Influence of Experimental Resolution on the Spectral Statistics Used to Show Quantum Chaos: The Case of Molecular Vibrational Chaos

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We show how the resolution of an experimental spectrum influences the standard statistical tests of random matrix theory such as the nearest neighbor distribution, the Fourier transform, or the number variance. A new experiment on very highly excited vibrational states of CS_2 is analyzed in light of these new results. The resolution problem in the published results concerning the molecular vibrational chaos is then examined. [S0031-9007(99)08658-5]

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The correlation properties of a Hamiltonian quantum spectrum, following the nature of the classical dynamics (chaotic or regular), are now well established. It has been shown that the quantum spectrum of a classically integrable system has the same correlation properties as a random spectrum [1]. The nearest neighbor distribution (NND) in this case is of a Poisson-type $P(s) = e^{-s}$. By contrast, the spectral fluctuations of the Sinai billiard, which is classically a strongly ergodic system, are similar to that of a random matrix of the GOE (Gaussian orthogonal ensemble) [2]. It was conjectured that this result holds for all chaotic systems. Quantum chaos is characterized by the level repulsion. The maximum of the NND is obtained for a nonvanishing spacing; this is the Wigner distribution. Another feature of quantum chaos is revealed by the spectral rigidity in the number variance Σ^2 statistics: small fluctuations of the number of levels contained in a given energy width. The statistical Fourier transform (FT) of a spectrum is also a test of quantum chaos: Its slow component is flat for a Poissonian spectrum, whereas it reveals a correlation hole for a GOE spectrum [3]. Up to now, quantum chaos has been observed in very few experimental cases. The nuclear ensemble data has shown exact GOE statistics [4]. The hydrogen atom (for a review article, see, for example, Ref. [5]) and the lithium atom [6] in strong magnetic field have been ideal systems for both the simulations and experiments. Finally, chaotic situations have been encountered in the vibrations of molecules. We distinguish the vibronic chaos (due to the interaction of several electronic energy surfaces) seen in NO_2 [7] from the vibrational chaos (due to nonlinear coupling between modes in the same electronic potential) observed in CS_2 [8], D_2CO [9], and C_2H_2 [10].

In order that the statistics have meaning, the spectrum of the system has to be complete and pure. What is quite straightforward in a simulation by the diagonalization of the Hamiltonian is very difficult in an experiment. From an experimental signal, it is necessary to "point out" the lines which are believed to be levels, obtaining what will be called an experimental stick spectrum. This pointing process is clearly influenced by the signal-to-noise ratio (S/N) and the resolution, which are the fundamental parameters of the experiment. In a spectrum with an insufficient S/N, some randomly distributed levels are embedded into the noise. The influence of randomly distributed missing levels of a GOE spectrum has been studied [11]. As expected, there is a transition from a GOE to a Poissonian NND as the fraction of missing levels goes from 0 to 1. Another effect of the noise leads us to point out lines which are not levels and which are randomly distributed. Berry and Robnik calculated the NND distribution of a spectrum resulting from the superposition of Poissonian and Wignerian sequences [12]. The Wigner-Poisson transition is once again observed when the noise is increased (the spurious random level fraction is increased). The effect of the experimental noise on the NND statistics is then quite well understood: The experimental statistics appear nearer to the Poisson distribution than they really are.

Up to now, the influence of the experimental resolution of spectra on the statistical analysis has not been investigated. The aim of this Letter is to evaluate the bias in the statistics that the resolution can introduce. Because of the linewidth, some levels are missed in the level pointing. Unlike the noise influence, the missed levels due to a lack of resolution are not randomly distributed in the spectrum; they are essentially close to another level. It is then obvious that the short distance correlations of the NND are biased by the pointing operation: The number of weak spacings in the experimental stick spectrum (list of the pointed lines with intensities) is lower than in the real spectrum (the spectrum obtained with infinite S/N and resolution). As a consequence, the experimental stick spectrum may reveal correlations which are only artifacts. It is then not only very important to study more quantitatively the effect of the resolution on the NND but also on the long distance correlation statistical tests such as the FT or the Σ^2.

Consider a random spectrum $E = \{E_i\}_{i=1,\ldots,N}$ whose mean level spacing is $\widetilde{\Delta E}$ and with all intensities equal to 1. This stick spectrum is supposed to be the real Hamiltonian spectrum of the considered system. Suppose now that one tries to obtain it in an experiment in which the resolution gives a linewidth equal to L. We then define the "experimental" stick spectrum E' as

$$\text{if } |E_{i+k} - E_i| < L \quad \text{and} \quad |E_{i+k+1} - E_i| > L,$$
$$\text{then } E'_p = \frac{1}{k} \sum_{n=i}^{i+k} E_n \,. \tag{1}$$

This algorithm takes the barycenter of all of the groups of levels included inside the linewidth L. This procedure is the simulation of the pointing operation on an "experimental spectrum" E_{exp} which would be the spectrum E convolved with a line function of width L. In a real experiment, E' is obtained from E_{exp} without knowing the real spectrum E. In the context of this model, a comparison between the statistics of E and E' shows the influence of the pointing operation on a spectrum whose linewidth is not negligible compared with the mean level spacing. In the experimental stick spectrum, the mean level spacing is now $\widetilde{\Delta E'}$ which is obviously greater than $\widetilde{\Delta E}$. In the following, the most important quantity is the ratio $\delta = L/\widetilde{\Delta E'}$ between the linewidth and the apparent mean level spacing.

Starting with a 600 level random spectrum (having a Poissonian NND), procedure (1) is applied. In order to eliminate the statistical fluctuations of the distribution, the procedure is carried out on 20 independent spectra with the same value of δ; the NND is then averaged over these 20 samples. The NND of the spectrum E' is calculated and is presented for some values of the parameter δ (Fig. 1).

The results show clearly that when the ratio δ is increased, the NND of the experimental stick spectrum E' reveals correlations; for $\delta = 1/2$ the NND of the spectrum looks like a Wignerian distribution. In conclusion, an experimental spectrum of a completely regular system can exhibit an artifact of chaos if it is not sufficiently well resolved.

The fact that the linewidth of the experiment modifies the small correlation distance through the NND may be considered as an intuitive result but one might think, *a priori*, that the long distance correlation statistics should not be affected by the resolution problem. As for the NND, we have taken 20 random independent spectra of 600 levels and for different values of δ, and we have computed the statistical Fourier transform (as in [13]) and the Σ^2.

Figure 2 shows that a correlation hole progressively appears in the FT as the ratio δ is increased. The calculation of the Σ^2 in Fig. 3 also shows that long distance correlations are dramatically modified by the pointing process of an insufficiently resolved spectrum.

The statistical properties go once more from a Poisson to a near-GOE statistic as δ is increased. In conclusion, the three statistical tests (NND, FT, and the Σ^2) are in good agreement and show that a perfectly uncorrelated Poisson spectrum, after the pointing simulated by the procedure (1), exhibits near-GOE correlation properties for $\delta \geqslant 1/2$.

The presented pointing model is very simple. All of the lines separated by a distance greater than L are resolved, whereas any two lines separated by a distance smaller than L stay unresolved [as a consequence, the NND statistics are pathological for the small spacings (Fig. 1)]. The experimental reality is quite different because of the intensities of the spectrum. It is quite simple to resolve two lines separated by $L/2$ if they have the same intensity. However, by contrast, it is hard to resolve two lines separated by L if the first is one hundred times more intense than the second. As a consequence, the pathology of the NND observed for small spacings disappears in the real experimental case. It is then clear that the pointing operation depends on the intensity

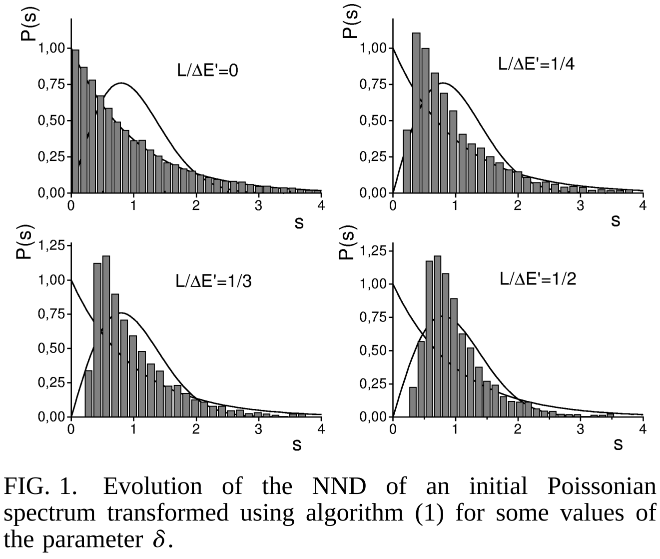

FIG. 1. Evolution of the NND of an initial Poissonian spectrum transformed using algorithm (1) for some values of the parameter δ.

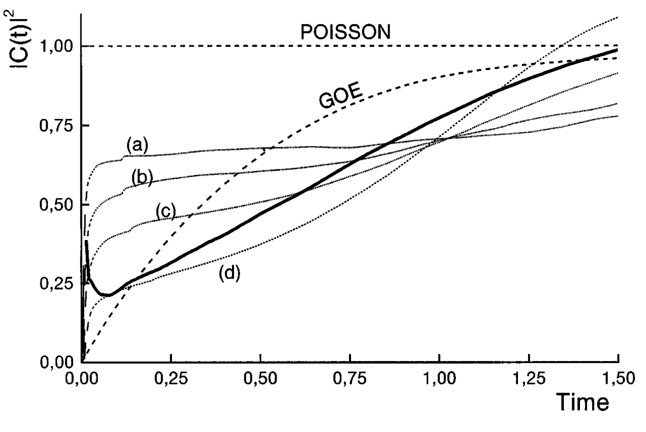

FIG. 2. Evolution of the FT of an initial Poissonian spectrum transformed using algorithm (1) for the following values of δ: (*a*) 1/5, (*b*) 1/4, (*c*) 1/3, and (*d*) 1/2. The thick curve represents the FT of the experimental CS_2 spectrum.

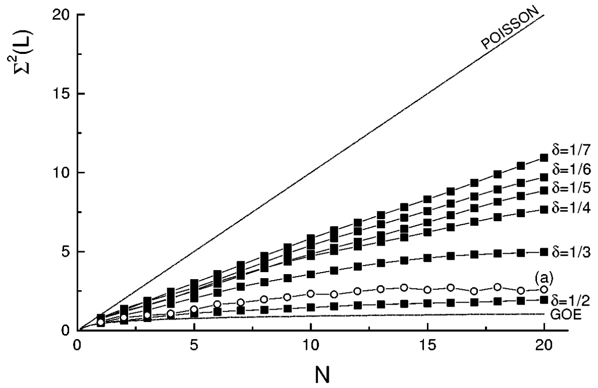

FIG. 3. Evolution of the Σ^2 of an initial Poissonian spectrum transformed using algorithm (1) for some values of δ. (*a*) represents the Σ^2 of the experimental CS_2 spectrum.

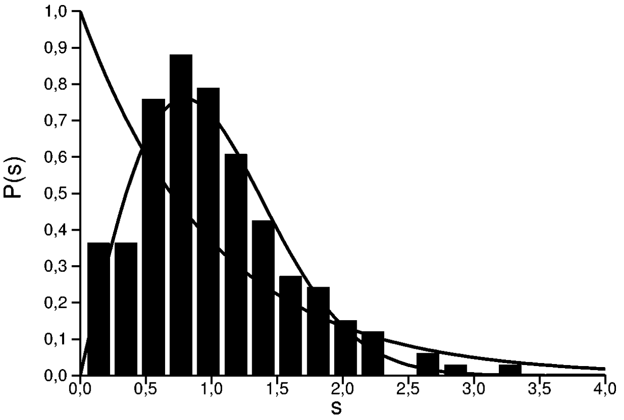

FIG. 4. Experimental NND distribution of the CS_2 spectrum on 200 levels between 19 100 and 19 300 cm^{-1}.

distribution of the spectrum. To estimate the influence of the intensity distribution of the initial spectrum on the statistics, we have developed another simple model. Starting with a random spectrum, supposing no correlation between the line position and its intensity, the intensities of the levels were fixed randomly to obtain a final given intensity distribution. More explicitly, we discretized the energy distribution chosen. To respect the intensity histogram, we assigned randomly N_1 levels with intensity I_1, N_2 levels with intensity I_2, etc. The obtained peak spectrum with intensities was convolved with a line form of Gaussian type of width L. A level was then pointed whenever there was a maximum in this convolved spectrum. We tested typical intensity distributions such as the Porter-Thomas distribution and the χ^2 with ν degrees of freedom, which represent, respectively, a completely chaotic system and a regular system [14]. The previous statistical tests were carried out on the pointed spectrum. It appears that the statistical results are about the same whatever the initial intensity distribution may be for a given value of δ, and are also really near the results obtained by (1) in Figs. 1, 2, and 3, which justifies the use of the universal model (1) [15].

The starting point of this work was the study of vibrational chaos in the molecule CS_2. In previous experiments, 900 vibrational levels in the ground electronic states of CS_2 from 0 to 19 000 cm^{-1} have been recorded with a laser induced fluorescence spectroscopy technique described in [16]. A transition to soft chaos has been observed at 13 000 cm^{-1} [8]. Since important improvements in the experimental setup have been realized, we have been able to obtain a spectrum at higher energy despite the fast decrease of the Frank-Condon. More than 400 new lines in the 19 000–19 600 cm^{-1} range have been measured. The NND distribution in the most dense region of the spectrum, including 200 levels, is presented in Fig. 4. This distribution is clearly of a Wigner-type.

This result is not contradictory to the previous soft chaotic situation described in [8] because a level density 3 times greater is observed in our experiment. Should we then conclude that the molecule has a completely chaotic dynamics? The key point is that the ratio δ for our experiment is equal to 0.45. We have shown that a completely random spectrum with $\delta = 0.5$ gives a pointed spectrum which has a NND distribution of Wigner-type. The correlation properties observed in our experimental spectrum can be explained only by the resolution influence without any correlations in the real spectrum. The same conclusion holds with the FT and the Σ^2 statistical tests. The FT (Fig. 2) and the Σ^2 (Fig. 3) of our CS_2 experimental spectrum are similar to those of a Poissonian spectrum with $\delta = 0.5$. We conclude that, even if all of the statistical tests reveal near-GOE correlation properties of the CS_2 vibrational spectrum, one can not conclude that a hard chaos exists in the molecule at 19 000 cm^{-1}.

The resolution is then a central problem for anyone who wants to give experimental evidence of vibrational chaos. Until now, situations of vibrational hard chaos characterized by non-Poissonian statistics have been observed in the acetylene molecule (C_2H_2) and in the formaldehyde molecule (D_2CO). In their pioneering experiment in 1983, Abramson *et al.* used a stimulated-emission pumping (SEP) spectroscopic technique to observe the vibrational spectrum of acetylene at about 28 000 cm^{-1} [10]. The vibrational spectrum of the ground state $\tilde{X}^1\Sigma_g^+$ is characterized by clumps of levels. The clump width is about 1 to 2 cm^{-1} and the density of states inside a clump is about 15 levels per cm^{-1}. It is supposed that a clump structure is associated with the coupling of one level carrying the oscillator strength (bright level) to nonoptically active states (dark states). Inside a clump, all of the lines have the same value of the total angular momentum J which is a good quantum number. For this reason, the statistics have been averaged over all clumps. This summation is also necessary because of the small number of levels in each clump (about 50). The obtained NND is of Wigner-type [17]. The second and third moments of the distribution

TABLE I. Summary of the experimental studies and the corresponding fits.

Molecule	CS_2	D_2CO	C_2H_2
$\left(\frac{R}{\widetilde{\Delta E'}}\right)_{\text{exp}}$	0.42	0.26 [9]	0.57 [10] 0.91 [18]
q_{model}	0.75	0.46	1
q_{exp}	1	0.71 [9]	$\sim$1

[10] as well as the Σ^2 and the Δ_3 [18] were calculated, leading to GOE results. It has been concluded that the vibrational spectrum inside each clump is of GOE-type. However, we believe that the lack of resolution is a central problem in this interpretation of the experimental results. The linewidth of the SEP spectra is fixed by the FWHM of the dump laser which is equal to 0.054 cm^{-1} for the best-resolved spectra. In the first publication [10], the averaged value of δ over all of the clumps is 0.57 while in the other publication [18] this value is equal to 0.91. From our previous analysis, it is no surprise that the correlation properties of the pointed spectrum are similar to that of a GOE spectrum (since $\delta > 0.5$). As for CS_2, it is not possible to conclude that there are correlations in the real spectrum of the molecule. We therefore believe that it is not possible to conclude that acetylene is chaotic at 28 000 cm^{-1} from the existing data.

Another important experiment reported in the literature concerns the formaldehyde D_2CO. The vibrational spectrum of the ground electronic state S_0 near the dissociation limit was studied by an anticrossing technique using the Stark effect [19]. All of the vibrational levels have the same values for the good quantum numbers. A statistical study was carried out; the NND and the Σ^2 statistics of the pointed spectrum are intermediate between Poisson and GOE. One way to analyze such an intermediate NND distribution consists of fitting it by the Brody distribution which smoothly interpolates between Poisson and Wigner as the only parameter of the distribution q is varied. The distribution is of Poisson-type when $q = 0$ and of Wigner-type when $q = 1$. The result of the experimental NND fit gives $q_{\text{exp}} = 0.71$ [9], revealing strongly non-Poissonian statistics. Once again, in this spectrum, the linewidth is not negligible compared to the observed mean level spacing since $\delta = 0.26$. Considering a random Poisson spectrum and applying procedure (1), the fit of the NND of the resulting spectrum gives a value equal to 0.46 for the Brody parameter q_{model}. The small difference between q_{exp} and q_{model} leaves the question of hard chaos unanswered. The summary of the experimental studies and the corresponding fits is given in Table I.

In conclusion, we have analyzed the influence of the resolution on the pointing of a spectrum and then on the statistical correlation tests of the random matrix theory: the NND, the FT, and the Σ^2. Starting with an initial Poissonian spectrum, we have shown that the correlation properties of the obtained pointed spectrum depend crucially on the parameter δ. All of the standard statistical tests reveal a near-GOE behavior for $\delta > 0.5$. In order that the resolution problem does not influence the statistics, δ should be less than $1/10$. We then analyzed new experimental data obtained for CS_2. With a value of δ equal to 0.45 in the experiment, one cannot conclude that the molecule is chaotic even if the pointed spectrum is near GOE. We believe that for C_2H_2 and D_2CO the situation is the same; the level of chaos found can be determined by the value of δ. Finally, we think that, until now, no clear proof of the existence of hard vibrational chaos in molecules has been given.

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