A local anharmonic treatment of vibrations of methane

R. Lemus[1], F. Pérez-Bernal[2], A. Frank[1,3], R. Bijker[1] and J.M. Arias[2]

[1] *Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, A.P. 70-543, 04510 México D.F., México*

[2] *Departamento de Física Atómica, Molecular y Nuclear, Facultad de Física, Universidad de Sevilla, Apdo. 1065, 41080 Sevilla, España*

[3] *Instituto de Física, Laboratorio de Cuernavaca, A.P. 139-B, Cuernavaca, Morelos, México*

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^{-1} (and a r.m.s. deviation of 1.16 cm^{-1}).

Key words: Molecular vibrations, anharmonic model, methane

Se hace una descripción de las vibraciones de tensión y flexión de metano en el marco de un modelo local anarmónico de vibraciones moleculares. El uso de operadores y funciones adaptadas por simetría permite reducir el problema de valores propios a una forma diagonal. Para las 44 energías observadas se obtiene un ajuste con una desviación estándar de 0.81 cm^{-1} (correspondiente a una desviación cuadrática media de 1.16 cm^{-1}).

Descriptores: Vibraciones moleculares, modelo anarmónico, metano

PACS numbers: 33.20.Tp, 33.15.Mt, 03.65.Fd

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$_4$ 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 *ab initio* calculations, see *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 [6].

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 [7].

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 [8,9]. 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]

$$S_{x,\Gamma_\gamma} = \sum_{i=1}^{10} \alpha^i_{x,\Gamma_\gamma} S_i , \qquad P_i = \sum_{x,\Gamma_\gamma} \alpha^i_{x,\Gamma_\gamma} P_{x,\Gamma_\gamma} , \qquad (1)$$

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 Γ 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 [8,9]. In the present discussion we prefer to keep the redundant coordinate (with symmetry labels $x = b$, $\Gamma = A_1$), 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

$$\sqrt{\frac{\beta_{x,\Gamma}}{2\hbar}}\, S_{x,\Gamma_\gamma} - \frac{1}{\sqrt{2\beta_{x,\Gamma}\hbar}}\, iP_{x,\Gamma_\gamma} = b^\dagger_{x,\Gamma_\gamma} ,$$

$$\sqrt{\frac{\beta_{x,\Gamma}}{2\hbar}}\, S_{x,\Gamma_\gamma} + \frac{1}{\sqrt{2\beta_{x,\Gamma}\hbar}}\, iP_{x,\Gamma_\gamma} = b_{x,\Gamma_\gamma} . \qquad (2)$$

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

$$b^\dagger_{x,\Gamma_\gamma} = \sum_{i=1}^{10} \alpha^i_{x,\Gamma_\gamma} b^\dagger_i , \qquad b_{x,\Gamma_\gamma} = \sum_{i=1}^{10} \alpha^i_{x,\Gamma_\gamma} b_i . \tag{3}$$

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]. Hereto we construct an anharmonic representation of the local operators $b^\dagger_i$ and b_i through the correspondence [13,14]

$$b^\dagger_i \rightarrow a^\dagger_i \equiv \frac{\hat{J}_{-,i}}{\sqrt{N_i}} , \qquad b_i \rightarrow a_i \equiv \frac{\hat{J}_{+,i}}{\sqrt{N_i}} , \tag{4}$$

where $\hat{J}^2_i = \hat{J}^2_{0,i} + (\hat{J}_{+,i}\hat{J}_{-,i} + \hat{J}_{-,i}\hat{J}_{+,i})/2 = \hat{N}_i(\hat{N}_i + 2)/4$, i.e. $N_i/2 = j_i$ [14]. The anharmonic operators satisfy the commutation relation

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

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

$$[a^\dagger_i, \hat{v}_j] = \frac{1}{\sqrt{N_i}}[\hat{J}_{-,i}, \frac{\hat{N}_j}{2} - \hat{J}_{0,j}] = -\delta_{ij} \frac{\hat{J}_{-,i}}{\sqrt{N_i}} = -\delta_{ij} a^\dagger_i . \tag{5}$$

The operators $J_{\mu,i}$ with $\mu = \pm, 0$ together with the number operator $\hat{N}_i$ are the generators of $U_i(2)$. In the limit $N_i \rightarrow \infty$ we recover the harmonic description in terms of $b^\dagger_i$, b_i and $\hat{v}_i = b^\dagger_i b_i$. 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

$$\mathcal{G} = U_1(2) \otimes U_2(2) \otimes \ldots \otimes U_{10}(2) . \tag{6}$$

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]

$$\hat{T}^{\Gamma_\gamma}_{\mu,x} = \sum_{i=1}^{10} \alpha^i_{x,\Gamma_\gamma} \hat{J}_{\mu,i} . \tag{7}$$

3

The coefficients $\alpha^i_{\Gamma_\gamma,x}$ are the same as in Eq. (1). 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 $\hat{T}^{A_1}_{\mu,b}$ 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 $\mathcal{T}_d$. We use the standard labelling for the vibrational basis states: $(\nu_1 \nu_2^{l_2} \nu_3^{l_3} \nu_4^{l_4})$, where ν_1, ν_3 and ν_2, ν_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 ν_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 $\mathcal{T}_d$ invariant interactions that are at most quadratic in the generators and conserve the total number of quanta

$$\hat{\mathcal{H}}_{x,\Gamma} = \frac{1}{2N_x} \sum_\gamma \left(\hat{T}^{\Gamma_\gamma}_{-,x} \hat{T}^{\Gamma_\gamma}_{+,x} + \hat{T}^{\Gamma_\gamma}_{+,x} \hat{T}^{\Gamma_\gamma}_{-,x} \right) ,$$

$$\hat{\mathcal{V}}_{x,\Gamma} = \frac{1}{N_x} \sum_\gamma \hat{T}^{\Gamma_\gamma}_{0,x} \hat{T}^{\Gamma_\gamma}_{0,x} . \tag{8}$$

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

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

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

The zeroth order vibrational Hamiltonian is now written as

$$\hat{H}_0 = \omega_1\,\hat{\mathcal{H}}_{s,A_1} + \omega_2\,\hat{\mathcal{H}}_{b,E} + \omega_3\,\hat{\mathcal{H}}_{s,F_2} + \omega_4\,\hat{\mathcal{H}}_{b,F_2} + \omega_{34}\,\hat{\mathcal{H}}_{sb}$$

$$+\alpha_2\,\hat{\mathcal{V}}_{b,E} + \alpha_3\,\hat{\mathcal{V}}_{s,F_2} + \alpha_4\,\hat{\mathcal{V}}_{b,F_2} + \alpha_{34}\,\hat{\mathcal{V}}_{sb} \ . \tag{10}$$

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 $\hat{\mathcal{V}}_{A_1,s}$ has not been included since the combination

$$\sum_{\Gamma=A_1,F_2} \left(\hat{\mathcal{H}}_{s,\Gamma} + \hat{\mathcal{V}}_{s,\Gamma}\right) = \frac{1}{4N_s}\sum_{i=1}^{4}\hat{N}_i(\hat{N}_i + 2) \ , \tag{11}$$

corresponds to a constant $N_s + 2$. A similar relation holds for the bending interactions, but in this case the interaction $\hat{\mathcal{V}}_{b,A_1}$ has already been excluded in order to remove the spurious A_1 bending mode. The subscripts of the parameters correspond to the $(\nu_1\nu_2^{l_2}\nu_3^{l_3}\nu_4^{l_4})$ 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)

$$\lim_{N_x\to\infty}\hat{\mathcal{H}}_{x,\Gamma} = \frac{1}{2}\sum_{\gamma}\left(b^\dagger_{x,\Gamma_\gamma}b_{x,\Gamma_\gamma} + b_{x,\Gamma_\gamma}b^\dagger_{x,\Gamma_\gamma}\right) \ ,$$

$$\lim_{N_x\to\infty}\hat{\mathcal{V}}_{x,\Gamma} = 0 \ ,$$

$$\lim_{N_s,N_b\to\infty}\hat{\mathcal{H}}_{sb} = \frac{1}{2}\sum_{\gamma}\left(b^\dagger_{s,F_{2\gamma}}b_{b,F_{2\gamma}} + b_{s,F_{2\gamma}}b^\dagger_{b,F_{2\gamma}}\right) \ ,$$

$$\lim_{N_s,N_b\to\infty}\hat{\mathcal{V}}_{sb} = 0 \ . \tag{12}$$

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

The zeroth order Hamiltonian of Eq. (10), 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. (7) 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 $\mathcal{T}_d$ invariant quartic Hamiltonian

$$\hat{H} = \omega_1\,\hat{\mathcal{H}}_{s,A_1} + \omega_2\,\hat{\mathcal{H}}_{b,E} + \omega_3\,\hat{\mathcal{H}}_{s,F_2} + \omega_4\,\hat{\mathcal{H}}_{b,F_2} + \alpha_3\,\hat{\mathcal{V}}_{s,F_2}$$

$$+X_{11}\left(\hat{\mathcal{H}}_{s,A_1}\right)^2 + X_{22}\left(\hat{\mathcal{H}}_{b,E}\right)^2 + X_{33}\left(\hat{\mathcal{H}}_{s,F_2}\right)^2 + X_{44}\left(\hat{\mathcal{H}}_{b,F_2}\right)^2$$

$$+X_{12}\left(\hat{\mathcal{H}}_{s,A_1}\,\hat{\mathcal{H}}_{b,E}\right) + X_{14}\left(\hat{\mathcal{H}}_{s,A_1}\,\hat{\mathcal{H}}_{b,F_2}\right)$$

$$+X_{23}\left(\hat{\mathcal{H}}_{b,E}\,\hat{\mathcal{H}}_{s,F_2}\right) + X_{24}\left(\hat{\mathcal{H}}_{b,E}\,\hat{\mathcal{H}}_{b,F_2}\right) + X_{34}\left(\hat{\mathcal{H}}_{s,F_2}\,\hat{\mathcal{H}}_{b,F_2}\right)$$

$$+g_{22}\left(\hat{l}_{A_2}\right)^2 + g_{33}\sum_\gamma \hat{l}^{F_1}_{s,\gamma}\hat{l}^{F_1}_{s,\gamma} + g_{44}\sum_\gamma \hat{l}^{F_1}_{b,\gamma}\hat{l}^{F_1}_{b,\gamma} + g_{34}\sum_\gamma \hat{l}^{F_1}_{s,\gamma}\hat{l}^{F_1}_{b,\gamma}$$

$$+t_{33}\,\hat{\mathcal{O}}_{ss} + t_{44}\,\hat{\mathcal{O}}_{bb} + t_{34}\,\hat{\mathcal{O}}_{sb} + t_{23}\,\hat{\mathcal{O}}_{2s} + t_{24}\,\hat{\mathcal{O}}_{2b}\ . \tag{13}$$

Each one of the interaction terms of the Hamiltonian of Eq. (13) has a direct physical interpretation and a specific action on the various modes. The ω_i and α_3 terms have already been discussed in Eq. (12). The X_{ij} terms are quadratic in the operators $\hat{\mathcal{H}}_{x,\Gamma}$ and hence represent anharmonic vibrational interactions. The g_{ij} terms are related to the vibrational angular momenta associated with the degenerate vibrations [2] 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

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

$$\hat{l}^{F_1\gamma}_x = +i\,\sqrt{2}\,\frac{1}{N_x}[\hat{T}^{F_2}_{-,x}\times\hat{T}^{F_2}_{+,x}]^{F_1\gamma}\ . \tag{14}$$

The square brackets in Eq. (14) denote the tensor coupling under the point group $\mathcal{T}_d$ [7]. In the harmonic limit, the expectation value of the ω_i, α_3, X_{ij} and g_{ij} terms in Eq. (13) leads to the familiar Dunham expansion [17]

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

where d_i is the degeneracy of the vibration. The t_{ij} terms are quartic operators of the type discussed by Hecht [2] 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

$$\hat{\mathcal{O}}_{xy} = \frac{1}{N_xN_y}\left(6\sum_\gamma[\hat{T}^{F_2}_{-,x}\times\hat{T}^{F_2}_{-,y}]^{E\gamma}\,[\hat{T}^{F_2}_{+,y}\times\hat{T}^{F_2}_{+,x}]^{E\gamma}\right.$$

$$\left.-4\sum_\gamma[\hat{T}^{F_2}_{-,x}\times\hat{T}^{F_2}_{-,y}]^{F_2\gamma}\,[\hat{T}^{F_2}_{+,y}\times\hat{T}^{F_2}_{+,x}]^{F_2\gamma}\right)\ ,$$

$$\hat{\mathcal{O}}_{2x} = \frac{1}{N_bN_x}\left(8\sum_\gamma[\hat{T}^{E}_{-,b}\times\hat{T}^{F_2}_{-,x}]^{F_1\gamma}\,[\hat{T}^{E}_{+,b}\times\hat{T}^{F_2}_{+,x}]^{F_1\gamma}\right.$$

$$\left.-8\sum_\gamma[\hat{T}^{E}_{-,b}\times\hat{T}^{F_2}_{-,x}]^{F_2\gamma}\,[\hat{T}^{E}_{+,b}\times\hat{T}^{F_2}_{+,x}]^{F_2\gamma}\right)\ . \tag{16}$$

In the harmonic limit the t_{ij} terms have the same interpretation as in [2,6]. The $\hat{\mathcal{O}}_{ss}$, $\hat{\mathcal{O}}_{bb}$ and $\hat{\mathcal{O}}_{sb}$ terms give rise to a splitting of the E and F_2 vibrations belonging to the $(\nu_1\nu_2^{l_2}\nu_3^{l_3}\nu_4^{l_4}) = (00^02^20^0)$, $(00^00^02^2)$ and $(00^01^11^1)$ levels, respectively. Similarly, the $\hat{\mathcal{O}}_{2s}$ and $\hat{\mathcal{O}}_{2b}$ 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 ω_i, α_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 ω_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

$$\delta = \left[\sum_{i=1}^{n} (E_{exp}^i - E_{cal}^i)^2 / (N_{exp} - N_{par}) \right]^{1/2} , \tag{17}$$

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 $\delta = 1.16$ cm^{-1} for 44 energies (and a standard deviation of $\sigma = 0.81$ cm^{-1}). The deviations with experiment are fairly constant over the entire energy range up to 9000 cm^{-1}, the largest one being $\Delta E = -2.22$ 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 $(\nu_10\nu_30)$ vibrations.

A particularly important role is played by the α_3 term. Eq. (5) shows that this type of terms can be rewritten as particular higher order interactions in the operators $\hat{J}_{\pm,i}$. 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 α_3 term vanishes and the Hamiltonian of Eq. (13) is equivalent to the vibrational Hamiltonian of [2], the harmonic frequencies ω_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 I shows that the α_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 $\delta = 1.16$ cm^{-1} for Fit 1 to $\delta = 20.42$ 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 $\delta = 1.16$ cm^{-1} (and a standard deviation of $\sigma = 0.81$ cm^{-1}), which can be considered of spectroscopic quality. We pointed out that the α_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].

REFERENCES

[1] B. Bobin and J. Moret-Bailly, Spectrochim. Acta **51A** (1995) 1231.

[2] K.T. Hecht, J. Mol. Spectr. **5** (1960) 355 and 390.

[3] D.L. Gray and A.G. Robiette, Mol. Phys. **37** (1979) 1901.

[4] W.T. Raynes, P. Lazzeretti, R. Zanasi, A.J. Sadlej and P.W. Fowler, Mol. Phys. **60** (1987) 509.

[5] T.J. Lee, J.M.L. Martin and P.R. Taylor, J. Chem. Phys. **102** (1995) 254.

[6] L. Halonen, J. Chem. Phys. **106** (1997) 831.

[7] R. Lemus and A. Frank, J. Chem Phys. **101** (1994) 8321.

[8] A.R. Hoy, I.M. Mills and G. Strey, Mol. Phys. **24** (1972) 1265.

[9] E.B. Wilson, J.C. Decius and P.C. Cross, 'Molecular vibrations', (Dover, 1980).

[10] Y. Alhassid, F. Gürsey and F. Iachello, Ann. Phys. (N.Y.) **148** (1983) 346.

[11] F. Iachello and R.D. Levine, 'Algebraic Theory of Molecules', (Oxford University Press, 1995).

[12] A. Frank and P. van Isacker, 'Algebraic Methods in Molecular & Nuclear Structure Physics', (Wiley Interscience, 1994).

[13] F. Pérez-Bernal, R. Bijker, A. Frank, R. Lemus and J.M. Arias, Chem. Phys. Lett. **258** (1996) 301.

[14] A. Frank, R. Lemus, R. Bijker, F. Pérez-Bernal and J.M. Arias, Ann. Phys. (N.Y.) **252** (1996) 211.

[15] R. Lemus, F. Pérez-Bernal, A. Frank, R. Bijker and J.M. Arias, Phys. Rev. A **56** (1997) 4337.

[16] A. Frank, R. Lemus, F. Pérez-Bernal and R. Bijker, preprint, submitted.

[17] G. Herzberg, 'The Spectra and Structures of Simple Radicals', (Dover, 1971).

[18] J.P. Champion, J.C. Hilico, C. Wenger and L.R. Brown, J. Mol. Spectrosc. **133** (1989) 256.

[19] J.C. Hilico (private communication, 1996).

[20] M. Chevalier, A. de Martino and F. Michelot, J. Mol. Spectrosc. **131** (1988) 382.

[21] D. Bermejo and S. Montero, J. Chem. Phys. **81** (1984) 3835.

[22] J.S. Margolis, Appl. Opt. **29** (1990) 2295.

[23] G. Herzberg, 'Infrared and Raman Spectra of Polyatomic Molecules', (Van Nostrand, 1945).

[24] Zhong-Qi Ma, Xi-Wen Hou and Mi Xie, Phys. Rev. **A53** (1996) 2173.

[25] Mi Xie, Xi-Wen Hou and Zhong-Qi Ma, Chem. Phys. Lett. **262** (1996) 1.

[26] A. Frank, R. Lemus, R. Bijker, F. Pérez-Bernal and J.M. Arias, Rev. Mex. Fís. **42**, Suplemento 1 (1996) 73.

[27] F. Pérez-Bernal, J.M. Arias, A. Frank, R. Lemus and R. Bijker, J. Mol. Spectrosc. **184** (1997) 1.

[28] L. Wiesenfeld, J. Molec. Spectrosc. **184** (1997) 277.

[29] R. Lemus, A. Frank and R. Bijker. Work in progress.

TABLES

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	∞
N_b	150	∞
ω_1	2977.60	2967.40
ω_2	1554.83	1558.38
ω_3	3076.45	3081.34
ω_4	1332.22	1337.51
α_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

10

TABLE II. Fit to vibrational excitations of CH$_4$. The values of the parameters are given in the second column of TableI. Here $\Delta E = E_{cal} - E_{exp}$. The experimental energies are taken from [6], [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}.

Γ	$(\nu_1\nu_2\nu_3\nu_4)$	E_{cal}	E_{exp}	ΔE	Γ	$(\nu_1\nu_2\nu_3\nu_4)$	E_{cal}	E_{exp}	ΔE
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	F_1	(0003)	3920.46	3920.50	−0.04
	(0020)	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)	4323.15	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			F_2	(0003)	3871.29	3870.49	0.80
	(0020)	6003.65	6004.65	−1.00		(0003)	3931.36	3930.92	0.44
						(0102)	4143.09	4142.86	0.23
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		

	(0021)	7300.85				(0111)	5848.46	
	(0120)	7562.91				(0210)	6054.58	
	(3000)	8583.81				(0210)	6067.03	
	(1020)	8727.97				(2001)	7094.16	
	(0030)	8975.64	8975.34	0.30		(1011)	7145.84	
A_2	(0102)	4161.52	4161.87	−0.35		(0021)	7266.11	
	(0300)	4595.28	4595.32	−0.04		(0021)	7303.38	
	(0111)	5844.61				(0021)	7344.87	
	(0120)	7550.53				(1110)	7365.83	
E	(0102)	4105.22	4105.15	0.07		(0120)	7514.67	7514[*)]
	(0102)	4152.15	4151.22	0.93		(2010)	8594.90	8604[*)]
	(0300)	4592.13	4592.03	0.10		(1020)	8786.05	8807[*)]
	(1002)	5535.04				(0030)	8907.91	8906.78	1.13
	(0012)	5620.36				(0030)	9045.36	9045.92	−0.56
	(0111)	5836.45						

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}	σ	δ
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 [6]	39	24	0.99	1.58
present	44	23	0.81	1.16