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Quantum chaotic behavior in vibro-roto-torsional levels of methanol and its isotopomers

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Abstract

A statistical analysis of experimental vibro-roto-torsional energy levels of CH_3OH, CD_3OH, CH_3OD, $^{13}CH_3OH$ and $^{13}CD_3OH$ molecules is performed, calculating the nearest neighbor spacing level distribution and the Dyson–Metha $\Delta_3(L)$. The interactions among the molecular internal motions are clearly proved by the departure of the statistics from the *regular* spectral behavior, in particular for the CH_3OD molecule, for both the NNLSD and the $\Delta_3(L)$. Increasing the torsional number n, an increasing in the *irregularity* of the spectra is also observed, accounting for a stronger interaction among the internal and global rotation. Strong differences are seen in the statistics of the various isotopomers, claiming for a future more accurate and conclusive study of the isotopic dependence in the global molecular energy levels dynamics.
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1. Introduction

By the improvement of both experimental and theoretical techniques, since the early 1980s it has been more and more frequent to have the availability of energetic spectra constituted of hundreds, or thousand, of levels. In such a situation, statistical study has proved its usefulness in an attempt to evidence global properties of the considered system, especially for systems where an accurate Hamiltonian is very hard to set up. In particular, molecular spectra have intrinsic complexity, that make the attempt of characterizing every single level quite demanding.

Historically, Wigner [1] was the first who faced this problem on dense nuclear spectra, proposing the technique to test correlation between energy levels based on the nearest neighbor level spacing distribution (NNLSD), followed by the definition of the Dyson–Metha statistics [2] $\Delta_3(L,i)$: statistical study to characterize energy spectra has proved to have universal validity by the development of the random matrix theory (RMT) [3,4]. The theory of *quantum chaos* classifies the spectra of non-interacting levels as *regular* (showing a Poisson statistics), whereas interacting level spectra are called *irregular* (showing a RMT statistical behavior).

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The use of this *global spectroscopy* has found interesting applications in the characterization of molecular vibrational spectra [5–10], concluding the strong coupling among vibrational motions in various regions of the spectra can be statistically evidenced. By contrary, up to now very few work has been done on the study of the molecular rotational motion, both internal and global [11]. The aim of this paper is to extend the analysis carried out on a preceding work on the vibro-roto-torsional spectrum of the methanol [12], which found a completely *regular* spectrum. As a general trend, derived by the quantum-mechanical perturbation theory point of view, it is expected the coupling among levels to be enforced by increasing the level energy: analyzing the more extended vibro-roto-torsional level set disposable now (having the maximum energy at about 2600 cm^{-1}, with respect to 80 cm^{-1} of the previous work), it is studied the possibility for a stronger coupling between rotational motions to take place in this molecule, evidenced by *irregularity* in the statistics. The work is also extended to the four isotopomers of the methanol CD_3OH, CH_3OD, $^{13}CH_3OH$ and $^{13}CD_3OH$, comparing the dynamical behavior of all the five molecules.

2. Experimental summary

In most investigations of molecular spectra, the work starts by comparing the experimental frequencies to the values predicted by available model Hamiltonians at low quantum numbers, where, in most cases, the predictions are very accurate. Then, one proceeds by iterative and interactive methods, notably the use of spreadsheets, following the line sequences toward higher quantum numbers. In many cases the new assignments can be used to improve the values of the parameters appearing in the model Hamiltonian, thus gaining a better insight into the physics of the molecule and improving the reliability of the calculations. At the end of the work, one has a list of experimental frequency values and more precise constants for the model Hamiltonian, which can provide accurate calculated energy-level values.

The difficulties encountered in the assignment of the far-infrared absorption spectra of the methyl-symmetric methanol isotopomers, for which satisfactory model Hamiltonians have been formulated only recently, have lead to a new assignment technique, based on the 'Ritz' computer program [13]. The idea behind this technique is to actually take advantage of one of the origins of the spectral complexity, namely the existence of non-stringent selection rules, in the assignment work. Non-stringent selection rules allow many transitions from each single level to other levels, so that the investigated spectral lines involve a number of levels much smaller (approximately by a factor 5 in the case of methanol) than the number of lines. Thus, in the Ritz method, the assignment work is done by following level sequences rather than line sequences. This procedure has two important advantages: (i) as stated above the number of levels is smaller than the number of investigated lines, and the energy-level values give a more direct insight into the physics of the molecule than the line frequencies, since energy-level values are the direct output of the model Hamiltonians. (ii) If a level sequence is perturbed by interactions with nearby levels, once it is assigned and its energy-level values are known, its perturbations do not hinder or complicate the assignment of the transitions from this sequence to other, unperturbed level sequences.

This is how the Ritz algorithm works: starting from an initial set of assigned lines, we evaluate the set of energy level values $\{E_i\}$ which minimize the chi square

$$\chi^2 = \sum_{i,j} \frac{(E_i - E_j - \nu_{ij})^2}{\epsilon_{ij}^2},$$

where E_i and E_j are the energies of the ith and jth level of the molecule, respectively, ν_{ij} is the experimental wavenumber of the corresponding transition, and ϵ_{ij} its experimental accuracy. Since, as stated above, the selection rules are not very stringent, each level is connected to many other levels (up to 20 or more) by observable transitions. Thus, this procedure provides very accurate 'experimental' values for the energies of the levels (accuracies of the order of 10^{-4} cm^{-1} for a good

Fourier transform spectrum). This accuracy allows an immediate identification of new transitions occurring between assigned levels. For transitions connecting to a new level (i.e. to a level not involved in any already assigned transition), extrapolations from the energies of levels already assigned are used for predicting new wavenumbers. A method for locating new level sequences is described in [14]. Thus, one proceeds by extrapolating energy-level values rather than line frequencies. The 'Ritz' method has proved very efficient in the assignment of dense rovibrational molecular spectra, notably of various methanol isotopomers, cyanamide and oxetane. An important 'byproduct' of the Ritz program, of great relevance for the present work, is the creation of a list of 'experimental' energy-level values, independent of any model Hamiltonian and its possible approximations. These energy level values constitute the most accurate possible Hamiltonian for the molecule, of course as far as assigned transition are involved. These are the data which are analyzed in the present work.

The spectra from which the energy-level values have been obtained have been measured on the Bruker Fourier transform spectrometer at the Physikalisch-Chemisches Institut the Justus Liebig University of Giessen. The spectra were calibrated using a selection of the H_2O lines in this region from Guelachvili and Rao. For the parent isotopic species the measurements were performed at pressures ranging from 10 to 200 Pa, with path lengths ranging from 145 to 284 cm. The spectrum of the CD_3OH isotopomer, for which the second largest number of energy-level values is available, was measured at a pressure of 50 Pa, with a path length of 284 cm. More experimental details can be found in [15,13,16–18,14].

3. Statistical techniques

For a sequence of energy levels $E_1, E_2, \ldots, E_n$ (i.e. an energy spectrum) consider the so-called integrated level density function, which gives the number $N(E)$ of levels with energy $\leqslant E$:

$$N(E) = \sum_{i=1}^{n} \Theta(E - E_i), \tag{1}$$

where $\Theta(E)$ is the Heaviside step-function. This function fluctuates about the smooth curve with represent the secular behavior of the energy spectra. In order to remove the variation in the mean level density between different regions of the spectra, the function $N(E)$ is approximated by a polynomial fitting [5] to obtain $\overline{N(E)}$. The original spectrum E_i is then mapped on the new spectrum ϵ_i:

$$\epsilon_i = \overline{N(E)}, \tag{2}$$

which has now a constant level density. The statistical analysis is carried out on the unfolded spectrum ϵ_i.

To characterize the fluctuations of the levels sequence, two are the most common tests:

1. the nearest neighbor spacing level distribution (NNLSD) [7], which accounts for the short range fluctuations. The NNLSD is represented as a histogram of spacings between two adjacent levels; the histogram is then fitted to the Brody distribution function $P_B(S)$

$$P_B(S) = \alpha S_i^{q_B} \exp(-\beta S_i^{1+q_B})$$
$$\alpha = (1 + q_B)\beta$$
$$\beta = \left[\bar{D}^{-1}\Gamma\left(\frac{2 + q_B}{1 + q_B}\right)\right]^{1+q_B},$$

   where $S_i = \epsilon_{i+1} - \epsilon_i$ is the spacing, $\bar{D}$ is the spectrum mean spacing and q_B is the Brody's parameter. The distribution interpolates the NNLSD between the Poisson distribution ($q_B = 0$) and the Wigner distribution ($q_B = 1$). The Poisson distribution is typical of a set of non-interacting levels, i.e. the levels could be though as being randomly distributed; a Wigner distribution is defined as the NNLSD of a set which represents the spectrum of a Gaussian orthogonal ensemble (GOE) [4], i.e. a set of pair-interacting levels. The Brody's parameter q_B is therefore used as a measure of the intensity of the interactions among level sets.
2. the Δ_3 statistic of Dyson and Metha [2], also called the *spectral rigidity*, which is a measure of the global behavior of a spectrum. It is defined by $\Delta_3(L) = \overline{\Delta_3(L, i)}$ (the over-lining indicates the average on i) with

$$\Delta_3(L,i) = \frac{1}{\epsilon_{L+i} - \epsilon_i} \min(a,b) \times \int_{\epsilon_i}^{\epsilon_{L+i}} [N(\epsilon) - a\epsilon - b]^2 \, d\epsilon,$$

where L is the number of levels considered, $N(\epsilon)$ is the staircase function and $a\epsilon + b$ is a best fit line. For a random set of levels with a Poisson distribution, $\Delta_3^{\mathrm{P}}(L)$ is equal to $L/15$, whereas for a GOE set $\Delta_3(L)$ shows a logarithmic dependence: $\Delta_3^{\mathrm{GOE}}(L) = \pi^{-2}[\ln(L) - 0.0687]$.

As the q_{B} value, the graph of $\Delta_3(L)$ can be used to determine the interaction strength among levels of a given spectrum.

Following a widely used nomenclature, throughout the rest of the paper a spectrum having a Poisson NNLSD and the linear behavior of $\Delta_3(L)$ will be called *regular*, whereas one having a Wigner NNLSD and the previously stated logarithmic behavior for $\Delta_3(L)$ will be called *irregular* (or GOE) spectrum [19].

4. Data analysis

4.1. Introductory remarks

For a set of energy levels to exhibit a possible deviation from the statistics of a random distributed spectrum, it must be homogeneous in all good quantum numbers [4]. The vibro-roto-torsional wave functions of the isotopomers has been classified by three quantum numbers: the one which defines the total angular momentum J, the torsional quantum number n [20] and the total symmetry of the vibro-roto-torsional level $S = A_1, A_2, E_1, E_2$. A_1 and A_2 is a notation introduced to denote torsional level of a k doublet A±, and total parity, $\pm(-1)^{J+n}$, respectively [21]. The statistical analysis has been carried out on sets homogeneous in one or more of the three quantum numbers. For the statistical measures to be confident, the resulting sets constituted of less that 100 levels have been rejected. The energy spectra belong to five isotopomers of the methanol molecule: CH_3OH, CD_3OH, CH_3OD, $^{13}CH_3OH$ and $^{13}CD_3OH$, constitute of about 6900, 6300, 3000, 6500 and 8200 levels respectively. These levels range in energy from the vibro-roto-torsional ground state up to 2600 cm^{-1} and, apart from the CH_3OD set, belong to various vibrational states (ground state, CO stretching, CH_3 in-plane rocking, CH_3 out-of-plane rocking, OH stretching, CH_3 symmetric bending).

4.2. Results and discussions

The analysis carried out on sets homogeneous in S, n or J quantum numbers only has shown a regular behavior for the spectra, so these results are not reported in this work. It has not been possible to carry out any analysis on sets with neither the same J and S nor the same J and n, due to the low number of levels at our disposal.

For every isotopomers previously listed, the data shown in the next pages belong to two different kind of spectra:

- sets of levels sharing the same symmetry S and torsional state n, belonging to all the possible vibrational and rotational states;
- sets of levels with the same S, with J in the ranges 10–12, 13–15, 16–18, 19–21, 22–24. This grouping has been done due the scarcity of levels sharing a single J value. These sets belong to all the possible vibrational and torsional states.

The value for q_{B} is reported in Fig. 1 for all the isotopomers; in order to make data clearer, the complete NNLSD histogram is reported only for the case of CH_3OD with $S = A_2$ in Fig. 3(a)–(d). In Fig. 2 the value of $\Delta_3(L)$ for $L = 15$ is reported: the value of $\Delta_3(15)$ for a *regular* spectrum is 1, whereas for a GOE spectrum the value is 0.11. It has been chosen $L = 15$ in order to avoid the $\Delta_3(L)$ saturation [7] (different author; report the values $L = 20$ [22] and $L = 30$ [23] as highest values of L to have $\Delta_3(L)$ free(of saturation). As for the NNLSD, only for the case of CH_3OD with $S = A_2$ the complete $\Delta_3(L)$ graph is reported in Fig. 4(a)–(d).

As a general consideration, from Figs. 1–4, a deviation from the behavior of random distributed spectra can be seen. Moreover, there are differences among the behaviors of the various isotopomers and of sets of different symmetry S.

Fig. 1(a)–(f) shows that there is a trend in the value of q_{B} with respect to n: all the sets of different S have the highest value of q_{B} for $n = 2$ or 3, and

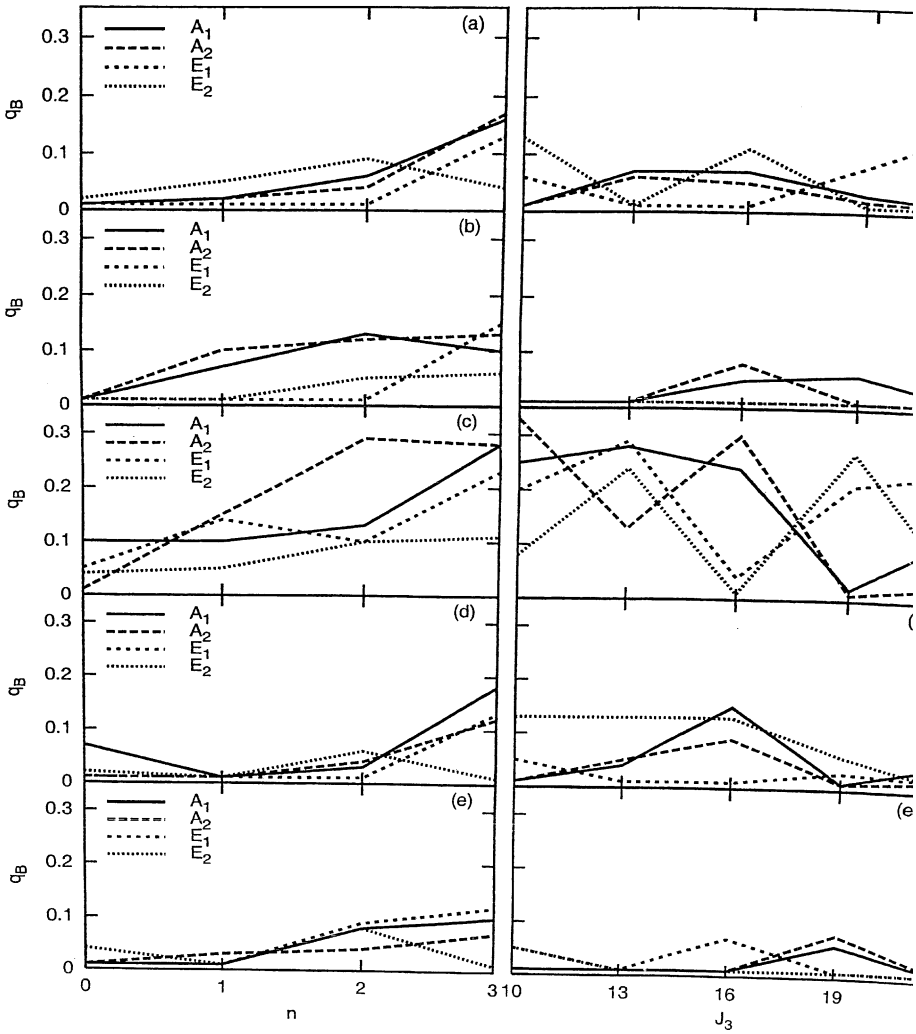

Fig. 1. Values of the Brody's parameter q_B for energy levels of symmetry $S = A_1, A_2, E_1, E_2$. On the left-hand side the abscissa is the torsional number $n = 0, 1, 2, 3$ whereas on the right-hand side is values of J in the ranges 10–12, 13–15, 16–18, 19–21, 22–24 respectively. (a and a′) CH_3OH, (b and b′) CD_3OH, (c and c′) CH_3OD, (d and d′) $^{13}CH_3OH$, (e and e′) $^{13}CD_3OH$. For a random spectrum $q_B = 0$, whereas for a GOE spectrum $q_B = 1$.

the lowest q_B occurs almost always for $n = 0$. From Fig. 2(a)–(f), the opposite can be said for $\Delta_3(15)$: for increasing n the value of $\Delta_3(15)$ diminishes. This behavior can be explained considering that the mean energy of a set increases for larger n: an increase in the energy means a larger coupling between the levels, because the global motion of the molecule can no longer be considered as a sum of distinct non-interacting degrees of freedom (i.e. torsional, rotational and vibrational motions). In particular, the levels of $n = 0$ reside in the bottom of the internal rotation potential well [16], whereas the levels with $n = 1, 2, 3$ are above this barrier, interacting more strongly with rotational motions. Transitions of spectra toward *irregular* ones, due to the increase of the mean energy of the sets, have already been seen in other molecules [24,25].

From Figs. 1(a′)–(f′) and 2(a′)–(f′), it is not possible to recognize any apparent trend in the

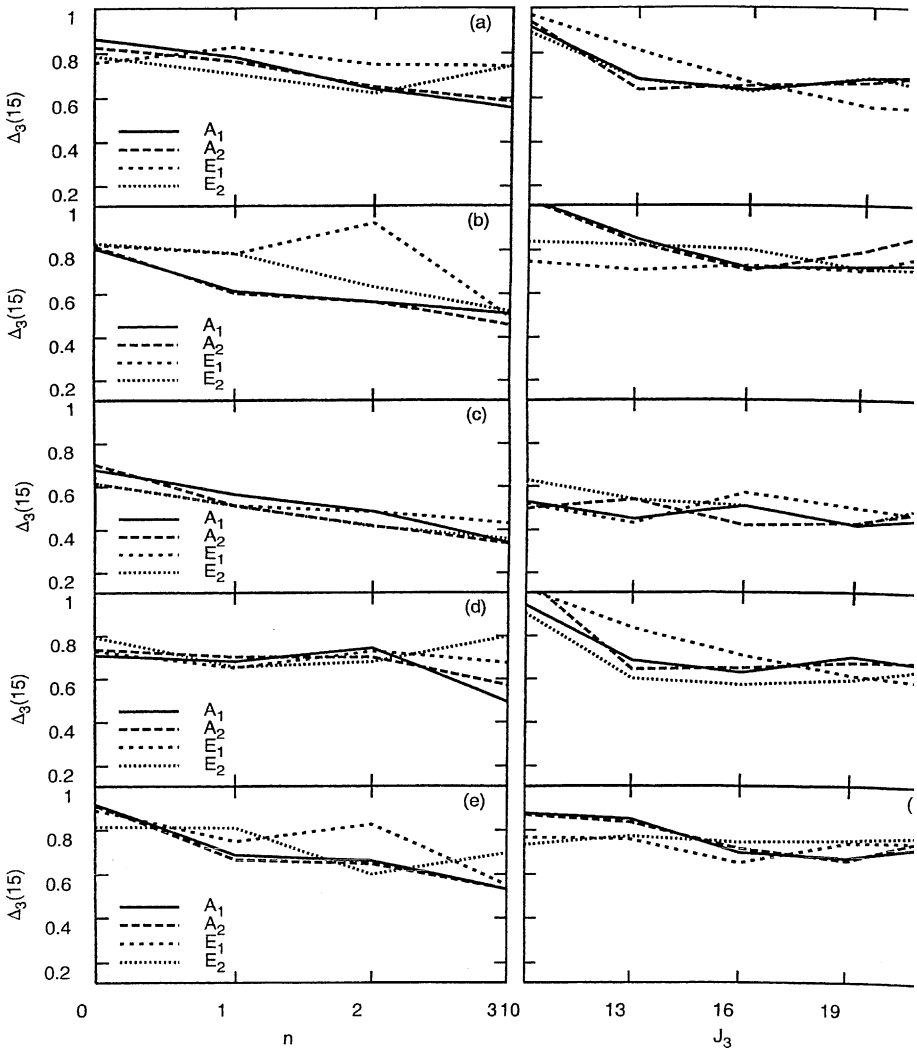

Fig. 2. Values of the Dyson–Metha $\Delta_3(15)$ for energy levels of symmetry $S = A_1, A_2, E_1, E_2$. On the left-hand side the abscissa is the torsional number $n = 0, 1, 2, 3$ whereas on the right-hand side is values of J in the ranges 10–12, 13–15, 16–18, 19–21, 22–24 respectively, (a and a′) CH_3OH, (b and b′) CD_3OH, (c and c′) CH_3OD, (d and d′) $^{13}CH_3OH$, (e and e′) $^{13}CD_3OH$. For a random spectrum $\Delta_3(15) = 1$, whereas for a GOE spectrum $\Delta_3(15) = 0.11$.

behavior of the sets with respect to the value of J. However, it is possible to achieve an interesting conclusion: in these sets, the major contribution to the *irregularity* of the spectra can be due to the perturbation among different torsional levels only. As for the former spectra sharing the n, it is possible to recognize the interaction among the molecular internal motions by a statistical point of view only.

The molecule of CH_3OD is the one exhibiting the largest deviation from a random spectral statistics, as show in Figs. 1(c) and (c′) and 2(c) and (c′). As stated above, all the roto-torsional levels for this molecule belong to the vibrational ground state, whereas for the others isotopomers data refer to two vibrational motions at least. This could be the reason for this behavior: being the sets more homogeneous, they are expected to show a more

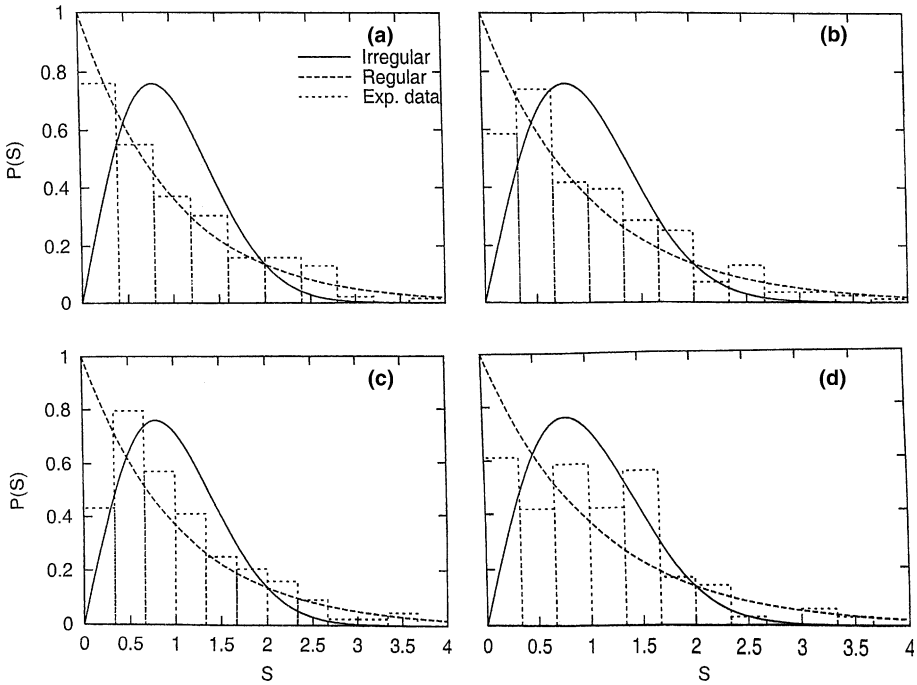

Fig. 3. NNLSD for energy levels of the CH_3OD molecule and symmetry $S = A_2$ corresponding to the torsional number: (a) $n = 0$, (b) $n = 1$, (c) $n = 2$, (d) $n = 3$. $P(S)$ is the fraction of levels with a given spacing S. The NNLSD for random *(regular)* and GOE *(irregular)* spectra are reported as well.

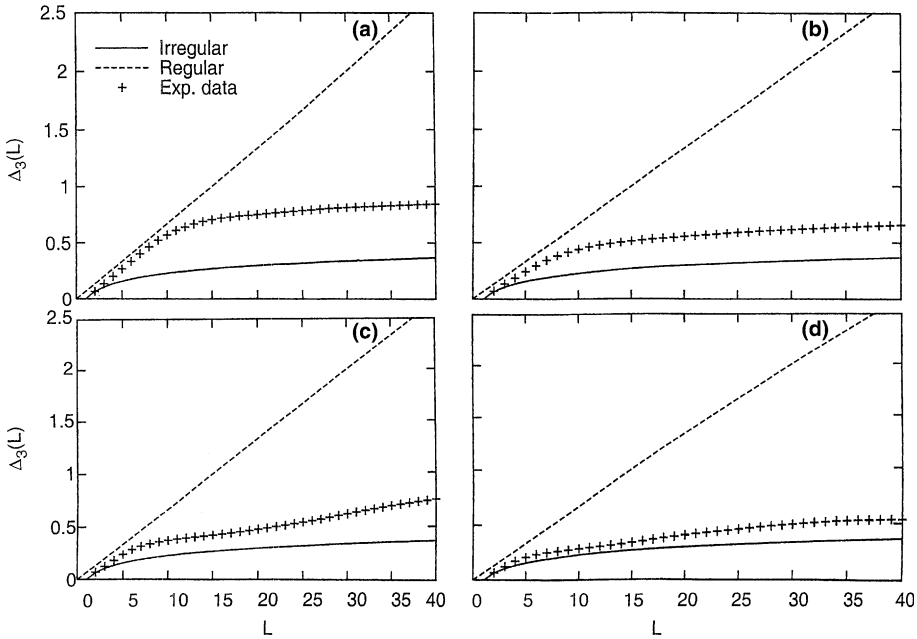

Fig. 4. $\Delta_3(L)$ for energy levels of the CH_3OD molecule and symmetry $S = A_2$ corresponding to the torsional number: (a) $n = 0$, (b) $n = 1$, (c) $n = 2$, (d) $n = 3$. The $\Delta_3(L)$ for random *(regular)* and GOE *(irregular)* spectra are reported as well.

apparent *irregular* behavior [4]. In order to test for this explanation, q_B and Δ_3 of sets built up of levels owing to the vibrational ground state only have been studied for all the remaining isotopomers. As a result, we have observed slight deviations (of the order of 10^{-2}) from the values of q_B and $\Delta_3(15)$ reported in Figs. 1 and 2, ruling out the simplest explanation of the CH_3OD molecule dynamical behavior.

Figs. 3 and 4(a–d) show CH_3OD energy levels of $S = A_2$ symmetry. It is now more apparent the departure of the level statistics from a random spectrum behavior with increasing n. In Figs. 3 and 4(a) in particular, the statistics is the one for a *regular* spectrum (the deviation of the Δ_3 curve in Fig. 4(a) with respect to the straight line is due to saturation), whereas in Figs. 3 and 4(c) is clear the disagreement with respect to the Poisson behavior (especially for the Δ_3). The strange NNLSD shown in Fig. 3(d) could be due to the incompleteness of the set: it is more and more difficult to experimentally determine levels with increasing energy, so sets of higher n are less reliable from a statistical point of view.

5. Conclusions

To our knowledge, up to now, extensive studies of the molecular roto-torsional motions have not been carried out using the global approach allowed by statistical tests. In the previous work done on the methanol molecule [12], it has not been observed any clear deviation from a random spectrum statistics of roto-torsional levels: it is now clear that this result is due to the levels energy, being the latter too low (at most 80 cm^{-1}). The data in this paper show that it is possible to have a strong interaction between the two rotational motions of a molecule (i.e. the internal rotation and the whole rotation), which turns out in a departure from the *regular* spectra statistics behavior.

As shown above, we have found differences among the various isotopomers: this could be expected, because a change in the isotopic mass of an atom in a molecule turns out in a change of the molecule dynamics [26]. However, it has to be pointed out that statistical discrepancies among the isotopomers (especially for the case of the CH_3OD molecule) could not be due entirely to the different structures of the molecules themselves: the data sets on which tests have been carried out do not contain exactly the same levels. Differences in the statistics could derive as well from differences in the regions of the spectra experimentally obtained for the various molecules. As a consequence, only with more complete data (experimentally or theoretically determined) it will be possible to study the effect of the isotopic substitution on the dynamics of the methanol molecule.

Previous works have been published on the classical dynamics of molecules as acetaldehyde and toluene, where torsion-rotation interactions take place [27–29], concluding there are strong couplings between the two motions (shown in the classical chaotic dynamics of the molecules themselves). Following conclusions of quantum chaos, a system which has a classical non-integrable Hamiltonian (i.e. presents chaotic regions in the phase space) should have a quantum discrete energy spectrum that resemble more and more a GOE spectrum as the classical dynamics becomes more chaotic. The present work confirms the relationship between classical and quantum chaos: the interaction of the rotational and torsional motions in the fully quantum mechanical system of the methanol and its isotopomers changes the statistics of the energy spectra toward a GOE-like behavior.

By the improving in the understanding of experimental energy level statistics, calculation of molecular spectra by theoretical Hamiltonian [30] will have to be tested for the capability of reproducing the right global spectral behavior [31]. By the enhancement in the quality of experimental measures as well, the use of statistical analysis could provide chemists of a tool to better understanding both intramolecular (for example, the way an excited molecule relaxes, where the motions coupling play a fundamental role [32–34]) and intermolecular dynamics (for example, the study of molecular reactive collisions [23,35]).

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