PHYSICAL REVIEW
LETTERS

VOLUME 61 4 JULY 1988 NUMBER 1

Confirmation of Random-Matrix Fluctuations in Molecular Spectra

Th. Zimmermann, H. Köppel, and L. S. Cederbaum
Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg,
D-6900 Heidelberg, West Germany

and

G. Persch and W. Demtröder
Fachbereich Physik, Universität Kaiserslautern, D-6750 Kaiserslautern, West Germany

(Received 10 November 1987)

Spectral fluctuation properties in the optical-fluorescence excitation spectrum of NO_2 are investigated. For this purpose new high-resolution measurements have been performed. We analyze the distribution of intensities and of level spacings and the spectral rigidity. Together with the consideration of effects of missing and spurious lines, the presence of random-matrix fluctuations is demonstrated unambiguously.

PACS numbers: 03.65.Ge, 05.40.+j, 05.45.+b, 33.20.Kf

The characterization of energy spectra by statistical methods has received much interest in the past years. It has been conjectured that "complex" systems exhibit universal fluctuation patterns of the spectral density. These have first been observed in a class of complicated experimental nuclear[1-3] and atomic[4] spectra. Typical statistical level-correlation properties could be modeled by ensembles of random matrices, in particular the Gaussian orthogonal ensemble (GOE).[5] The recent interest was particularly stimulated by numerical studies of simple model systems[6] and semiclassical theories,[7] which established a close connection between quantum energy-level statistics and classical ergodic properties.

The presence of GOE-type level statistics in numerically obtained model spectra is by now demonstrated by a large number of investigations.[6] However, the *experimental* verification of random-matrix (GOE) predictions is still of particular importance because so far there is no general theory which fully explains the success of the GOE and defines the range of its validity. The number of such analyses is very small. From a set of highly resolved *nuclear* resonance spectra, GOE-type statistical properties have been revealed unambiguously.[3] Similarly, significant results have been reported for selected *atomic* spectra.[4] *Molecules* form an important class of systems where the unambiguous verification of GOE predictions has been missing.

The basic prerequisite for such a statistical analysis is to have a sufficiently large and complete level sequence which corresponds to quantum states of the same symmetry species. In molecular spectroscopy this is a very difficult task,[8] mainly because of the very high density of states produced by rotational, vibrational, and electronic degrees of freedom.

The first signatures of GOE-type spectral fluctuations in molecular spectra have been found in the visible absorption spectrum of NO_2,[9] and in the following also in stimulated-emission pumping spectra of acetylene.[10] GOE statistics are also indicated by an investigation of the Fourier transform of a spectrum of methylglyoxal.[11] These examples, however, all suffer from the smallness of the data sample and from experimental uncertainties, such as missing lines or spurious lines of wrong symmetry. In particular, the previous statistical analysis of the NO_2 spectrum[9] was based on comparatively old data. The possibility of many spurious and mixing levels thus could not be excluded for that example, and the validity of the statistical results has been doubted.[12] The experiment therefore has been redone with special emphasis on our obtaining maximal spectral resolution. Special care has been taken in the interpretation of experimental raw data to obtain a level sequence of maximum quality. In this way we arrive at significant statistical results for the level statistics and confirm earlier conclusions on GOE-type level correlations in NO_2.

In the following we analyze a supersonic-beam fluorescence excitation spectrum of NO_2 corresponding to the transition $^2B_2 \leftarrow {}^2A_1$. Through adiabatic expansion and seeding with argon, low rotational temperatures are achieved (≈ 10 K). The resulting spectrum shows nearly unperturbed rotational line progressions (bands), indicating that molecular rotation separates to a good approximation from vibronic motion. In the statistical analysis, in order to have only levels of the same symmetry (i.e., with the same set of good quantum numbers), therefore only the origins of the rotational bands (*vibronic band origins*) are considered. These represent molecular states which are of pure vibrational and electronic (i.e., vibronic) character. The typical appearance of a rotational band in the experimental spectrum is shown schematically in the inset of Fig. 2(a). We confine our analysis to the energy interval from 14 879.8 to 17 518.1 cm^{-1}, where we have the most reliable experimental data. In this range 145 vibronic band origins were deduced from the raw spectrum. In dubious cases of nearly overlapping bands, additional high-resolution measurements with resolved hyperfine structure were made. Four band origins have been identified as hot bands (transitions between two excited states), so that we finally arrive at a sample of 141 vibronic energy levels for a subsequent statistical analysis. Vibronic intensities associated with the band origins have been obtained by the summing up of all line intensities of the respective rotational bands. By the variation of the laser power it was checked that these numbers are not affected by saturation effects. For all experimental and technical details we refer to the literature.[13]

We discuss three statistical measures: the frequency distributions $\rho(I)$ and $P(S)$ of intensities I and spacings S between neighboring levels, respectively, and the Δ_3 statistic (*spectral rigidity*). The definition of $\rho(I)$ and $P(S)$ is obvious; the less-known quantity $\bar{\Delta}_3(L)$ is defined by[14]

$$\bar{\Delta}_3(L) = \left\langle \frac{1}{L} \min_{A,B} \left\{ \int_E^{E+L} [N(E') - AE' - B]^2 dE' \right\} \right\rangle_E, \tag{1}$$

where $N(E)$ is the number of levels below energy E and $\langle \ldots \rangle_E$ denotes spectral averaging.[15] $\bar{\Delta}_3(L)$ is a measure for the averaged least-squares fluctuations of the spectral density around its mean behavior. $\bar{\Delta}_3(L)$ and $P(S)$ are independent statistics and give complementary information in the sense that they are mainly sensitive to long- and short-range spectral correlations, respectively.

The numerical results of the analysis of our experimentally deduced set of 141 levels are shown in Figs. 1 and 2. Figure 1 gives the histogram of intensities on a doubly logarithmic scale. The full line gives the GOE prediction, namely the Porter-Thomas distribution[16]

$$\rho(I) = (2\pi I)^{-1/2} e^{-I/2}, \tag{2}$$

where intensities I are normalized to unit mean. Since this distribution diverges for $I=0$, the histogram gives the scaled values $\sqrt{I} N(I)$, where $N(I)\, dI$ is the number of intensities in the interval $[I, I+dI]$. Above a threshold of $I_s \approx 0.01$, the histogram follows the theoretical distribution, Eq. (2). A χ^2 test for this range gives a confidence level of 37%, which indicates good agreement with Eq. (2). The intensity threshold I_s is imposed by experimental conditions and leads to a fraction α of missing levels which, with use of Eq. (2), is given by

$$\alpha = \int_0^{I_s} \rho(I)\, dI = \mathrm{erf}[(I_s/2)^{1/2}]. \tag{3}$$

From our data we estimate that approximately twelve levels are missing ($\alpha \approx 0.08$).[17] Because of these missing lines, the experimental mean intensity $\langle I_{\mathrm{exp}} \rangle$ used for the normalization of the intensities in Fig. 1 has to be renormalized to obtain the true mean $\langle I \rangle$. Using Eq. (2) we find

$$\frac{\langle I_{\mathrm{exp}} \rangle}{\langle I \rangle} = 1 + (1-\alpha)^{-1} \left(\frac{2I_s}{\pi} \right)^{1/2} \exp\left(\frac{-I_s}{2} \right), \tag{4}$$

where I_s is the true threshold. From this in our case we find that the above estimates for I_s and α do not change significantly. For a discussion of missing-line effects on $\rho(I)$, also compare Ref. 10b. For a theoretical discussion of intensity fluctuations, also see the work of Stechel.[18]

In Fig. 2(a) the NO_2 spacing histogram is compared with the corresponding GOE result, which is closely approximated by the Wigner distribution,

$$P_0(S) = \tfrac{1}{2} \pi S e^{-\pi S^2/4}, \tag{5}$$

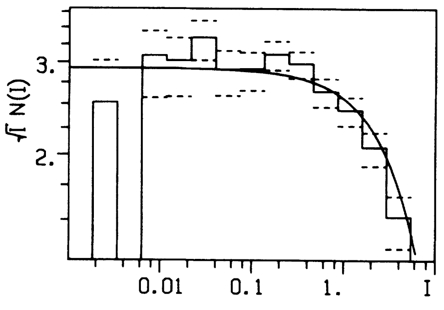

FIG. 1. Histogram of experimental intensities I. The abscissa is in mean intensity units; the ordinate gives the scaled number of intensities $\sqrt{I} N(I)$. The solid line is the GOE prediction [Porter-Thomas distribution, Eq. (2)]. The dashed-line bars indicate the statistical sampling error (one standard deviation). Also, see caption of Fig. 2(a).

drawn as a solid line. For comparison, the dashed line shows $P(S)$ for an uncorrelated sequence, where successive levels arrive randomly, and which gives an exponential, $P(S)=\exp(-S)$.[7] The agreement of the empirical histogram with the Wigner distribution, Eq. (5), is good, with a χ^2 confidence level of 23%. To strengthen this significance we have to discuss the effect on $P(S)$ when levels are randomly eliminated from a pure GOE sequence. For a small relative fraction α of eliminated levels we find the spacing distribution to be generally given by (S in mean spacing units)

$$P(S)=(1+\alpha)[(1-\alpha)P_0((1+\alpha)S)+\alpha P_1((1+\alpha)S)]. \tag{6}$$

$P_0(S)$ is the undisturbed spacing distribution, in our case given by Eq. (5), and $P_1(S)$ is the distribution of next-nearest level spacings. $P_1(S)$ for the GOE is known.[19] Together with the value for α estimated above, it follows that in the GOE case the normalized $P(S)$ differs at most by 0.04 from $P_0(S)$, which, in our case, is negligible.

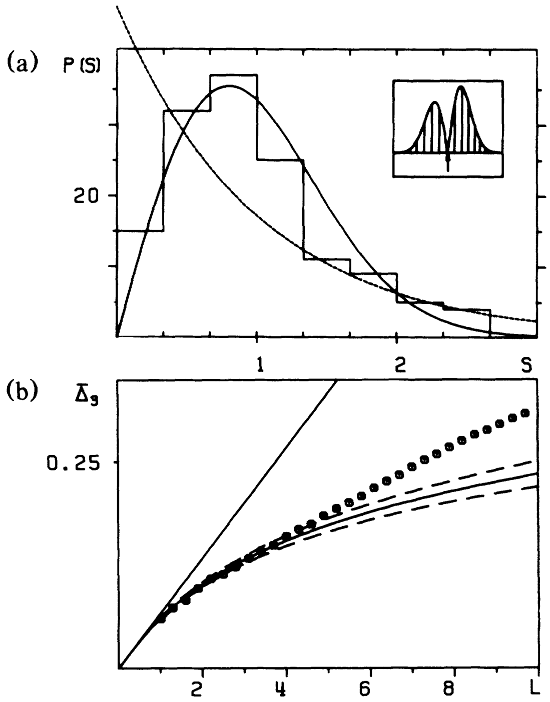

FIG. 2. (a) Histogram of experimental spacings S between adjacent band origins. The abscissa is in mean spacing units; the ordinate gives the number of spacings per bin. The solid line is the Wigner distribution (GOE), Eq. (5); the dashed line indicates the prediction for an uncorrelated level sequence. Inset: Schematic of a typical rotational band (P and R branch) as found in the experimental spectrum, from which the origin is extracted (indicated by an arrow). The spacings S shown here are spacings between adjacent band origins derived in that way, and the intensities shown in Fig. 1 are obtained as the total intensity of the band. (b) Empirical $\bar{\Delta}_3(L)$ values (circles) for the sequence of band origins. The abscissa is in mean spacing units. The solid curve gives the GOE prediction; the dashed lines indicate the theoretical standard deviation as obtained from a Monte Carlo calculation (see text). The straight line is the prediction for a spectrum without any level correlations.

For the spectral rigidity the situation is different. Figure 2(b) shows the NO_2 $\bar{\Delta}_3(L)$ values (circles) and the GOE prediction (solid curve). The latter is (for large L) given by

$$\bar{\Delta}_3(L)=\pi^{-2}\ln(L)-0.007. \tag{7}$$

L is always measured in mean spacing units. For an uncorrelated level sequence one finds a linear dependence of $\bar{\Delta}_3$ on L, $\bar{\Delta}_3=L/15$, depicted by the straight line. The agreement of the empirical $\bar{\Delta}_3(L)$ values with the GOE prediction up to $L=5$ is good; for $L>5$ the empirical data points deviate towards higher values. The broken lines in Fig. 2(b) give the standard deviations of $\bar{\Delta}_3(L)$. They have been calculated by a Monte Carlo calculation with use of an ensemble of 100 GOE matrices of dimension 300. The effect of randomly eliminating twelve lines from a GOE sequence of 153 levels was determined by our averaging over the same ensemble (also see Cocera and Stefanon[20]). To account for further experimental problems, we also included the effect of having spurious lines (e.g., hot bands) among the set of 141 levels, assuming four such levels as a reasonable estimate. The result is shown in Fig. 3, which is analogous to Fig. 2(b). Our Monte Carlo simulation reproduces the experimental deviations of $\bar{\Delta}_3(L)$ from the GOE prediction quite well. The remaining discrepancies for large L are within one standard deviation.

The optical spectrum of NO_2 is long known for its complexity.[21] The reason is indicated by theoretical *ab initio* calculations which show that the $^2A_1$ electronic

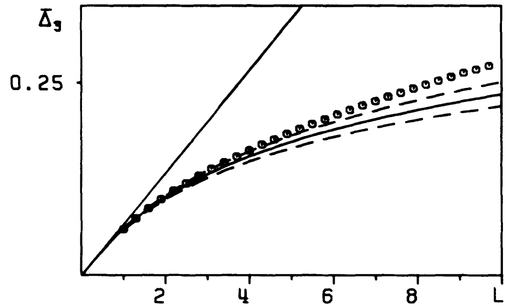

FIG. 3. As in Fig. 2(b), but $\bar{\Delta}_3(L)$ (circles) obtained from a Monte Carlo calculation to demonstrate the effect of twelve missing and four spurious lines on a GOE sequence of 141 levels.

ground state and the ${}^2B_2$ first excited state become degenerate near the equilibrium geometry of the ${}^2B_2$ state.[22] Dynamical calculations show that this leads to a breakdown of the usual adiabatic (Born-Oppenheimer) separability of electronic and nuclear motion (i.e., strong vibronic coupling).[23] As a consequence, also the different vibrational modes are strongly intermixed. The statistical properties of the NO_2 spectrum which we have found in the present work are a direct manifestation of this situation and thus verify these predictions. More precisely, since uncoupled (*regular*) systems exhibit different statistical properties[7] (such spectra are locally uncorrelated), we can now infer from the experimental data *alone* that the vibronic levels in the analyzed energy range cannot be further characterized by vibrational and electronic quantum numbers.

We conclude that typical random-matrix (GOE) spectral fluctuations have been identified in the optical vibronic spectrum of NO_2. The incorporation of missing-line effects gives a consistent picture for short- and long-range level correlations as well as for the distribution of intensities. We confirm earlier conclusions based on a less complete experiment and statistical analysis. Our findings strongly support the conjectured universality of spectral fluctuations in systems with strongly coupled degrees of freedom and strengthen the validity of random-matrix models.

---

[1] *Statistical Theories of Spectra: Fluctuations,* edited by C. E. Porter (Academic, New York, 1965).

[2] T. A. Brody *et al.*, Rev. Mod. Phys. **53**, 385 (1981).

[3] R. U. Haq, A. Pandey, and O. Bohigas, Phys. Rev. Lett. **48**, 1086 (1982); O. Bohigas, R. U. Haq, and A. Pandey, Phys. Rev. Lett. **54**, 1645 (1985).

[4] N. Rosenzweig and C. E. Porter, Phys. Rev. **120**, 1698 (1960); H. S. Camarda and P. D. Georgopulos, Phys. Rev. Lett. **50**, 492 (1983).

[5] M. Mehta, *Random Matrices and the Statistical Theory of Energy Levels* (Academic, New York, 1967).

[6] See, e.g., *Quantum Chaos and Statistical Nuclear Physics,* edited by T. H. Seligman and H. Nishioka, Lecture Notes in Physics Vol. 263 (Springer-Verlag, Heidelberg, 1986), in particular O. Bohigas, M.-J. Giannoni, and C. Schmit, p. 18, and references therein.

[7] M. V. Berry and M. Tabor, Proc. Roy. Soc. London A **356**, 375 (1977); M. V. Berry, Proc. Roy. Soc. London A **400**, 229 (1985).

[8] See, e.g., Th. Zimmermann, L. S. Cederbaum, H.-D. Meyer, and H. Köppel, J. Phys. Chem. **91**, 4446 (1987).

[9] E. Haller, H. Köppel, and L. S. Cederbaum, Chem. Phys. Lett. **101**, 215 (1983).

[10a] E. Abramson *et al.*, J. Chem. Phys. **80**, 2298 (1984).

[10b] S. Mukamel, J. Sue, and A. Pandey, Chem. Phys. Lett. **105**, 134 (1984).

[10c] R. L. Sundberg *et al.*, J. Chem. Phys. **83**, 466 (1985).

[11] L. Leviandier *et al.*, Phys. Rev. Lett. **56**, 2449 (1986).

[12] R. Jost and M. Lombardi, in Ref. 6, p. 72; K. K. Lehmann and S. L. Coy, J. Chem. Phys. **87**, 5415 (1987).

[13] G. Persch, W. Demtröder, Th. Zimmermann, H. Köppel, and L. S. Cederbaum, to be published.

[14] F. J. Dyson and M. L. Mehta, J. Math. Phys. **4**, 701 (1963).

[15] The spectrum is first scaled to constant mean level density since only density fluctuations are to be considered (see, e.g., Refs. 2 and 9).

[16] C. E. Porter and R. G. Thomas, Phys. Rev. **104**, 483 (1956).

[17] The χ^2 confidence level for the hypothesis that our experimental intensities follow the Porter-Thomas distribution improves when $\rho(I)$, Eq. (2), is normalized according to the true number of levels.

[18] E. B. Stechel, in Ref. 6, p. 182, and references therein.

[19] P. B Kahn, Nucl. Phys. **41**, 159 (1963).

[20] C. Cocera and M. Stefanon, Nucl. Phys. A **315**, 1 (1979).

[21] D. K. Hsu, D. L. Monts, and R. N. Zare, *Spectral Atlas of Nitrogen Dioxide* (Academic, New York, 1978).

[22] C. F. Jackels and E. R. Davidson, J. Chem. Phys. **65**, 2941 (1976).

[23] E. Haller, H. Köppel, and L. S. Cederbaum, J. Mol. Spectrosc. **111**, 377 (1985).