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Ethane Internal Rotation -Vibrational Hamiltonian

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Abstract One of the main purposes of a theoretical spectroscopist is to propose a model to reproduce the experimental spectra available in the literature as accurate and with as much physical information as possible. In this case it has been studied the Far infrared and Infrared spectra of non-rigid molecules, introducing in the Vibrational Potential their dependence on the large amplitude variables. The molecule that has been selected to test our proposed Hamiltonian is ethane which is a very well studied molecule. The molecule is a non-rigid molecule and their experimental spectra have been reported in the literature.

Keywords: Ethane, *ab initio*, FIR-IR Spectrum.

Resumen Uno de los objetivos principales de un espectroscopista teórico es generar un modelo que reproduzca los espectros experimentales con la mayor precisión e información física posible. En este caso se estudió el espectro en el Infrarrojo lejano e Infrarrojo de moléculas no rígidas introduciendo en el potencial vibracional su dependencia de las variables de gran amplitud. La molécula de etano fue seleccionada para comprobar nuestro Hamiltoniano propuesto, ya que es una molécula ampliamente estudiada.; además de ser una molécula no rígida cuyo espectro experimental ha sido reportado en la literatura.

Palabras clave: Etano, *ab initio*, espectro de ir lejano.

Introduction

A non-rigid molecule [1,2] is a molecule with internal motions (large amplitude motions) associated to low energy barriers, that interchange various isoenergetic structures, giving rise to a Far-Infrared spectrum. At the same time these molecules have normal modes of vibration (variations of angles and distances) associated to the vibrational spectrum in the Infrared region.

One can use a theoretical model in order to reproduce the experimental spectra reported in the literature. Both motions can be considered independent at a first approach due to its difference in energy, even though in order to have a more accurate reproduction of the experimental spectra one has to consider the interaction between both motions.

The purpose of this work is to generate a theoretical and systematic model that will take in consideration the vibrational (Infrared) spectrum dependence with respect to the large amplitude coordinates. Using the model previously mention the final idea is to obtain a theoretical spectrum that can reproduce more precisely the experimental data available and at the same time to contain more physical information of the system.

One has to choose a widely studied theoretically and experimentally molecule in order to give support to our study, ethane [3, 4, 5] will be used as good example in this study. The coordinates to be considered are the internal large amplitude rotational angle 'θ' which defines the rotation of one methyl group with respect to the other one and the normal vibrational C-C stretching coordinate. This work will contribute to the high resolution spectroscopy of ethane. In general the model that is developed can be generalized to study the IR spectra of non rigid molecules.

Theory

As mention in the introduction, the molecular system selected for the present study is ethane.

The Hamiltonian to be solved can be associated to three different motions (external rotation, internal rotation and vibrational motion). Considering the difference in energy the hamiltonian at a first approach can be solved separately:

$$\hat{H} = \hat{H}_{\text{ext-rot}} + \hat{H}_{\text{int-rot}} + \hat{H}_{\text{vib}} \dots \dots \quad (1)$$

The total Hamiltonian must represent the non-rigid symmetry group (SG) of the molecule^[1]

$$S = [e_3^1 \wedge U^1] \wedge D_3 \sim G_{36}. \quad (2)$$

Each partial Hamiltonian can be written as follows:

External rotational Hamiltonian:

$$\hat{H}_{\text{ext-rot}} = hA\hat{J}_a^2 + hB\hat{J}_b^2 + hC\hat{J}_c^2 \quad (3)$$

where A B and C are the moments of inertia, *h* is the Plank Constant and \hat{J}_a^2 , \hat{J}_b^2 , \hat{J}_c^2 the corresponding angular momentum operators, in the principal axes system.

Internal rotational Hamiltonian:

For this case in order to make the Hamiltonian simpler it will be taken only the H-C-C-H dihedral angle (θ) as internal variable:

$$\hat{H}_{\text{int-rot}} = -\frac{\partial}{\partial \theta} \beta_{\text{int-rot}}(\theta) \frac{\partial}{\partial \theta} + V_{\text{int-rot}}(\theta). \quad (4)$$

For simplicity, the only internal variable considered in this Hamiltonian is the H-C-C-H dihedral angle.

$$\hat{H}_{\text{int-rot}} = -\beta_{\text{int-rot}} \frac{\partial^2}{\partial \theta^2} + V_{\text{int-rot}}(\theta). \quad (5)$$

The int-rot potential is expressed as an expansion in terms of $\cos(\theta)$ functions and it has to be a symmetry adapted θ function ($f(\theta) = f(\theta+120^\circ)$).

$$V_{\text{int-rot}}(\theta) = \sum_n V_{\text{int-rot},3n} \cos(3n\theta). \quad (6)$$

The potential will be truncated up to third order terms:

$$V_{\text{int-rot}}(\theta) = V_{\text{int-rot},0} + V_{\text{int-rot},3} \cos(3\theta) + V_{\text{int-rot},6} \cos(6\theta) + V_{\text{int-rot},9} \cos(9\theta) \quad (7)$$

Vibrational Hamiltonian

Only one normal vibrational mode (C-C stretching) is being considered:

$$\hat{H}_{\text{vib}} = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial S^2} + V_{\text{vib}}(S). \quad (8)$$

The Hamiltonian is written as a function of the internal displacement coordinate defined in terms of the carbon-carbon distance displacement ($\Delta(\text{C-C})$) around the equilibrium position:

$$S = \sqrt{\mu} (\Delta(\text{C-C})), \quad (9)$$

Where μ is the reduce mass of two carbon atoms, each one with mass m_c .

$$\mu = \frac{m_c^2}{2m_c}. \quad (10)$$

The vibrational potential energy ($V_{\text{vib}}(S)$) can be written as a Taylor expansion

$$V_{\text{vib}}(S) = \sum_n \frac{1}{n!} V_{\text{vib}}^{(n)} S^n, \quad (11)$$

Where:

$$V_{\text{vib}}^{(n)} = \left(\frac{\partial^n V_{\text{vib}}(S)}{\partial S^n} \right)_{eq}. \quad (12)$$

Each term must be of a certain order of magnitude in order for the series to converge, and in this particular case the function will be truncated up to the third order term:

$$V_{\text{vib}}(S) = V_0 + \frac{1}{2} V_{\text{vib}}'' S^2 + \frac{1}{6} V_{\text{vib}}''' S^3. \quad (13)$$

Up to this point the internal rotation and vibrational Hamiltonians have been considered as independent. In order to consider the dependence of the vibrational Hamiltonian (H_{vib}) in terms of the internal variable θ , the potential function can be written as function of both variables (S and θ):

$$V_{\text{vib}}(S, \theta) = V_0(\theta) + \frac{1}{2} V(\theta)''_{\text{vib}} S^2 + \frac{1}{6} V(\theta)'''_{\text{vib}} S^3. \quad (14)$$

Vibrational Spectra can be obtained by calculating the vibrational part in two different ways: a) θ -independent (equation 10) and b) θ -dependent (equation 11)

Methodology

Once that the system and the methodology have been selected the first thing to be done is to obtain the minimum energy conformation by using the Gaussian03 program, MP2 method, 6-311G** basis set. At the same time the harmonic analysis of the minimum was also done.

In Table 1 it is observed that the method and the basis used in this work reproduce quite reasonably the more precise methods reported in the literature. Other results obtained are the Rotational constants and the frequencies under study (Tables 2 and 3).

The method for calculating the β parameter from the optimized geometry is well described in the literature [7, 8] and it has been used for the ethane molecule.

$$\beta = 10.76190 \text{ cm}^{-1} \quad (15)$$

As it was mentioned before, it will be considered a constant and not q dependent.

By using the same method the energies at different values of θ (each $\Delta\theta = 10^\circ$) were calculated:

Table 1. Minimum energy Conformation ($\theta = 60^\circ$)

parameters	6-311G**	CC-pCVTZ [6]
C-C	1.5420 Å	1.5265 Å
C-H	1.0954 Å	1.0908 Å
H-C-H	107.8368°	107.68°
H-C-C	111.0652°	111.21°
θ	60°	60°
E(cm ⁻¹)	17,428,896.3	

Table 2. Rotational constants.

A (cm ⁻¹)	B (cm ⁻¹)	C (cm ⁻¹)
2.6680	0.6577	0.6577

Table 3. Frequencies.

Frequency (cm ⁻¹)	Normal mode
327.5665	CH ₃ Rotation
1012.7524	C-C Stretching

Table 4. Potential Energies at different θ angle.

	0°	10°	20°	30°	40°	50°	60°
E (cm ⁻¹)	1135.07	1057.8	847.399	562.385	280.037	74.897	0

Each value and conformation is considered a partial minimum, and the int-rot potential energy is obtained by fitting the energies to the symmetry adapted function expressed in eq. (7):

$$V_{\text{int-rot}}(\theta) = 565.0016 \text{ cm}^{-1} + 567.4783 \text{ cm}^{-1} \cos 3\theta + 2.5786 \text{ cm}^{-1} \cos 6\theta + 0.0576 \text{ cm}^{-1} \cos 9\theta. \quad (16)$$

For each partial minimum conformation the C-C distance is varied from -0.04 Å up to 0.04 Å in 0.005 Å increments and keeping constant the other molecular parameters. The results are fitted to the V_{vib} function (eq. 14) for each θ angle. This vibrational potentials are the ones called non θ -dependent, because θ is a parameter and not a function.

Vibrational potentials for each θ angle

$$\begin{aligned} V_{\text{vib}}(S, 0^\circ) &= 35.6086 S^2 - 1.0556 S^3 \\ V_{\text{vib}}(S, 10^\circ) &= 35.6303 S^2 - 1.0576 S^3 \\ V_{\text{vib}}(S, 20^\circ) &= 35.7150 S^2 - 1.0587 S_1^3 \\ V_{\text{vib}}(S, 30^\circ) &= 35.8320 S^2 - 1.0634 S_1^3 \\ V_{\text{vib}}(S, 40^\circ) &= 35.9457 S^2 - 1.0687 S_1^3 \\ V_{\text{vib}}(S, 50^\circ) &= 36.0297 S^2 - 1.0729 S_1^3 \\ V_{\text{vib}}(S, 60^\circ) &= 35.9539 S^2 - 1.0688 S_1^3 \end{aligned} \quad (17)$$

This potentials will be useful to obtained the so called non coupled spectra because the vibrational potential is not θ -dependent.

In order to introduce the angle dependence into the V vibrational potential each of the parameters $V(S, \theta)^n_{\text{vib}}$ in equation (17) are fitted to a symmetry function of the θ angle:

$$V(\theta)^n_{\text{vib}} = V^n_0 + V^n_3 \cos 3\theta + V^n_6 \cos 6\theta + V^n_9 \cos 9\theta \quad (18)$$

The final result is a θ -dependent vibrational potential, similar to eq. (14), which will be used for obtaining the so called coupled spectra where the vibrational potential includes the θ dependence which is our main purpose:

$$\begin{aligned} V(S, \theta) &= 0.2179 S - 0.2644 S \cos 3\theta + 0.3068 S \cos 6\theta \\ &\quad - 0.5569 S \cos 9\theta + 35.8196 S^2 - 0.2074 S^2 \cos 3\theta \\ &\quad - 0.0223 S^2 \cos 6\theta + 0.0232 S^2 \cos 9\theta - 1.0637 S^3 \\ &\quad + 0.0081 S^3 \cos 3\theta + 0.0003 S^3 \cos 6\theta \\ &\quad - 0.0012 S^3 \cos 9\theta \end{aligned} \quad (19)$$

Spectra

The energy levels are calculated variationally using a two-dimensional flexible model where the torsional and the vibrational modes are considered independent variables and the remaining $3N-8$ coordinates are allowed to be relaxed.

The program bidim [9] has been used for calculating the spectra.

a) With the internal rotation potential and (eq. 16) and the one-dimensional vibrational potentials (eq. 17) a non-coupled spectra is calculated for each θ . In Table 5 only the results for θ (0,30,60) are shown:

The vibrational energy levels have been classified by the vibrational (n_{vib}) and rotational (n_{rot}) quantum numbers. It is important to note the triple degeneracy of the energy levels, in accordance to the molecular symmetry and the angle dependence of the vibrational frequency (ν)

b) The coupled spectra is calculated by using the internal rotation potential and the two-dimensional (S, θ) vibrational potential (eq. 19).

Table 5. Uncoupled energy levels (cm⁻¹).

n_{vib}	n_{rot}	0°	30°	60°
0	0	0.0000	0.0000	0.0000
0	0	0.0032	0.0032	0.0032
0	0	0.0032	0.0032	0.0032
0	1	303.2862	303.2862	303.2862
0	1	303.2862	303.2862	303.2862
0	1	303.4232	303.4232	303.4232
0	2	575.5118	575.5118	575.5118
0	2	577.9414	577.9414	577.9414
0	2	577.9414	577.9414	577.9414
0	3	804.7870	804.7870	804.7870
0	3	804.7870	804.7870	804.7870
0	3	827.1955	827.1955	827.1955
1	1	997.8629 v	1001.2754 v	1003.5018 v
1	1	997.8660 v	1001.2785 v	1003.5050 v
1	1	997.8660 v	1001.2785 v	1003.5050 v

Table 6. Coupled energy levels.

N_{vib}	N_{rot}	Energy (cm^{-1})
0	0	0.0000
0	0	0.0032
0	0	0.0031
0	1	303.0751
0	1	303.0751
0	1	303.2141
1	0	1003.2811
1	0	1003.2844
1	0	1003.2844

Table 7. Rotational frequency (cm^{-1}).

Experimental ^[6]	MP2/6-311G** [4,10]	This work
278	333	303.2861

Table 8. Vibrational frequencies C-C.

Experimental [6,8]	MP2/6-311G** [4,10]	These work
945	1034	1003.2844

Results

The energy barrier ($E(0) - E(60) = 1113.07 \text{ cm}^{-1}$) does not reproduce quite precisely the experimental value (1008.009 cm^{-1} [5]) due to the short basis set 6-311G** and the method used in the calculation. Nevertheless our main purpose is not to reproduce the rotational barrier but to obtain a more precise spectra.

With this method the rotational frequency is improved with respect to the one calculated by the Gaussian03 program package.

The vibrational frequencies calculated by including the torsional dependence of the vibrational potential and the anharmonic term are closer to the experimental results than the Gaussian calculation reported in the literature:

Discussion

In this work it has been studied the internal rotation and vibrational spectra in the case of ethane which is a simple and well known non-rigid molecule.

A systematic method for introducing in the vibrational Hamiltonian the anharmonic correction term and their dependence on the internal variables has been presented.

The method is mainly based on the difference in energies of both motions under study, and the results obtained reproduce quite reasonably the experimental results reported in the literature, and improves the theoretical values in available in the literature.

The study performed in this paper can be applied to other non-rigid molecules.

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