A local anharmonic treatment of vibrations of methane

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Abstract

The stretching and bending vibrations of methane are studied in a local anharmonic model of molecular vibrations. The use of symmetry-adapted operators reduces the eigenvalue problem to block diagonal form. For the 44 observed energies we obtain a fit with a standard deviation of 0.81 cm\textsuperscript{-1} (and a r.m.s. deviation of 1.16 cm\textsuperscript{-1}).

Key words: Molecular vibrations, anharmonic model, methane

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I. INTRODUCTION

The development and refinement of experimental techniques in high resolution spectroscopy has generated a wealth of new data on rovibrational spectra of polyatomic molecules. Highly symmetric molecules, such as tetrahedral XY\textsubscript{4} systems, form an ideal testing ground for models of molecular structure. On the one hand, the high degree of symmetry tends to reduce the complexity of the spectrum and on the other hand, the use of symmetry concepts and group theoretical techniques may help to interpret the data and eventually suggest new experiments [1]. A good example is the methane molecule, for which there exists a large amount of information on vibrational energies.
Theoretically, the force field constants of methane from which the spectrum can be generated \([2]\) can be obtained from anharmonic force field calculations \([3]\) or \textit{ab initio} calculations, see \textit{e.g.} \([4,5]\). In a more empirical approach, the vibrational Hamiltonian is expressed in terms of curvilinear internal coordinates, which are symmetrized for the bending variables, but not for the stretching variables. The model parameters are optimized in a fit to experimental vibrational energies \([1]\).

The aim of this paper is to investigate the stretching and bending vibrations of methane up to three quanta in a symmetry-adapted vibrational model. The method is based on the use of symmetrized (both for bending and stretching variables) internal coordinates. The fundamental idea is to incorporate anharmonic effects in the local modes from the outset. This is done by substituting the standard creation and annihilation operators associated with the internal coordinates by \(SU(2)\) operators which carry the intrinsic anharmonicity of the local modes. The result can be viewed as a symmetrized (and in other ways improved) version of our previous work on methane \([4]\).

II. LOCAL ANHARMONIC SYMMETRIZED COORDINATES

The vibrational Hamiltonian of methane is usually expressed in terms of curvilinear internal coordinates \(S_i\) and their conjugate momenta \(P_i\) \([3]\). Both the kinetic and potential energy are then expanded as a Taylor series around the equilibrium configurations. In practice, it is convenient to introduce symmetry-adapted curvilinear internal coordinates and their conjugate momenta \([3]\)

\[
S_{x,\Gamma,\gamma} = \sum_{i=1}^{10} \alpha_{x,\Gamma,\gamma}^i S_i, \quad P_i = \sum_{x,\Gamma,\gamma} \alpha_{x,\Gamma,\gamma}^i P_{x,\Gamma,\gamma}, \quad (1)
\]

since it reduces the Hamiltonian to block diagonal form. In the case of methane there is a redundancy between the curvilinear coordinates which describe the bending degrees of freedom. The redundant or spurious combination can be removed from the outset by restricting the labels \(\Gamma\) and \(x\) to the fundamental modes only: \(\Gamma = A_1, F_2\) for stretching vibrations \((x = s)\) and \(\Gamma = E, F_2\) for bending vibrations \((x = b)\). However, as a consequence the inverse transformations of Eq. (1) become nonlinear \([3,4]\). In the present discussion we prefer to keep the redundant coordinate \((x = b, \Gamma = A_1)\), and to remove the spurious states at a later stage. In this case the inverse relations are linear just as Eq. (1) itself.

Next we introduce instead of the symmetrized coordinates and momenta of Eq. (1) creation and annihilation operators

\[
\sqrt{\beta_{x,\Gamma,\gamma}} S_{x,\Gamma,\gamma} - \frac{1}{\sqrt{2\beta_{x,\Gamma,\gamma}}} i P_{x,\Gamma,\gamma} = b_{x,\Gamma,\gamma}^\dagger, \\
\sqrt{\beta_{x,\Gamma,\gamma}} S_{x,\Gamma,\gamma} + \frac{1}{\sqrt{2\beta_{x,\Gamma,\gamma}}} i P_{x,\Gamma,\gamma} = b_{x,\Gamma,\gamma}. \quad (2)
\]
The coefficients \( \beta_{x,\Gamma} \) represent scaling factors for each vibrational mode. According to the discussion following Eq. (1) the symmetrized operators can be expanded in terms of local operators as

\[
 b_{x,\Gamma,\gamma}^\dagger = \sum_{i=1}^{10} \alpha_{x,\Gamma,\gamma}^i b_i^\dagger, \quad b_{x,\Gamma,\gamma} = \sum_{i=1}^{10} \alpha_{x,\Gamma,\gamma}^i b_i.
\]  

(3)

As mentioned before, the basic idea of the present approach is to explicitly incorporate anharmonic effects in the local modes. It has been shown that the anharmonicities induced by potentials such as the Morse and Pöschl-Teller oscillators can be described in terms of \( U(2) \) algebras \([10,11]\). Here we construct an anharmonic representation of the local operators \( b_i^\dagger \) and \( b_i \) through the correspondence \([13,14]\).

\[
b_i^\dagger \rightarrow a_i^\dagger \equiv \frac{\hat{J}_{+,i}}{\sqrt{N_i}}, \quad b_i \rightarrow a_i \equiv \frac{\hat{J}_{+,i}}{\sqrt{N_i}},
\]  

(4)

where \( \hat{J}_{+,i}^2 = \hat{J}_{+,i}^2 + (\hat{J}_{+,i} \hat{J}_{-,i} + \hat{J}_{-,i} \hat{J}_{+,i})/2 = \hat{N}_i(\hat{N}_i + 2)/4 \), \( i.e. \ N_i/2 = j_i \) \([14]\). The anharmonic operators satisfy the commutation relation

\[
[a_i, a_j^\dagger] = \frac{1}{\sqrt{N_i N_j}} [\hat{J}_{+,i} \hat{J}_{-,j}] = \delta_{ij} \frac{2 \hat{J}_{0,i}}{N_i} = \delta_{ij} \left( 1 - \frac{2 \hat{v}_i}{N_i} \right),
\]

\[
[a_i, \hat{v}_j] = \frac{1}{\sqrt{N_i}} [\hat{J}_{+,i}, \frac{\hat{N}_j}{2} - \hat{J}_{0,j}] = \delta_{ij} \frac{\hat{J}_{+,i}}{\sqrt{N_i}} = \delta_{ij} a_i,
\]

\[
[a_i^\dagger, \hat{v}_j] = \frac{1}{\sqrt{N_i}} [\hat{J}_{-,i}, \frac{\hat{N}_j}{2} - \hat{J}_{0,j}] = -\delta_{ij} \frac{\hat{J}_{-,i}}{\sqrt{N_i}} = -\delta_{ij} a_i^\dagger.
\]  

(5)

The operators \( \hat{J}_{\mu,i} \) with \( \mu = \pm, 0 \) together with the number operator \( \hat{N}_i \) are the generators of \( U_i(2) \). In the limit \( N_i \to \infty \) we recover the harmonic description in terms of \( b_i^\dagger \), \( b_i \) and \( \hat{v}_i = b_i^\dagger b_i \). With each internal coordinate we associate a \( U(2) \) algebra. For the methane molecule this leads to four \( U(2) \) algebras for the stretching degrees of freedom and six more for the bending degrees of freedom (of the latter, one linear combination is spurious).

The molecular dynamical group is then given by

\[
\mathcal{G} = U_1(2) \otimes U_2(2) \otimes \ldots \otimes U_{10}(2).
\]  

(6)

The Hamiltonian and other operators of interest are expressed in terms of the generators \( \hat{J}_{\mu,i}, \hat{N}_i \) of the \( U_i(2) \) algebras in Eq. (6). The local basis states for each oscillator are \( |N_i, v_i \rangle \), where \( v_i = 0, 1, \ldots [N_i/2] \) denotes the number of oscillator quanta in the \( i \)-th oscillator and \( N_i \) is related to the depth of the anharmonic potential \([11,12,14]\).

For the CH\(_4\) molecule there are two different boson numbers: \( N_s \) for the stretching modes and \( N_b \) for the bending modes. The tetrahedral symmetry of methane is taken into account by symmetrizing the local operators \( \hat{J}_{\mu,i} \) \([7]\)

\[
\hat{T}_{\mu,i} = \sum_{i=1}^{10} \alpha_{\mu,i}^j \hat{J}_{\mu,i}.
\]  

(7)
The coefficients $\alpha_{1,\gamma,x}^\Gamma$ are the same as in Eq. (4). The symmetrized tensor operators of Eq. (7) correspond to ten degrees of freedom, four of which ($A_1 \oplus F_2$) are related to stretching modes and six ($A_1 \oplus E \oplus F_2$) to the bendings. Consequently we can identify the tensor with $x = b$ and $\Gamma = A_1$ as the operator associated to a spurious mode. This identification makes it possible to eliminate the spurious states exactly. This is achieved by (i) ignoring the $\hat{T}_{\mu,b}^{A_1}$ tensor in the construction of the Hamiltonian, and (ii) diagonalizing this Hamiltonian in a symmetry-adapted basis from which the spurious mode has been removed [15,16]. It is important to note that, although in general in the presence of anharmonic interactions only approximate methods can be developed to eliminate spurious degrees of freedom, the particular anharmonization provided by $U(2)$ admits a symmetry procedure to exclude the unphysical states exactly [16].

III. THE VIBRATIONAL HAMILTONIAN

The vibrational Hamiltonian for methane can now be constructed by repeated couplings of the tensors of Eq. (7) to a scalar ($\Gamma = A_1$) under the tetrahedral group $T_d$. We use the standard labelling for the vibrational basis states: $(\nu_1 \nu_2 \nu_3 \nu_4)$, where $\nu_1, \nu_2$ and $\nu_2, \nu_4$ denote the number of quanta in the $A_1, F_2$ stretching modes, and in the $E, F_2$ bending modes, respectively. The labels $l_i$ are related to the vibrational angular momentum associated with degenerate vibrations. The allowed values are $l_i = \nu_i, \nu_i - 2, \ldots, 1$ or 0 for $\nu_i$ odd or even [17].

In this paper, the Hamiltonian is taken to be diagonal in the total number of quanta $V = \nu_1 + \nu_2 + \nu_3 + \nu_4$, and in the polyad $V' = 2\nu_1 + \nu_2 + 2\nu_3 + \nu_4$, but does not contain explicit Fermi interactions between the stretching and bending vibrations. Fermi interactions can be included in the model by means of additional interactions which are diagonal in the polyad $V' = 2\nu_1 + \nu_2 + 2\nu_3 + \nu_4$ and exchange quanta between the stretching and bending modes. In that case the number of quanta $V$ ceases to be conserved.

According to the above procedure, we now construct the $T_d$ invariant interactions that are at most quadratic in the generators and conserve the total number of quanta

$$\hat{H}_{x,\Gamma} = \frac{1}{2N_x} \sum_{\gamma} \left( \hat{T}_{-x}^{\Gamma_1} \hat{T}_{+x}^{\Gamma_2} + \hat{\bar{T}}_{+x}^{\Gamma_3} \hat{\bar{T}}_{-x}^{\Gamma_4} \right),$$

$$\hat{V}_{x,\Gamma} = \frac{1}{N_x} \sum_{\gamma} \hat{T}_{0,x}^{\Gamma_1} \hat{\bar{T}}_{0,x}^{\Gamma_2}. \quad (8)$$

Here $\Gamma = A_1, F_2$ for the stretching vibrations $x = s$ and $\Gamma = E, F_2$ for the bending vibrations $x = b$. In addition to Eq. (8), there are two stretching-bending interactions

$$\hat{H}_{sb} = \frac{1}{2\sqrt{N_s N_b}} \sum_{\gamma} \left( \hat{T}_{-s}^{F_2_1} \hat{T}_{+s,b}^{F_2} + \hat{\bar{T}}_{+s}^{F_2_2} \hat{\bar{T}}_{-s,b}^{F_2} \right),$$

$$\hat{V}_{sb} = \frac{1}{\sqrt{N_s N_b}} \sum_{\gamma} \hat{T}_{0,s}^{F_2} \hat{\bar{T}}_{0,b}^{F_2}. \quad (9)$$

The zeroth order vibrational Hamiltonian is now written as
\[\hat{H}_0 = \omega_1 \hat{H}_{s,A_1} + \omega_2 \hat{H}_{b,E} + \omega_3 \hat{H}_{s,F_2} + \omega_4 \hat{H}_{b,F_2} + \omega_{34} \hat{H}_{sb} + \alpha_2 \hat{V}_{b,E} + \alpha_3 \hat{V}_{s,F_2} + \alpha_4 \hat{V}_{b,F_2} + \alpha_{34} \hat{V}_{sb}.\]  

(10)

The interaction terms of \(\hat{H}_0\) can be rewritten in terms of the Casimir operators of subgroups of Eq. (6) which were used in [7]. The interaction \(\hat{V}_{A_1,s}\) has not been included since the combination

\[\sum_{\Gamma=A_1,F_2} (\hat{H}_{s,\Gamma} + \hat{V}_{s,\Gamma}) = \frac{1}{4N_s} \sum_{i=1}^{4} \hat{N}_i(\hat{N}_i + 2),\]  

(11)

corresponds to a constant \(N_s + 2\). A similar relation holds for the bending interactions, but in this case the interaction \(\hat{V}_{b,A_1}\) has already been excluded in order to remove the spurious \(A_1\) bending mode. The subscripts of the parameters correspond to the \((\nu_1 \nu_2 \nu_3 \nu_4)\) labeling of a set of basis states for the vibrational levels of CH\(_4\).

In the harmonic limit the interactions of Eqs. (8) and (9) attain a particularly simple form, which can be directly related to configuration space interactions [2,6]. This limit is obtained by interpreting Eq. (4) in the opposite sense [13,14], and corresponds group theoretically to the contraction of the SU(2) algebra to the Weyl algebra. In the harmonic limit the interactions of Eqs. (8) and (9) can be expressed in terms of the symmetrized harmonic operators of Eq. (3)

\[\lim_{N_s \to \infty} \hat{H}_{s,\Gamma} = \frac{1}{2} \sum_{\gamma} \left( \hat{b}_{s,\Gamma} \hat{b}_{s,\Gamma} \right),\]  

\[\lim_{N_s \to \infty} \hat{V}_{s,\Gamma} = 0,\]  

\[\lim_{N_s,N_b \to \infty} \hat{H}_{sb} = \frac{1}{2} \sum_{\gamma} \left( \hat{b}_{s,F_2} \hat{b}_{b,F_2} \right),\]  

\[\lim_{N_s,N_b \to \infty} \hat{V}_{sb} = 0.\]  

(12)

From Eq. (12) we find a direct physical interpretation for the interaction terms. The \(\hat{H}_{x,\Gamma}\) terms represent the anharmonic counterpart of the harmonic interactions, while the \(\hat{V}_{x,\Gamma}\) terms are purely anharmonic contributions which vanish in the harmonic limit.

The zeroth order Hamiltonian of Eq. (11), however, is not sufficient to obtain a high-quality fit of the vibrations of methane (see also [6]. The use of symmetrized operators of Eq. (9) makes it possible to construct higher order (quartic) terms in a straightforward and systematic way. For the study of the vibrational excitations of methane we propose to use the following \(T_d\) invariant quartic Hamiltonian

\[\hat{H} = \omega_1 \hat{H}_{s,A_1} + \omega_2 \hat{H}_{b,E} + \omega_3 \hat{H}_{s,F_2} + \omega_4 \hat{H}_{b,F_2} + \alpha_3 \hat{V}_{s,F_2} + \alpha_{34} \hat{V}_{sb} + X_{11} \left( \hat{H}_{s,A_1} \right)^2 + X_{22} \left( \hat{H}_{b,E} \right)^2 + X_{33} \left( \hat{H}_{s,F_2} \right)^2 + X_{44} \left( \hat{H}_{b,F_2} \right)^2 + X_{12} \left( \hat{H}_{s,A_1} \hat{H}_{b,E} \right) + X_{14} \left( \hat{H}_{s,A_1} \hat{H}_{b,F_2} \right) + X_{23} \left( \hat{H}_{b,E} \hat{H}_{s,F_2} \right) + X_{24} \left( \hat{H}_{b,E} \hat{H}_{b,F_2} \right) + X_{34} \left( \hat{H}_{s,F_2} \hat{H}_{b,F_2} \right)\]  

(13)
overtones, respectively.

The square brackets in Eq. (14) denote the tensor coupling under the point group $T_d$ and hence represent anharmonic vibrational interactions. The $g_{ij}$ terms are related to the vibrational angular momenta associated with the degenerate vibrations and give rise to a splitting of vibrational levels with the same values of $(\nu_1\nu_2\nu_3\nu_4)$ but with different $l_2$, $l_3$ and/or $l_4$. They can be expressed in terms of the symmetrized tensors of Eq. (7) as

$$\hat{l}^A_2 = -i \sqrt{2} \frac{1}{N_b} [\hat{T}^E_{-b} \times \hat{T}^E_{+,b}]^A_2 ,$$

$$\hat{l}^F_{x\gamma} = +i \sqrt{2} \frac{1}{N_x} [\hat{T}^F_{2-} \times \hat{T}^F_{+,x}]^F_{x\gamma} . \tag{14}$$

The square brackets in Eq. (14) denote the tensor coupling under the point group $T_d$. In the harmonic limit, the expectation value of the $\omega_i$, $\alpha_3$, $X_{ij}$ and $g_{ij}$ terms in Eq. (13) leads to the familiar Dunham expansion [7].

$$\sum_i \omega_i (v_i + \frac{d_i}{2}) + \sum_{i,j} X_{ij} (v_i + \frac{d_i}{2})(v_j + \frac{d_j}{2}) + \sum_{i,j} g_{ij} l_i l_j , \tag{15}$$

where $d_i$ is the degeneracy of the vibration. The $t_{ij}$ terms are quartic operators of the type discussed by Hecht [3] and give rise to further splittings of the vibrational levels $(\nu_1\nu_2\nu_3\nu_4)$ into its possible sublevels. They can be expressed in terms of the tensor operators of Eq. (7) as

$$\hat{O}_{xy} = \frac{1}{N_x N_y} \left( 6 \sum_{\gamma} [\hat{T}^F_{-x} \times \hat{T}^F_{-y}]^E_{\gamma} [\hat{T}^F_{+,y} \times \hat{T}^F_{+,x}]^E_{\gamma} -4 \sum_{\gamma} [\hat{T}^F_{-,x} \times \hat{T}^F_{-,y}]^F_{2\gamma} [\hat{T}^F_{+,y} \times \hat{T}^F_{+,x}]^F_{2\gamma} \right) ,$$

$$\hat{O}_{xx} = \frac{1}{N_x} \left( 8 \sum_{\gamma} [\hat{T}^E_{-,b} \times \hat{T}^F_{+,x}]^F_{1\gamma} [\hat{T}^E_{+,b} \times \hat{T}^F_{+,x}]^F_{1\gamma} -8 \sum_{\gamma} [\hat{T}^E_{-,b} \times \hat{T}^F_{-,x}]^F_{2\gamma} [\hat{T}^E_{+,b} \times \hat{T}^F_{+,x}]^F_{2\gamma} \right) . \tag{16}$$

In the harmonic limit the $t_{ij}$ terms have the same interpretation as in [2,8]. The $\hat{O}_{ss}$, $\hat{O}_{bb}$ and $\hat{O}_{sb}$ terms give rise to a splitting of the $E$ and $F_2$ vibrations belonging to the $(\nu_1\nu_2\nu_3\nu_4) = (00^02^02^0)$, $(00^00^22^0)$ and $(00^11^11^1)$ levels, respectively. Similarly, the $\hat{O}_{2s}$ and $\hat{O}_{2b}$ terms split the $F_1$ and $F_2$ vibrations belonging to the $(01^11^10^0)$ and $(01^10^01^1)$ overtones, respectively.
We remark that, whereas the $\omega_i$, $\alpha_3$ and $X_{ij}$ terms can be rewritten in terms of the Casimir invariants of $[7]$ and products thereof, the $g_{ij}$ and $t_{ij}$ terms cannot be expressed in this way. These interactions involve intermediate couplings with $\Gamma = A_2, F_1, E, F_2$ symmetry, that are not symmetric ($\Gamma = A_1$) as is the case for the invariant operators.

**IV. RESULTS**

The Hamiltonian of Eq. (13) involves 23 interaction strengths and the two boson numbers, $N_s$ and $N_b$. The vibron number associated with the stretching vibrations is determined from the spectroscopic constants $\omega_e$ and $x_e\omega_e$ for the CH molecule to be $N_s = 43$ $[11,7]$. The vibron number for the bending vibrations, which are far more harmonic than the stretching vibrations, is taken to be $N_b = 150$. We have carried out a least-square fit to the vibrational spectrum of methane including 44 experimental energies from $[6], [18] – [22]$ with equal weights.

The values of the fitted parameters are presented in the second column of Table I (Fit 1). In Table II we compare the results of our calculation with the experimentally observed energies. All predicted levels up to $V = \nu_1 + \nu_2 + \nu_3 + \nu_4 = 3$ quanta are included. The quality of the fit is expressed in terms of the r.m.s. deviation

$$\delta = \left[ \frac{\sum_{i=1}^{n} (E_{exp}^i - E_{cal}^i)^2}{(N_{exp} - N_{par})} \right]^{1/2},$$

where $N_{exp}$ is the total number of experimental energies and $N_{par}$ the number of parameters used in the fit. We find a good overall fit to the observed levels with a r.m.s. deviation of $\delta = 1.16 \text{ cm}^{-1}$ for 44 energies (and a standard deviation of $\sigma = 0.81 \text{ cm}^{-1}$). The deviations with experiment are fairly constant over the entire energy range up to 9000 cm$^{-1}$, the largest one being $\Delta E = -2.22 \text{ cm}^{-1}$. A statistical analysis of the error in the parameters (i.e. the variation in a given parameter such that the r.m.s. does not increase more than a certain fraction) shows that the fitted parameters are well determined. The cross-anharmonicity $X_{13}$ was not included in the fit, due to lack of data for the $(\nu_1 \nu_2 \nu_3 0)$ vibrations.

A particularly important role is played by the $\alpha_3$ term. Eq. (3) shows that this type of terms can be rewritten as particular higher order interactions in the operators $J_{\pm,i}$. In order to address the importance of this term, we have carried out a fit in the harmonic limit ($N_s \to \infty, N_b \to \infty$). In this limit the $\alpha_3$ term vanishes and the Hamiltonian of Eq. (13) is equivalent to the vibrational Hamiltonian of $[2]$, the harmonic frequencies $\omega_i$ and anharmonic constants $X_{ij}$, $g_{ij}$ and $t_{ij}$ having the same meaning. A comparison between the parameter values and the r.m.s. deviations of Fits 1 and 2 in Table II shows that the $\alpha_3$ term and the anharmonic effects in the interaction terms of Eq. (13) can only be compensated for in part by the anharmonicity constants $X_{ij}$. The r.m.s. deviation increases from $\delta = 1.16 \text{ cm}^{-1}$ for Fit 1 to $\delta = 20.42 \text{ cm}^{-1}$ for Fit 2.

For comparison we show in Table III the results of some other recent model calculations.
V. SUMMARY AND CONCLUSIONS

In summary, in this paper we have studied the vibrational excitations of methane in a model based on the use of symmetry-adapted internal coordinates, in which anharmonic effects are introduced in the local modes. We find an overall fit to the 44 observed levels with a r.m.s. deviation of $\delta = 1.16 \text{ cm}^{-1}$ (and a standard deviation of $\sigma = 0.81 \text{ cm}^{-1}$), which can be considered of spectroscopic quality. We pointed out that the $\alpha_3$ term in combination with the anharmonic effects in the other interaction terms plays an important role in obtaining a fit of this quality. Physically, these contributions arise from the anharmonic character of the local modes. They play an important role to describe the anharmonicities, especially for higher number of quanta. This conclusion is supported by earlier applications of this model to the Be$_4$ cluster \[13,26\], the H$_3^+$, Be$_3^+$ and Na$_3^+$ molecules \[14\], and two isotopes of the ozone molecule \[27\].

The present calculations only include interaction terms that are simultaneously diagonal in the total number of quanta $V = \nu_1 + \nu_2 + \nu_3 + \nu_4$, and in the polyad $V' = 2(\nu_1 + \nu_3) + \nu_2 + \nu_4$, but do not contain explicit Fermi interactions between the stretching and bending vibrations. It is interesting to note that despite the absence of these interactions which are generally considered to be necessary for an adequate description of methane, we do obtain a high quality fit. Fermi interactions can be included in the present model by constructing a Hamiltonian which is still diagonal in the polyad $V' = 2\nu_1 + \nu_2 + 2\nu_3 + \nu_4$ but that mixes the stretching and bending modes \[29\]. It is well-known that energies only are not sufficient to distinguish between various model calculations. Other quantities, such as infrared and Raman transitions or Franck-Condon factors are more sensitive to details in the wave functions than energies, and provide a better test of different models of molecular structure. Work along these directions is in progress \[29\].

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TABLE I. Parameters in cm$^{-1}$ obtained in the fit to the vibrational energies of CH$_4$. The last column shows the results in the harmonic limit ($N_s \to \infty$, $N_b \to \infty$).

| Parameter | Fit 1        | Fit 2        |
|-----------|--------------|--------------|
| $N_s$     | 43           | $\infty$    |
| $N_b$     | 150          | $\infty$    |
| $\omega_1$| 2977.60      | 2967.40      |
| $\omega_2$| 1554.83      | 1558.38      |
| $\omega_3$| 3076.45      | 3081.34      |
| $\omega_4$| 1332.22      | 1337.51      |
| $\alpha_3$| 582.87       | –            |
| $X_{11}$  | 3.69         | –21.30       |
| $X_{22}$  | 1.30         | –1.17        |
| $X_{33}$  | 5.43         | –10.79       |
| $X_{44}$  | –3.47        | –6.26        |
| $X_{12}$  | –3.60        | –3.39        |
| $X_{13}$  | –            | –            |
| $X_{14}$  | –2.86        | –3.10        |
| $X_{23}$  | –11.14       | –7.97        |
| $X_{24}$  | 1.00         | –5.37        |
| $X_{34}$  | –5.60        | –3.46        |
| $g_{22}$  | –0.46        | 0.37         |
| $g_{33}$  | 0.19         | –4.35        |
| $g_{44}$  | 4.07         | 4.98         |
| $g_{34}$  | –0.65        | –0.74        |
| $t_{33}$  | 0.40         | –1.25        |
| $t_{44}$  | 1.00         | 0.56         |
| $t_{34}$  | 0.21         | 0.24         |
| $t_{23}$  | –0.39        | –0.39        |
| $t_{24}$  | 0.13         | 0.91         |
| r.m.s.    | 1.16         | 20.42        |
TABLE II. Fit to vibrational excitations of CH$_4$. The values of the parameters are given in the second column of Table I. Here $\Delta E = E_{cal} - E_{exp}$. The experimental energies are taken from [3], [18]–[22]. The levels marked with an asterisk are taken from [23], but were not included in the fit. The wave numbers are given in cm$^{-1}$.

| $\Gamma$ | $(\nu_1\nu_2\nu_3\nu_4)$ | $E_{cal}$ | $E_{exp}$ | $\Delta E$ | $\Gamma$ | $(\nu_1\nu_2\nu_3\nu_4)$ | $E_{cal}$ | $E_{exp}$ | $\Delta E$ |
|----------|--------------------------|-----------|-----------|-----------|----------|--------------------------|-----------|-----------|-----------|
| $A_1$    | (1000)                   | 2916.32   | 2916.48   | -0.16     | (0111)   |                         | 5844.98   |           |           |
| $E$      | (0100)                   | 1533.46   | 1533.33   | 0.13      | (1200)   |                         | 5974.81   |           |           |
| $F_2$    | (0001)                   | 1309.86   | 1310.76   | -0.90     | (1011)   |                         | 7147.49   |           |           |
|          | (0010)                   | 3018.09   | 3019.49   | -1.40     | (0021)   |                         | 7303.38   |           |           |
|          |                          |           |           |           | (2100)   |                         | 7315.60   |           |           |
| $A_1$    | (0002)                   | 2587.77   | 2587.04   | 0.73      | (0120)   |                         | 7479.48   |           |           |
|          | (0200)                   | 3063.66   | 3063.65   | 0.01      | (0120)   |                         | 7557.17   |           |           |
|          | (0011)                   | 4323.81   | 4322.72   | 1.09      | (1020)   |                         | 8833.05   |           |           |
|          | (2000)                   | 5790.13   | 5790      | 0.13      | (0102)   |                         | 7147.53   |           |           |
|          | (0200)                   | 5966.57   | 5968.1    | -1.53     | (0102)   |                         | 4128.38   | 4128.57   | -0.19     |
| $E$      | (0002)                   | 2624.14   | 2624.62   | -0.48     | (0201)   |                         | 4364.39   | 4363.31   | 1.08      |
|          | (0200)                   | 3065.22   | 3065.14   | 0.08      | (0012)   |                         | 5620.08   |           |           |
|          | (0011)                   | 4323.09   | 4322.15   | 0.94      | (0012)   |                         | 5630.76   |           |           |
|          | (1100)                   | 4446.41   | 4446.41   | 0.00      | (1101)   |                         | 5755.58   |           |           |
|          | (0020)                   | 6045.03   | 6043.8    | 1.23      | (0111)   |                         | 5829.79   |           |           |
| $F_1$    | (0101)                   | 2845.35   | 2846.08   | -0.73     | (0111)   |                         | 5848.94   |           |           |
|          | (0011)                   | 4323.45   | 4322.58   | 0.57      | (0210)   |                         | 6061.57   |           |           |
|          | (0110)                   | 4537.57   | 4537.57   | 0.00      | (1011)   |                         | 7147.53   |           |           |
| $F_2$    | (0002)                   | 2612.93   | 2614.26   | -1.33     | (0021)   |                         | 7303.29   |           |           |
|          | (0101)                   | 2830.61   | 2830.32   | 0.29      | (0021)   |                         | 7343.21   |           |           |
|          | (1001)                   | 4223.46   | 4223.46   | 0.00      | (1110)   |                         | 7361.79   |           |           |
|          | (0011)                   | 4321.02   | 4319.21   | 1.81      | (0120)   |                         | 7518.70   |           |           |
|          | (0110)                   | 4543.76   | 4543.76   | 0.00      | (0030)   |                         | 8947.65   | 8947.95   | -0.30     |
|          | (1010)                   | 5845.53   |           |           | (0102)   |                         | 4143.09   | 4142.86   | 0.23      |
|          | (0020)                   | 6003.65   | 6004.65   | -1.00     | (0003)   |                         | 3931.36   | 3930.92   | 0.44      |
| $A_1$    | (0003)                   | 3909.20   | 3909.18   | 0.02      | (0201)   |                         | 4349.01   | 4348.77   | 0.24      |
|          | (0102)                   | 4131.92   | 4132.99   | -1.07     | (0201)   |                         | 4378.38   | 4379.10   | -0.72     |
|          | (0300)                   | 4595.26   | 4595.55   | -0.29     | (1002)   |                         | 5523.80   |           |           |
|          | (1002)                   | 5498.66   |           |           | (0012)   |                         | 5594.92   | 5597.14   | -2.22     |
|          | (0012)                   | 5617.16   |           |           | (0012)   |                         | 5620.68   |           |           |
|          | (0111)                   | 5836.11   |           |           | (0012)   |                         | 5632.36   |           |           |
|          | (1200)                   | 5973.26   |           |           | (1101)   |                         | 5740.86   |           |           |
|          | (1011)                   | 7147.56   |           |           | (0111)   |                         | 5830.28   |           |           |
|    | 7300.85 | 5848.46 |
|----|--------|---------|
| 0021 | 7300.85 | 5848.46 |
| 0120 | 7562.91 | 6054.58 |
| 3000 | 8583.81 | 6067.03 |
| 1020 | 8727.97 | 7094.16 |
| 0030 | 8975.64 | 7145.84 |
| A2   | 4161.52 | 4161.87 |
| 0012 | 8975.34 | -0.35   |
| 0102 | 4595.28 | 4595.32 |
| 0300 | 4161.87 | -0.04   |
| 0111 | 5844.61 | (0021)  |
| 0120 | 7550.53 | 7344.87 |
| E    | 4105.22 | 4105.15 |
| 0012 | 4105.15 | 0.07    |
| 0102 | 4152.15 | 4151.22 |
| 0300 | 4592.13 | 4592.03 |
| 0102 | 4151.22 | 0.93    |
| 0012 | 4592.03 | 0.10    |
| 1002 | 5535.04 | (0020)  |
| 0012 | 8594.90 | 8604.04 |
| 0012 | 5535.04 | (0020)  |
| 0012 | 9045.36 | 9045.92 |
TABLE III. Standard and r.m.s. deviations in cm$^{-1}$ of some recent calculations of vibrational energies of CH$_4$.

| Reference          | $N_{exp}$ | $N_{par}$ | $\sigma$ | $\delta$ |
|--------------------|-----------|-----------|----------|----------|
| Lemus and Frank [7]| 19        | 8         | 9.50     | 12.16    |
| Ma et al [24]      | 19        | 8         | 9.08     | 11.61    |
| Xie et al [25]     | 19        | 7         | 8.26     | 10.12    |
| Wiesenfeld [28]    | 35        | 9         | 8.80     | 10.21    |
| Halonen [8]        | 39        | 24        | 0.99     | 1.58     |
| present            | 44        | 23        | 0.81     | 1.16     |