Application of a symmetry adapted algebraic model to the vibrational spectrum of methane

R. Lemus, F. Pérez-Bernal, A. Frank, R. Bijker and J.M. Arias

1 Instituto de Ciencias Nucleares, U.N.A.M., 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

1 Algebraic model

Recently, a symmetry-adapted version of the vibron model has been developed [1-4]. The aim of this work is to present the description of all stretching and bending vibrations of the methane molecule in the framework of such a model.

In the present algebraic approach a $U(2)$ algebra is associated with each relevant interatomic interaction. For the CH$_4$ molecule we have four $U(2)$ algebras corresponding to the C-H interactions and six more representing the H-H couplings. The assignments and the choice of the Cartesian coordinate system are the same as in [1]. The molecular dynamical group is then given by the product $U_1(2) \otimes \ldots \otimes U_{10}(2)$, where each $U_i(2)$ algebra $(i = 1, \ldots, 10)$ is generated by the set $\{ \hat{G}_i \} \equiv \{ \hat{N}_i, \hat{J}_{+i}, \hat{J}_{-i}, \hat{J}_{0,i} \}$, which satisfies the commutation relations

\[
\begin{align*}
[\hat{J}_{0,i}, \hat{J}_{\pm,i}] &= \pm \hat{J}_{\pm,i}, \\
[\hat{J}_{+i}, \hat{J}_{-i}] &= 2 \hat{J}_{0,i}, \\
[\hat{N}_i, \hat{J}_{\mu,i}] &= 0,
\end{align*}
\]

with $\mu = \pm, 0$. The labeling is such that $i = 1, \ldots, 4$ correspond to the C-H couplings while the other values of $i$ are associated with H-H interactions [1]. Here $\hat{N}_i$ is the $i$-th boson number operator. All physical operators are expressed in terms of the generators $\{ \hat{G}_i \}$, and hence commute with the number operators $\hat{N}_i$. Since $\hat{J}_{0,i}^2 = \hat{N}_i(\hat{N}_i + 2)/4$ we can make the identification $j_i = \hat{N}_i/2$. The eigenvalues of $\hat{J}_{0,i}$ are restricted to $m_i \geq 0$ and can have the values $m_i = N_i/2, (N_i - 2)/2, \ldots, 1/2$ or $0$ for $N_i$ odd or even, respectively [1]. The local basis states for each oscillator are usually written as $|N_i,v_i\rangle$, where $v_i = (N_i - 2m_i)/2 = 0, 1, \ldots, [N_i/2]$ denotes the number of oscillator quanta in the $i$-th oscillator. For the CH$_4$ molecule there are two different boson numbers, $N_s$ for the C-H couplings and $N_b$ for the H-H couplings, which correspond to the stretching and bending modes, respectively.

The symmetry of methane is taken into account by projecting the local operators $\{ \hat{G}_i \}$, which act on bond $i$, on the irreducible representations $\Gamma$ of the tetrahedral
group $\mathcal{T}_d$. For the $\hat{J}_{\mu,i}$ generators of Eq. (1) we obtain the $\mathcal{T}_d$ tensors

$$\hat{T}_{\mu,\gamma}^{x} = \sum_{i=1}^{10} \alpha_{\gamma,i}^{x} \hat{J}_{\mu,i},$$

where $\gamma$ denotes the component of $\Gamma$, and the label $x$ refers to stretching (s) or bending (b). The explicit expressions for the tensors are similar to the one phonon wave functions expansions given in []. The algebraic Hamiltonian is constructed by repeated couplings of these tensors to a total symmetry $A_1$.

The methane molecule has nine vibrational degrees of freedom. Four of them correspond to the fundamental stretching modes ($A_1 \oplus F_2$) and the other five to the fundamental bending modes ($E \oplus F_2$) []. The projected tensors of Eq. (2) 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 $\hat{T}_{\mu,1}^{A_1,b}$ as the operator associated to a spurious mode. This identification makes it possible to eliminate the spurious states exactly. This can be achieved by (i) constructing the physical Hamiltonian by simply ignoring the $\hat{T}_{\mu,1}^{A_1,b}$ tensor in the coupling procedure, and (ii) diagonalizing this Hamiltonian in a symmetry-adapted basis from which the spurious mode has been removed following the procedure of [].

According to the above procedure, we construct the $\mathcal{T}_d$ invariant interactions that are at most quadratic in the generators and conserve the total number of quanta

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

$$\hat{V}_{\Gamma_x} = \frac{1}{N_x} \sum_{\gamma} \hat{T}_{0,\gamma}^{x} \hat{T}_{0,\gamma}^{x}. \quad (3)$$

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. (3), there are two stretching-bending interactions which will not be considered at the moment.

The zeroth order vibrational Hamiltonian is then written as

$$\hat{H}_0 = \omega_1 \hat{H}_{A_1,s} + \omega_2 \hat{H}_{E,b} + \omega_3 \hat{H}_{F_2,s} + \omega_4 \hat{H}_{F_2,b} + \alpha_2 \hat{V}_{E,b} + \alpha_3 \hat{V}_{F_2,s} + \alpha_4 \hat{V}_{F_2,b} \quad (4)$$

The interaction $\hat{V}_{A_1,s}$ has not been included since the combination $\sum_{\Gamma}(\hat{H}_{\Gamma_x} + \hat{V}_{\Gamma_x})$ corresponds to the constant $N_s + 2$. A similar situation is present for the bending interactions, but in this case the interaction $\hat{V}_{A_1,b}$ 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$_4$. Here $\nu_1, \nu_2, \nu_3$ and $\nu_4$ denote the number of quanta in the $A_1,s, E_b, F_2,s$ and $F_2,b$ modes, respectively. The labels $l_i$ are related to the vibrational angular momentum associated with degenerate vibrations []. In the harmonic limit the interactions
of Eqs. (3) and (4) attain a particularly simple form, which can be directly related to configuration space interactions [1-4]. The $\hat{H}_{T_s}$ terms represent the anharmonic counterpart of the harmonic interactions, while the $\hat{V}_{T_s}$ terms are purely anharmonic contributions which vanish in the harmonic limit.

The zeroth order Hamiltonian of Eq. (1) is not sufficient to obtain a high-quality fit of the vibrations of methane. Several other physically meaningful interaction are essential for such a fit. For the study of the vibrational excitations of methane we use the $T_d$ invariant Hamiltonian

$$\hat{H} = \omega_1 \hat{H}_{A_1, s} + \omega_2 \hat{H}_{E_b} + \omega_3 \hat{H}_{F_{2, s}} + \omega_4 \hat{H}_{F_{2, b}} + \alpha_3 \hat{V}_{F_{2, s}} + X_{11} \left( \hat{H}_{A_1, s} \right)^2 + X_{22} \left( \hat{H}_{E_b} \right)^2 + X_{33} \left( \hat{H}_{F_{2, s}} \right)^2 + X_{44} \left( \hat{H}_{F_{2, b}} \right)^2 + X_{12} \left( \hat{H}_{A_1, s} \hat{H}_{E_b} \right) + X_{14} \left( \hat{H}_{A_1, s} \hat{H}_{F_{2, b}} \right) + X_{23} \left( \hat{H}_{E_b} \hat{H}_{F_{2, s}} \right) + X_{24} \left( \hat{H}_{E_b} \hat{H}_{F_{2, b}} \right) + X_{34} \left( \hat{H}_{F_{2, s}} \hat{H}_{F_{2, b}} \right) + g_{22} \left( \hat{i}^2 \right)^2 + g_{33} \sum_{\gamma} \hat{i}^2 \hat{i}^2 + g_{34} \sum_{\gamma} \hat{i}^2 \hat{i}^2 + g_{44} \sum_{\gamma} \hat{i}^2 \hat{i}^2 + t_{33} \hat{O}_{ss} + t_{44} \hat{O}_{bb} + t_{34} \hat{O}_{sb} + t_{23} \hat{O}_{gs} + t_{24} \hat{O}_{gb} . \tag{5}$$

The $X_{ij}$ terms are quadratic in the operators $\hat{H}_{T_s}$ and hence represent anharmonic vibrational interactions. The $g_{ij}$ terms are related to the vibrational angular momenta associated with the degenerate vibrations [1-3].

In the harmonic limit the expectation value of the diagonal terms in Eq. (5) leads to the familiar Dunham expansion [1].

$$\sum_i \omega_i \left( v_i + \frac{d_i}{2} \right) + \sum_{j \geq i} \sum_i X_{ij} \left( v_i + \frac{d_i}{2} \right) \left( v_j + \frac{d_j}{2} \right) + \sum_{j \geq i} \sum_i g_{ij} l_i l_j . \tag{6}$$

Here $d_i$ is the degeneracy of the vibration. The $t_{ij}$ terms in Eq. (5) give rise to further splittings of the vibrational levels $(\nu_1, \nu_2, \nu_3, \nu_4)$ into its possible sublevels [1]. Their explicit expressions are given in ref. [2].

## 2 Results

The Hamiltonian of Eq. (5) 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 $N_s = 43$ [1]. 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 energies. We find an overall fit to the observed levels with a r.m.s. deviation which is an order of magnitude better than in previous studies. While the r.m.s. deviations of [1] and [2] are 12.16 and 11.61 cm$^{-1}$ for 19 energies, we find a r.m.s. of 1.16 cm$^{-1}$ for 44 energies.
The values of the fitted parameters as well as all predicted levels up to $V = 3$ are given in ref. [1].

The $\alpha_3$ term is completely anharmonic in origin and has no counterpart in the harmonic limit. In order to address the importance of this term in Eq. (5) we have carried out another calculation without this term. With one less interaction term the r.m.s. deviation increases from 1.16 to 4.48 cm$^{-1}$. This shows the importance of the term proportional to $\alpha_3$ to obtain an accurate description of the anharmonicities that are present in the data. The absence of the $\alpha_3$ term in the second calculation can only partially be compensated by the anharmonicity constants $X_{ij}$ [2].

3 Conclusions

In summary, in this work we present the description of vibrational excitations of methane in a symmetry-adapted algebraic model. We find an overall fit to the 44 observed levels with a r.m.s. deviation of 1.16 cm$^{-1}$, which can be considered of spectroscopic quality. We pointed out that the $V_{F_2,s}$ term in combination with the anharmonic effects in the other interaction terms plays a crucial role in obtaining a fit of this quality. Purely anharmonic terms of this sort arise naturally in the symmetry-adapted algebraic model, but vanish in the harmonic limit. Physically, these contributions arise from the anharmonic character of the interatomic interactions, and seem to play an important role when dealing with molecular anharmonicities.

These studies suggest that the symmetry-adapted algebraic model provides a numerically efficient tool to study molecular vibrations with high precision. The main difference with other algebraic methods is the use of symmetry-adapted tensors in the construction of the Hamiltonian. In this approach, the interactions can be constructed in a systematic way, each term has a direct physical interpretation, and spurious modes can be eliminated exactly.

Acknowledgments

We thank Prof. J.C. Hilico for his interest and for making available to us his compilation of observed level energies. This work was supported in part by the European Community under contract nr. C11*-CT94-0072, DGAPA-UNAM under project IN105194, CONACyT-México under project 400340-5-3401E and Spanish DGCYT under project PB92-0663.
References

[1] A. Frank, R. Lemus, R. Bijker, F. Pérez-Bernal and J.M. Arias, preprint [chem-ph/9603002], Revista Mexicana de Física, as Proceedings of the ‘XIX Oaxtepec Symposium on Nuclear Physics’, Oaxtepec, January 3-6, 1996.

[2] F. Pérez-Bernal, R. Bijker, A. Frank, R. Lemus and J.M. Arias, *Chem. Phys. Lett.* **258**, 301-306 (1996).

[3] A. Frank, R. Lemus, R. Bijker, F. Pérez-Bernal and J.M. Arias, *Ann. of Phys.* Nov. (1996) In press.

[4] F. Pérez-Bernal, J.M. Arias, A. Frank, R. Lemus and R. Bijker, preprint [chem-ph/9605001], submitted to *Journal of Molecular Spectroscopy*.

[5] R. Lemus and A. Frank, *J. Chem Phys.* **101**, 8321-8332 (1994).

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

[7] G. Herzberg, ‘Infrared and Raman Spectra of Polyatomic Molecules’, (Van Nostrand, 1945).

[8] F. Iachello and S. Oss, *Phys. Rev. Lett.* **66**, 2976-2980 (1991).

[9] A. Frank and R. Lemus, *Phys. Rev. Lett.* **68**, 413 (1992).

[10] K.T. Hecht, *J. Mol. Spectr.* **5**, 355-389 (1960).

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

[12] Zhong-Qi Ma, Xi-Wen Hou and Mi Xie, preprint [chem-ph/9604002], to be published in Physical Review A.