-1}. This results in a mixing of less than 1% of the two types of vibrations, so that for a low resolution work, it can safely be neglected. At higher quantum levels, however, the anharmonicity of the stretch vibration greatly reduces the energy difference. For example, the level corresponding to eight stretch quanta on the same CH bond is only $\Delta = \omega - 16\epsilon - \Omega \simeq 840$ cm^{-1} higher in energy than the level of seven stretches + one bend, while the interaction between them is of the order of $g\sqrt{8} \simeq 160$ cm^{-1}. This implies that for the interpretation of overtone spectra even of low resolution the stretch–bend mixing has to be taken into account. We apply once more the technique of transforming the Hamiltonian by a unitary operator so that the interaction $H_1 = H_{SB}$ is diagonalized up to third order, while $H_0 = H_S + H_B$. The first-order energy correction is given by the diagonal elements of H_1 and is $D_1 = 0$. The unitary transformation e^{iK_1}, which upon application to $H = H_S + H_B + H_{SB}$ gives the second-order energy correction D_2, satisfies

$$i[H_0, K_1] = H_1 - D_1 = H_1, \tag{A3}$$

and can be shown to be

$$iK_1 = \frac{\sqrt{3}}{2} \sum_{i=1}^{4} [g(G_i^N b_i^* B_i - b_i B_i^* G_i^N) + h(H_i^N b_i^* B_i^* - b_i B_i H_i^N)], \tag{A4}$$

where

$$G_i^N = (\omega - \Omega - 2\epsilon N_i)^{-1}$$

and

$$H_i^N = (\omega + \Omega - 2\epsilon N_i)^{-1}.$$

The second-order energy correction is then obtained as

$$D_2 = \frac{3}{4} \sum_{i=1}^{4} [g^2 G_i^N (N_i - B_i^* B_i) - h^2 H_i^N (N_i + B_i^* B_i)], \tag{A5}$$

while the higher-order contributions are obtained by diagonalizing

$$C = \frac{i}{2}[K_1, H_1] - D_2 = \frac{1}{8} \sum_{i\neq j} b_i^* b_j [h^2(H_i^{N+1} + H_j^N) - g^2(G_i^{N+1} + G_j^N)], \tag{A6}$$

where terms having a magnitude smaller than a few cm^{-1} and linking states differing by two stretch or bend quanta have been neglected. We note that the interaction of Eq. (A6) links states that may be degenerate, and thus cannot be diagonalized perturbatively any further. It may, however, be combined with Eqs. (A2b) and (A2c) and diagonalized numerically.

Finally, we may diagonalize the two-quantum stretch–stretch interactions of Eq. (A2b). Since this term links states that differ by $\Delta = 2\omega - 2\epsilon(N_i + N_j) \simeq 6200 - 120(N_i + N_j)$ neglect of the anharmonicity will introduce a very small error even for the most anharmonic levels of interest $(N_i + N_j = 8$ or 9). We may therefore take

$$H_0 = \omega \sum_{i=1}^{4} N_i, \tag{A7a}$$

$$H_1 = \eta \sum_{i>j} (b_i^* b_j^* + b_i b_j), \tag{A7b}$$

giving $D_1 = 0$, \hfill (A8a)

$$iK_1 = \frac{\eta}{2\omega} \sum_{i>j} (b_i^* b_j^* - b_i b_j), \tag{A8b}$$

so that

$$D_2 = -\frac{3}{2} \frac{\eta^2}{\omega} \sum_{i=1}^{4} N_i, \tag{A9a}$$

and

$$C = -\frac{\eta^2}{\omega} \sum_{i\neq j} b_i^* b_j. \tag{A9b}$$

Incorporating Eq. (A9b) into Eq. (A2b), we can write the overall transformed Hamiltonian as

$$H = \sum_{i=1}^{4} [\tilde{\omega}(N_i) N_i - \epsilon N_i^2] + Z_1 \sum_{i>j} N_i N_j \tag{A10a}$$

$$+ \sum_{i\neq j} b_i^* b_j \bar{\gamma}(N_i, N_j) + Z_2 \sum_{i\neq j} b_i^* b_i^* b_j b_j \tag{A10b}$$

$$+ \frac{3}{4} \sum_{i=1}^{4} \bar{\Omega}(N_i) B_i^* B_i, \tag{A10c}$$

where $Z_1 = 72(\beta/\omega)^2(\eta+\gamma)$, $Z_2 = 2(\beta/\omega)^2(5\gamma - 6\eta)$, and $\tilde{\omega}, \bar{\gamma}$, and $\bar{\Omega}$ are slow functions of the number operators, given by

$$\tilde{\omega}(N_i) = \omega - \epsilon - \frac{3}{2}\frac{\eta^2}{\omega} + \frac{1}{2}Z_1 + \frac{3}{4}(g^2 G_i^N - h^2 H_i^N),$$

$$\bar{\gamma}(N_i, N_j) = \gamma - \frac{\eta^2}{\omega} + 8\left(\frac{\beta}{\omega}\right)^2 (2\eta - \gamma)(N_i + N_j + 1)$$

$$+ \frac{1}{8}[h^2(H_i^{N+1} + H_j^N) - g^2(G_i^{N+1} + G_j^N)],$$

$$\bar{\Omega}(N_i) = \Omega - g^2 G_i^N - h^2 H_i^N.$$

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