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VIBRATIONAL ENERGY LEVELS AND VIBRONIC STRUCTURE OF ELECTRONIC SPECTRA IN MOLECULES WITH LARGE AMPLITUDE MOTIONS

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Abstract—This paper presents a software tool for determining the vibrational energy levels and the vibronic structure of electronic spectra in molecules showing one, two or more large amplitude motions. The program, ROVI, uses the potential functions and the kinetic terms for each electronic state in the construction of the hamiltonian matrix. The hamiltonian is solved variationally in a free rotor basis to obtain the energy levels and the wavefunctions. In addition, the temperature and the transition dipole moment are used for the calculation of the vibronic structure of the electronic spectrum. ROVI simulates the transitions as vertical lines or by a superposition of lorentzian functions. The program is used to illustrate the change in the vibronic structure of the $S_0 \rightarrow T_1$ electronic spectrum of acetaldehyde with the temperature.

INTRODUCTION

The classical study of molecular vibrations is restricted to small amplitude, harmonic motions. However, large amplitude anharmonic vibrations appear frequently, playing an important role in the conformational behaviour of biomolecular compounds. From an experimental standpoint the use of electronic spectroscopy techniques permits to obtain useful information about these motions. However, when one or more large amplitude modes appear in a molecule, its electronic spectrum is usually difficult to resolve. The problem is specially important when the molecule experiences structural changes on excitation to a higher electronic state. This is the case for the carbonyl and thiocarbonyl compounds. These molecules suffer a change in the preferred methyl conformation and a pyramidalization of the carbonyl moiety (Clouthier & Moule, 1989). In these cases the Franck-Condon principle predicts long progressions in the vibronic structure of the electronic spectrum.

From a theoretical point of view, the use of information obtained from *ab initio* calculations has shown to be very useful in the construction of anharmonic models for describing the rotation of one or two methyl tops (Ozkabak *et al.*, 1990; Ozkabak & Goodman, 1991, 1992; Smeyers *et al.*, 1993). In these studies the hamiltonian for the nuclear motion is solved variationally in a free rotor basis. Considering that the free rotor functions represent a basis for the angular space, the variational approach can be

used for any large amplitude vibration described through the change in an angle. In this context, some calculations of the vibrational structure arising from simultaneous methyl torsion and hydrogen wagging in different electronic states have been performed on some carbonyl and thiocarbonyl compounds (Smeyers *et al.*, 1990; Moule *et al.*, 1992; Niño *et al.*, 1994; Muñoz-Caro *et al.*, 1994). These studies have been useful for the assignment of electronic spectra. In this paper we present a software tool (ROVI) able to obtain the energy levels for one or more large amplitude vibrations expressed as a function of an angle (Niño & Muñoz-Caro, 1994a) and to simulate the vibronic structure of an electronic spectrum. The program works with two electronic states using the dipole transition moment, the kinetic and potential energy terms expressed as trigonometric expansions on the angular coordinates. The program can use symmetry considerations to simplify the computation and to classify the energy levels.

THEORETICAL BASIS

The nuclear hamiltonian used in ROVI for n large amplitude vibrations is (Harthcock & Laane, 1985; Niño & Muñoz-Caro, 1994b):

$$\hat{H} = \sum_{i=1}^n \sum_{j=1}^n \left[B_{ij} \frac{\partial^2}{\partial q_i \partial q_j} + \left(\frac{\partial B_{ij}}{\partial q_i} \right) \frac{\partial}{\partial q_j} \right] + V(q_1, \dots, q_n) \quad (1)$$

where q_i represents a vibrational coordinate, B_{ij} are the kinetic elements related to the g_{ij} of the

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ro-vibrational \mathbf{G} matrix (Pickett, 1972; Harthcock & Laane, 1985) through $B_{ij} = -\hbar^2 g_{ij}/2$, and V is the potential function that depends on the vibrational coordinates.

When the large amplitude vibrations are expressed as a function of an angle, a useful approximation is to use Fourier series expansions for the dipole moment, the potential and the kinetic functions (Muñoz-Caro *et al.*, 1994). Thus,

$$\mu = \sum_i^{N_\mu} \mu_i^0 \cdot f_i \quad (2)$$

$$V = \sum_i^{N_V} V_i^0 \cdot f_i \quad (3)$$

$$B_{ij} = \sum_k^{N_B} B_{ijk}^0 \cdot f_{ijk} \quad (4)$$

where f represents trigonometric terms of the form

$$f(\alpha_k) = \begin{cases} \cos(K\alpha_k); & K = 0, 1, \dots \\ \sin(K\alpha_k); & K = 1, 2, \dots \end{cases} \quad (5)$$

Expanding the wave function for the nuclear motion on the basis of the free rotor we obtain

$$\Psi = \sum_i^{N_F} c_i \left[\prod_j^n f_{ij} \right] \quad (6)$$

where N_F represents the number of basis functions, n the number of large amplitude vibrations and f_{ij} the normalized trigonometric free rotor wavefunctions:

$$f_{ij} = \begin{cases} 1/\sqrt{\pi} \cdot \cos(N\alpha_j) & \text{for } N = 1, 2, \dots \\ 1/\sqrt{\pi} \cdot \sin(N\alpha_j) & \text{for } N = 1, 2, \dots \\ 1/\sqrt{2\pi} & \text{for } N = 0. \end{cases} \quad (7)$$

Using the variational principle (Niño *et al.*, 1994; Muñoz-Caro *et al.*, 1994), the kinetic term of the hamiltonian matrix adopts the form

$$\begin{aligned} \langle \varphi_m | \hat{T} | \varphi_n \rangle &= \sum_i^n \sum_j^n \sum_k^{N_B} B_{ijk}^0 \\ &\times [\langle f_{mi} | f_{ijk} | f'_{ni} \rangle \langle f_{mj} | f_{ijk} | f'_{nj} \rangle \\ &+ \langle f_{mi} | f'_{ijk} | f_{ni} \rangle \langle f_{mj} | f_{ijk} | f'_{nj} \rangle] \\ &\times \prod_{p \neq i, j}^n \langle f_{mp} | f_{ijkp} | f_{np} \rangle \end{aligned} \quad (8)$$

where $i \neq j$ and

$$\langle \varphi_m | \hat{T} | \varphi_n \rangle = \sum_i^n \sum_k^{N_B} \left(B_{ijk}^0 [\langle f_{mi} | f_{ijk} | f'_{ni} \rangle + \langle f_{mi} | f'_{ijk} | f_{ni} \rangle] \prod_{p \neq i}^n \langle f_{mp} | f_{ijkp} | f_{np} \rangle \right) \quad (9)$$

for $i = j$. The potential term becomes

$$\langle \varphi_m | \hat{V} | \varphi_n \rangle = \sum_i^{N_V} V_i^0 \prod_p^n \langle f_{mp} | f_{ip} | f_{np} \rangle. \quad (10)$$

These equations permit to calculate the energy levels for each state.

Using equation (2), the matrix elements for the transition dipole moment become

$$\mu_{nm} = \sum_i^{N_F} \sum_j^{N_F} c_{in} c_{im} \mu_j^0 \prod_p^n \langle f_{ip} | f_{jp} | f_{jp} \rangle \quad (11)$$

being c_{in} and c_{im} the coefficients of the wavefunction.

For the above expressions it is necessary to determine the value of the trigonometric integrals. The use of three trigonometric terms leads to 27 different integrals that reduce to the 11 where the product of the trigonometric has even symmetry. The values of the integrals are shown in Table 1.

Relative intensities are obtained by the expression

$$I \propto (g_n - g_m) \mu_{nm}^2 \quad (12)$$

where g represents the population of each vibrational state calculated from the Boltzman distribution

$$g_n = e^{-\epsilon_n/kT} / \sum_i^{N_F} e^{-\epsilon_i/kT}. \quad (13)$$

The structure of the electronic spectrum is simulated representing each transition as a vertical line with a height proportional to the relative intensity. An additional simulation is obtained by fitting each transition to a lorentzian function of the form

$$L(v) = \frac{a}{\frac{a}{I_0} + (v_{mn} - v)^2} \quad (14)$$

where I_0 is the relative intensity and a is a parameter related to the width of the function. Equation (14) reduces to $L(v) = I_0$ when $v = v_{mn}$. The spectrum is obtained by superposition of the lorentzian functions.

PROGRAM DESCRIPTION

The program has been developed and implemented in standard FORTRAN 77 language (Niño &

Table 1. The values of the trigonometric integrals in the non-vanishing cases. Normalization constants are not shown. K and L are positive integers and δ represents the Kronecker delta

Type	Number of integrals	Value
$\cos K\theta \cos L\theta \cos M\theta$	1	$(\pi/2)(\delta_{K+M-L} + \delta_{M-K-L} + \delta_{K+M,L} + \delta_{K-M,L})$
$\sin K\theta \cos L\theta \sin M\theta$	3	$(\pi/2)(\delta_{M-K,L} + \delta_{K-M,L} - \delta_{K+M,L} - \delta_{K-M,L})$
$\cos K\theta \cos L\theta \cos 0$	3	$\pi(\delta_{K-L} + \delta_{K,L})$
$\sin K\theta \sin L\theta \cos 0$	3	$\pi(\delta_{K,L} - \delta_{K-L})$
$\cos 0 \cos 0 \cos 0$	1	2π

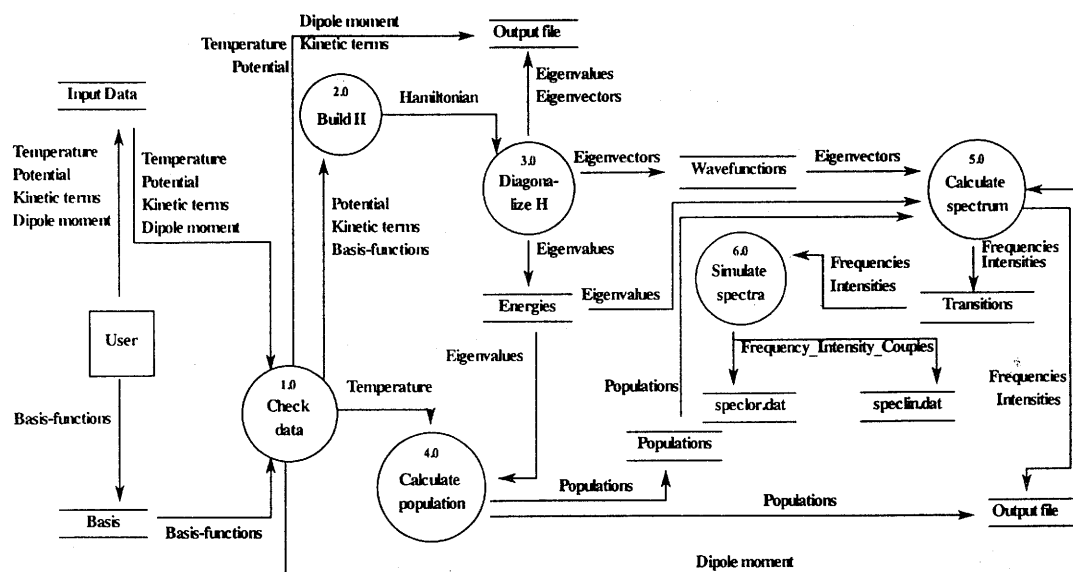


Fig. 1. Data flow diagram showing the functional logical model of the ROVI program.

Muñoz-Caro, 1994a) running under the UNIX operating system.

The design of the system has been based in the functional behavior of the program. Thus, a logical model has been constructed through a Data Flow Diagram (Martin & McClure, 1988; Yourdon, 1989) as shown in Fig. 1. In this diagram arrows represent flow of data, squares represent terminal entities (the user), double lines represent files and bubbles represent processes that transform input data in output data.

The input data for the program is partitioned in nine groups identified with a key word. Group theory for non rigid molecules can be used introducing the number of irreducible representations and their degeneracies. The Tape3 file stores the basis functions following the order of the irreducible representations. ROVI factorizes the hamiltonian matrix using as many blocks as the number of representations and classifies the eigenvalues and eigenfunctions accordingly. The transition dipole moment is introduced as a Fourier expansion for each cartesian component (usually the projections on the principal axis). The selection rules are introduced specifying the irreducible representations and the dipole moment component involved.

At present, the study of large amplitude motions considers usually one or two simultaneous vibrations. In these conditions and using the factorization introduced by the group theory, the maximum size for the hamiltonian matrix is expected to be about 1000×1000 . We have selected the Givens-Householder technique using standard algorithms (Michels & Prosser, 1965) for diagonalizing these medium size matrices.

The program uses nine files. The input and output data are written to Tape5 and Tape6 respectively. The

energy levels are stored in Tape7, the eigenvectors in Tape8 and the populations in Tape2. These files are unformatted and direct access files. Tape9 stores the allowed transitions as an unformatted sequential file whereas the basis functions are stored in Tape3. Finally, specin.dat and specclor.dat store in ASCII format the data for drawing the linear and the lorentzian spectra as a series of frequency-intensity couples. Thus, a graphical program able to draw a line between two adjacent points can be used for the generation of the graphical output. The algorithm used for the simulation of the spectrum through a superposition of lorentzian functions is shown in Fig. 2.

PERFORMANCE

The amounts of disk space and RAM memory depend on the basis size and the number of energy levels considered. This is a consequence of the variational principle used to solve the molecular hamiltonian. Figures 3 and 4 represent the RAM and the disk space as a function of the basis size and the number of energy levels. These figures have been obtained considering 64 bits for a floating point number in double precision, 32 bits for an integer, 24 bytes for each unformatted record in the sequential file and 8 bytes for the unformatted record in a direct access file.

The two figures show that the disk space increases with the basis functions and the number of levels whereas the amount of RAM depends principally on the basis size. It is also clear that the disk space increases with the basis size and the levels faster than the amount of RAM. These facts are a consequence of the semi-direct approach used for some consuming-resources entities in the design phase of the

```

Increment ← Maximum_frequency - Minimum_frequency
Maximum ← Maximum_frequency + Increment/10
Minimum ← Minimum_frequency - Increment/10
Increment ← (Maximum - Minimum)/200
Energy ← Minimum
Factor ← 2000

Open file speclor.dat

For i=1 to 200
  Rewind file Tape4
  Intensity ← 0

  For j=1 to Number_of_transitions
    Read Frequency, Intensity in Tape4
    Omega ← (Frequency - Energy)^2
    Intensity ← Intensity + Factor/(Factor/Intensity + Omega)
  end_for

  Write (Energy, Intensity) in file speclor.dat
  Energy ← Energy + Increment
end_for

Close file speclor.dat

```

Fig. 2. Pseudocode for the simulation of the spectrum by a superposition of lorentzian functions.

program. Thus, eigenvalues, eigenvectors, populations, transitions and intensities are calculated and stored on disk. They are loaded in central memory only when are needed.

APPLICATION

The use of the program is illustrated analyzing the dependence with the temperature of the vibrational structure in the $S_0 \rightarrow T_1$ electronic spectrum of acetaldehyde. In the first triplet state, T_1 , this molecule exhibits two large amplitude motions, the torsion of the methyl group and the wagging (planar bending) of the carbonyl hydrogen. Thus, the vibrational

energy levels and the spectrum are calculated solving a two dimensional problem with the torsion, θ , and wagging, α , angles as angular coordinates. The potential functions were obtained from *ab initio* results at the RHF and UHF/MP2/6-311G(d, p) level (Niño *et al.*, 1994). The kinetic terms $B_{\theta\theta}$, $B_{\theta\alpha}$, $B_{\alpha\alpha}$ were calculated from the *ab initio* data with the KICO program (Muñoz-Caro & Niño, 1993). In this study acetaldehyde is classified under the G_6 non rigid group that exhibits three irreducible representations, a_1 , a_2 , e . This group accounts for the rotation of the methyl group and the simultaneous inversion of the θ and α angles (Niño *et al.*, 1994; Muñoz-Caro *et al.*, 1994). Thus, the following symmetrized set of basis functions has been used

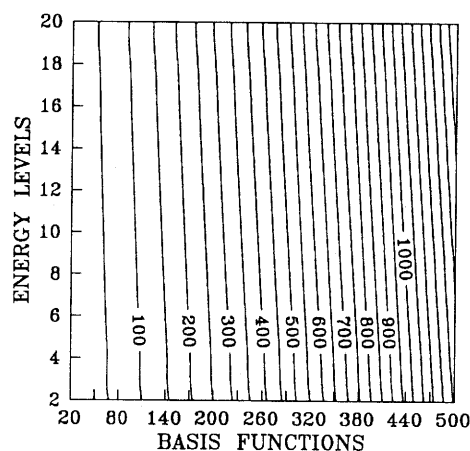


Fig. 3. Contour map, in Kbytes, for the variation of central memory (RAM) with the number of energy levels and basis functions in the ROVI program.

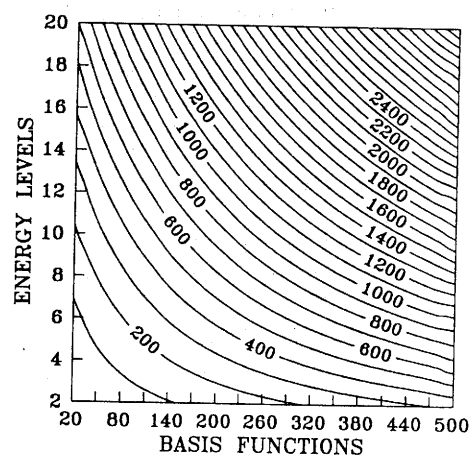


Fig. 4. Contour map, in Kbytes, for the variation of hard disk space with the number of energy levels and basis functions in the ROVI program.

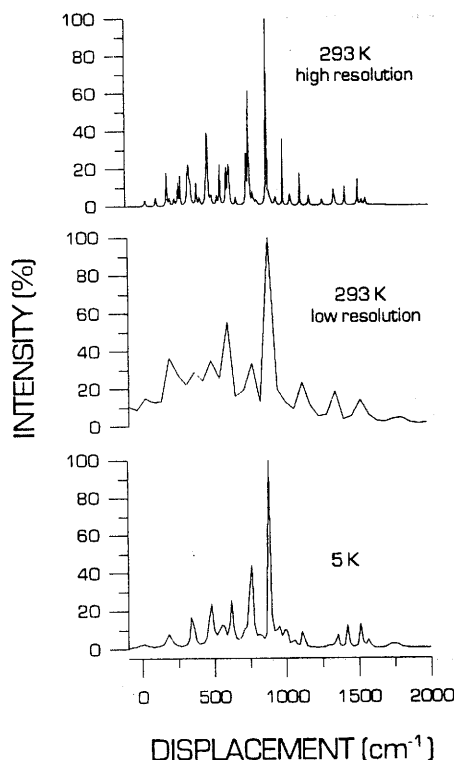


Fig. 5. The vibrational structure of the $S_0 \rightarrow T_1$ electronic spectrum of acetaldehyde at low (5 K) and room (293 K) temperatures.

$$\begin{aligned}
 a_1 & \begin{cases} N \cos 3L\theta \cdot \cos M\alpha \\ N \sin 3L\theta \cdot \sin M\alpha \end{cases} \\
 a_2 & \begin{cases} N \cos 3L\theta \cdot \sin M\alpha \\ N \sin 3L\theta \cdot \cos M\alpha \end{cases} \\
 e & \begin{cases} N \cos 3(L \pm 1)\theta \cdot \cos M\alpha \\ N \sin 3(L \pm 1)\theta \cdot \sin M\alpha \\ N \cos 3(L \pm 1)\theta \cdot \sin M\alpha \\ N \sin 3(L \pm 1)\theta \cdot \cos M\alpha \end{cases} \quad (15)
 \end{aligned}$$

where N is the normalization constant and L, M are positive integers (Smeyers *et al.*, 1990). In the present case the limits used for L and M were 5 and 15, respectively. Thus, it is obtained a 961×961 hamiltonian matrix factorized by symmetry in boxes of 171×171 (a_1) 170×170 (a_2) and 620×620 (e). In the simulated spectra only Franck-Condon transitions were considered and they were calculated assuming a constant transition dipole moment. The value for μ was introduced as a one term expansion:

$$\mu = 1.0 \cdot \cos(0 \cdot \theta) \cos(0 \cdot \alpha). \quad (16)$$

The spectra simulated at low (5 K) and room (293 K) temperatures are shown in Fig. 5. At low temperature (jet-cooled simulated spectrum) only the lowest torsional a_1 and e symmetry energy levels are populated in the S_0 . Consequently, transitions

between levels of a_2 symmetry do not appear. The strongest bands correspond to an $a_1 \rightarrow a_1$ transition with a 100% of intensity placed at 881.5 cm^{-1} and two degenerate $e \rightarrow e$ transitions with a 92% of intensity placed at 883.4 cm^{-1} (Niño *et al.*, 1994). Figure 5 shows that the pattern of intensities is sensible to the change of temperature. In the spectrum at 293 K the vibronic structure appears more congested. This is a consequence of the population of the methyl torsional energy levels in the S_0 ground state (the KT factor equals 203.6 cm^{-1} whereas the calculated barrier to rotation equals 415.2 cm^{-1}). The transitions observed at 5 K maintain their intensities but the population of higher torsional energy levels in the S_0 state produces an additional set of bands. These bands show several transitions of $a_2 \rightarrow a_2$ symmetry, the strongest placed at 887.7 cm^{-1} with intensity 58.2%. A more detailed picture can be obtained with the high resolution spectrum of Fig. 5. This spectrum has been simulated using 2000 points in the interpolation of the lorentzian functions. Clearly the broad bands observed in the low resolution spectrum are the result of the combination of very close transitions. Thus, the room temperature spectrum has a complex structure which from an experimental point of view is difficult to resolve.

Program availability—The program is distributed through the Quantum Chemistry Program Exchange as QCPE program number 648. Included in the distribution are a User's manual and a detailed example.

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