

## SURVEY ARTICLE

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# STATISTICAL STUDIES OF LEVEL CORRELATIONS AND CHAOTIC PHENOMENA IN SPECTROSCOPY

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This review covers some modern applications of statistical methods in the analysis of complicated molecular spectra, obtained usually with laser excitation. Among the available fluctuation measures, special emphasis is given to the nearest neighbour separation and spectral rigidity measures, and attention is called to the power spectrum (or statistical Fourier-transform) method.

From the high-resolution spectroscopic techniques used to obtain spectra of highly vibrationally excited molecules, the stimulated emission pumping (SEP) scheme is very successful in simplifying the high excitation regions. Examples of SEP applications are given, especially to acetylene, in greater details. Finally the role of molecular rotation in molecular dynamical and statistical studies is stressed.

## 1. Introduction

In recent years there is an increased interest in the interpretation of complex molecular spectra obtained usually with laser excitation. With high energy excitation it is possible to reach large values of vibrational quantum numbers. Traditional spectroscopy deals with spectra wherein each transition can be assigned to valid quantum numbers and thus can be analyzed in a conventional fashion. With the coming of lasers and their applications in laser-induced processes it became evident that the common methods of spectroscopic analysis are not always easily applicable at high vibrational excitation where the energy level density is extremely large. On the other hand, e.g. chemical applications of lasers demand an understanding of this energy region.

In this review we shall cover some relatively recent techniques that allow us to gain at least a partial explanation of complex spectra. Such studies inevitably lead to basic questions concerning regularity in molecular spectra and involve problems about ergodic or chaotic behaviour in quantum systems. We shall shortly summarize recent views on quantum ergodicity in molecular spectra. The relevance to laser-excited molecular processes shall occasionally be emphasized as it is this aspect that provides the most important impetus for such studies.

## 2. A short historical overview

As we shall see the analytical approach to high energy density regions is mostly statistical in nature. It is through a statistical study of energy level systems or even actual spectral features from which we hope to extract information on regularity and dynamical behaviour. Such studies were pioneered by Wigner in nuclear physics [118,119,120,121] who proposed a form for the distribution of first neighbour spacings in highly excited nuclear spectra.

This statistical approach is closely linked to the theory of random matrices (Bohigas and Giannoni [17], Brody et al [20], Carmeli [23], Mehta [84], Porter [102] because — as Wigner pointed out — the statistical properties of spectra of complicated Hamiltonians are similar to those of random Hamiltonians. The applications of random matrix statistics to atomic spectra have emerged in the last twenty years (Camarda and Georgopoulos [22], Rosenzweig and Porter [107]) with a rapid expansion to molecular spectroscopy (for NO<sub>2</sub>: Haller, Koppel and Cederbaum [56,57], Hardwick [59], Lehmann and Coy [75,76], Smalley et al [108], Zimmerman, Koppel and Cederbaum [117] — for acetylene: Abramson et al [1,2,3], Engel and Levine [37], Farantos [39], Holme and Levine [63,64,65], McIlroy and Nesbitt [86], Pique et al [94,95,97], Sumpter and Thompson [109], Sundberg et al [110], — for Ar<sub>3</sub>: Leitner, Berry and Whitnell [77] — for formaldehyde: Miller et al [87], Polik et al [99,100].

Following the simple applications of first neighbour spacing statistics, more advanced statistical tools have been worked out. Thus the spectral rigidity measure ( $\Delta_3$ ) was introduced by Dyson and Mehta [32], and Bohigas and Giannoni [16] to test long-range correlations among levels, the so-called *F*-statistics (Dyson [33]) to find levels in sequences to be eliminated from the analysis, and several other correlation and fluctuation measures (Brody et al [20]).

For modern polyatomic applications not only the various spacing distributions and the  $\Delta_3$ -statistics became widely used, but additional fluctuation measures have been developed for spectral line strength (Alhassid, Levine [4], Brickman, Engel and Levine [19], Coy, Hernandez and Lehmann [27], Heller, Sundberg [61], Kommandeur et al [73], Porter, Thomas [101]), and for fluorescent lifetimes (Engel et al [35]). In this review we shall deal only with energy level statistics, occasionally mentioning spectral line strength distributions.

An additional technique for testing long-range order or correlatedness in optical spectra is the statistical Fourier-transform of energy level sequences or experimental frequency spectra (Jost, Lombardi [69]), Leviandier, Lombardi, Jost, Pique [78], Levine, Kinsey [79], Lombardi, Labastie, Bordas, Broyer [81], Lorquet, Engel, Levine [82], Pique, Joyeux, Manners, Sitja [98], Remacle, Levine [106]). This method provides information on the time-scale of various processes leading to the experimental spectra. Ergodic behaviour in spectra may also be quantified by the fractal dimension of the trajectories in phase space (Grassberger and Procaccia [47]), and by Kolmogorov entropy (Pesin [93]). Excellent examples for this approach are in the recent literature (Beck, Leitner, Berry [9], Berry [14]).

### 3. Regularity, ergodicity and chaos in spectroscopy

One of the interesting questions of contemporary physics is whether chaotic phenomena in classical dynamics appear in some form in the quantum mechanical description. The literature on this subject is very extensive (e.g., Berry [10,11,12,13], Casati et al [24], Heller [62], Tabor [112]).

It is characteristic of classically chaotic dynamics that it grows from the non-linearity in the governing system of dynamical equations. Chaos means the irregular and unpredictable evolution of a non-linear system in time. Quantum systems are not chaotic in the way classical systems are. The Schroedinger equation that is the basis of the wave mechanical description is a linear equation in the sense that if two different wavefunctions satisfy it then also does any linear combination of those functions. Thus a linear superposition is maintained indefinitely and the solutions are periodic and quasi-periodic. In contrast to classical dynamics, molecular systems do not have well-defined trajectories in phase space on time scales long relative to the excitation time of internal motions. Due to the Heisenberg uncertainty relationship it is not possible to prepare an individual spectroscopic state in which the position and momentum coordinates of the nuclei and electrons are sharply defined; they have a finite distribution instead. While in classical chaos particle trajectories have an infinitely complicated substructure (Gutzwiller [55]), in the quantum mechanical description these trajectories are blurred.

There are several terms that are frequently used in the discussion of the dynamical behaviour; regularity, ergodicity and chaoticity. In addition one encounters frequently the qualification: "stochastic". It is not attempted here to separate clearly the meaning of these terms (in relation to spectroscopic behaviour) but a few words are appropriate.

A stochastic process is one that is a function of a random variable (in addition of being a function of time), and the random element is usually some external influence on the system. The irregular behaviour of a classical system, modelling a quantum system like molecules, is not a result of some random external influence but is due to the intrinsic properties of the system itself. Therefore, strictly speaking molecular systems cannot properly be regarded as stochastic. Still this term is very widely used.

Ergodic behaviour is defined in statistical mechanics. When we have a classical system where the trajectory of motion in phase space samples uniformly the latter, the time average of a given quantity equals its phase (ensemble) average.

Bohr's correspondence principle requires that in a high excitation state, like nearly dissociated or nearly ionized molecular states, where the energy density is very great, the molecular quantum system should correlate with the classical description. Therefore one would expect some manifestation of classically chaotic behaviour in a quantum system, or quantum phenomenon, like molecular spectra. This manifestation is found in the statistical properties of molecular energy levels and in transitions among them. Ergodicity or regular behaviour, and chaotic limits shall in the following be studied from a statistical viewpoint. Regular spectroscopic behaviour may be related to the regularity of the underlying classical motion,

whereas irregular (or chaotic) behaviour of the corresponding classical system manifests itself in a very different statistical behaviour in spectroscopy. The transition between regular and irregular (chaotic) classical systems is provided by the KAM theorem (Kolmogorov–Arnold–Moser) (Arnold [15], Kolmogorov [72], Moser [88]). It is possible to study the statistical properties of energy levels in the semiclassical limit;  $\hbar \rightarrow 0$ , as was shown by Berry [11,12] using Gutzwiller’s method (Gutzwiller [48,49,50,51,52], see also: Balian and Bloch [7]). In this way classical periodic orbits may be related to semiclassical energy levels. In the semiclassical description quantization is provided by the Einstein–Brillouin–Keller (EBK) quantization (based on Einstein’s paper in 1917; [34]). This corresponds to ‘old quantum theory’ which was superseded by wave mechanics, but for the study of molecular chaos in the semiclassical limit has been rediscovered and widely used (see: Tabor [112], Section 6, pp. 228–279). In terms of EBK quantization rules a regular spectrum corresponds to regions of integrable (regular) motion that can be quantized according to these rules, whereas irregular (chaotic) spectra cannot be so quantized. As we shall see, one may model certain spectroscopic observations on this semiclassical approach that provides insight into spectral statistical characteristics.

#### 4. The mathematical apparatus of statistical spectroscopy

Before applying most of the statistical probes to molecular energy levels or actual molecular spectra a procedure is needed to place those sequences on the same footing. For this purpose one has to separate the average density of levels from fluctuations about that average (Brody et al [20], Bohigas and Giannoni [17], Haller, Koppel and Cederbaum [56]). This is because we want to reduce different energy level systems to the same basis that then allows a comparison of the statistical behaviour of highly excited nuclear levels to those of molecular excitations. This is achieved by a suitable mapping of the original energy level system:  $E \rightarrow \tilde{E}$ . Taking  $N(E)$  as the cumulative density of the energy levels it is seen to fluctuate about a smooth average:  $N_{av}(E)$ :

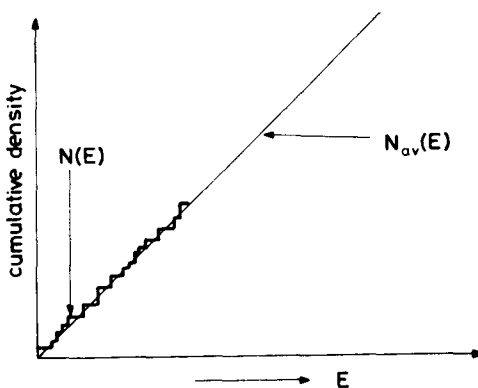


Fig. 1. Cumulative energy level distribution

Now if

$$\begin{aligned} \tilde{E}_i &= N_{\text{av}}(E_i); \quad i = 1, 2, 3, \dots \\ N_{\text{av}}(E) &= \int_0^E \varrho_{\text{av}}(E') dE' = \int_0^{\tilde{E}} \varrho_{\text{av}}(\tilde{E}') d\tilde{E} = \tilde{E} = \hat{N}_{\text{av}}(\tilde{E}). \end{aligned} \quad (1)$$

The new energy level sequence  $\tilde{E}_i$  has a constant density;  $\varrho_{\text{av}}(\tilde{E}) = 1$ , and it may be split up to a secular part (showing a smooth change with energy, that is universal) and a fluctuation part (that is specific to the system):

$$\hat{N}(\tilde{E}) = \hat{N}_{\text{av}}(\tilde{E}) + \hat{N}_{\text{fl}}(\tilde{E}) = \tilde{E} + \hat{N}_{\text{fl}}(\tilde{E}). \quad (2)$$

We shall be concerned only about the fluctuation part  $\hat{N}_{\text{fl}}(\tilde{E})$ . This carries the statistical information on the energy level system. Taking into account the fact that energies (eigenvalues) are not continuous functions, Eq. (1) can be rewritten:

$$N_{\text{av}}(E) = \sum_{i=1}^n \Theta(E - E_i), \quad (3)$$

where  $\Theta(E)$  is the Heaviside step function, and  $\tilde{E}$  can be given as:

$$\tilde{E} = b_1^{-1}[N_{\text{av}}(E) - b_0], \quad (4)$$

so that:

$$\hat{N}_{\text{av}}(\tilde{E}) = b_0 + b_1 \tilde{E}. \quad (5)$$

This procedure is called “unfolding” (“deconvolution” or “mapping”) and might be a sensitive function of the choice for  $N_{\text{av}}(E)$ , i.e. of the way we approximate the average behaviour of the energy level system. There are various possibilities for this, one of these is the use of a polynomial expansion:

$$N_{\text{av}}(E) = \sum_{k=1}^m a_k E^k. \quad (6)$$

Alternatively, one may use a cubic spline function smoothing (Press et al [103], Chapter 3), or apply a moving average (Wong, French [122], Venkataraman [115]):

$$\tilde{E}_{i+1} = \tilde{E}_i + (2k + 1)(E_{i+1} - E_i)/(E_{j_2+1} - E_{j_1}), \quad (7)$$

where  $i$  runs over the energy levels, and  $j_1 = \max(1, i - k)$  and  $j_2 = \min(n - 1, i + k)$ ,  $n$  is the total number of energy levels and  $k$  is the number of consecutive spacings between the energy levels over which averaging is done.

All these unfolding methods produce level sequences of nearly unit local mean spacing (density). The fluctuation properties of spectra may either be stationary (invariant to translation along the energy axis), or not stationary. In the latter case one is interested in asymptotic properties of energy level sequences.

#### 4.1. Fluctuation measures

With respect to the statistical nature of  $\hat{N}_R(\tilde{E})$  in Eq. (2) there are two extreme cases, the case of a complete lack of correlation among energy levels, and the case of very strong correlations. There are a number of mathematical techniques to test such correlations. Historically the first of these was suggested by Wigner (Wigner [118,119]) that relates to the distribution of spacings among adjacent levels:  $P(S)$  ( $S$  stands for first neighbour spacing between unfolded energies:  $\tilde{E}$ ). This method relies on the absence or presence of repulsion between levels.<sup>1</sup>

For a completely random energy level sequence, the probability of a spacing is independent of the magnitude of the spacing and one has a Poissonian distribution law: (using first neighbour spacings ( $S$ ) in terms of local spacing units. The local spacing unit is 1 for an unfolded energy level sequence):

$$P(S) = \exp(-S). \quad (8)$$

On the other hand when there is (linear) level repulsion, the probability of a spacing is proportional to the spacing magnitude:

$$P(S) = (\pi/2)S \exp(-\pi S^2/4). \quad (9)$$

There is an important difference between the Poisson (Eq. (8)) and Wigner (Eq. (9)) distributions; for a random energy level sequence the most probable spacing is zero (level clustering), whereas for the Wigner (strongly correlated) distribution zero spacing has zero probability (level repulsion).

In order to model strong correlations among energy levels, which is the case for highly excited nuclear spectra, Wigner proposed random matrix theory (Wigner [118,119], Brody et al [20]). Random matrix theory is reminiscent of statistical mechanics in the sense that it deals with ensemble averages over stochastic quantities. These ensembles are formed of matrices possessing random structure. Depending on the way such a random matrix is defined there are three types of matrix ensembles: the Gaussian orthogonal ensembles (GOE), the Gaussian unitary ensembles (GUE), and the symplectic ones. If the physical system is invariant under time-reversal and under rotations the matrices are real symmetric with random elements having independent Gaussian distributions. The ensemble must be invariant to orthogonal transformations and consists of matrices of identical dimension. The GOE model

<sup>1</sup>Repulsion between energy levels may be understood in terms of avoided crossings, or the "non-crossing rule" (Neumann and Wigner [89], Berry [11]). This rule applies only when we select energy levels possessing the same symmetry. In the case of vibronic energy levels this involves the same electronic state and vibrational quantum numbers (or combinations of vibrational quantum numbers that correspond to the same symmetry of the product of vibrational wavefunctions), the same total angular momentum quantum number (usually  $J$ ) and the same parity (behaviour towards space inversion). In addition there is a need to study as complete as possible level systems in the given symmetry, so that no (or a minimal number of) energy levels should be missing, and no spurious levels should occur. All the following statistical measures presuppose this kind of symmetry selection, the use of so-called "pure sequences".

represents the strongest possible level correlations and it is frequently feasible to give analytical formulae for this limit of the various fluctuation measures. The GUE limit corresponds to systems for which the Hamiltonian does not possess time reversal and rotation symmetry, such matrices have complex Hermitian structure. Finally the symplectic ensembles correspond to systems that are time-reversal invariant but not invariant under rotations, and if the system has half-odd-integer total angular momentum the matrices of the ensemble are quaternion real. The importance of GUE and symplectic ensembles is little in the field of molecular spectroscopy.

Random matrices also show ergodic property so that their ensemble averages are equal to spectral averages of a member (Pandey [91]). As a consequence when we choose one member of the ensemble it will be representative of the whole ensemble. This ergodicity property shall be utilized in the application of the various fluctuation measures.

We can now return to the discussion of the fluctuation measures with these two limits in mind; the completely random Poissonian sequences and the strongly correlated GOE limit.

The spacing distribution discussed previously does not include information on spacing correlations. This is obtained for two adjacent nearest-neighbour spacings, as a spectral average, by:

$$c = \sum_i (S_i - 1)(S_{i+1} - 1) / \sum_i (S_i + 1)^2. \tag{10}$$

For the Poissonian case  $c = 0$ , while in the GOE limit the first-order spacings are anticorrelated:  $c = -0.271$  (Brody et al [20], Garrison [43]).

Another very useful statistics is the spectral rigidity;  $\Delta_3(L)$  (Bohigas, Giannoni [16], Dyson, Mehta [32], French et al [41,42]). Spectral rigidity measures the least-squares deviation of the cumulative energy density  $\hat{N}(\tilde{E})$  in Eq. (2) from the best straight line fitting it:

$$\Delta_3(\alpha; L) = (1/L) \min_{A,B} \int_{\alpha}^{\alpha+L} [\hat{N}(\tilde{E}) - A\tilde{E} - B]^2 d\tilde{E}, \tag{11}$$

where  $\hat{N}(\tilde{E})$  is the number of levels below  $\tilde{E}$ ,  $A$  and  $B$  are constants of the fitting,  $L$  measures the length of the level sequence, and  $\alpha$  is the beginning of the  $L$  interval. The value actually used in the analysis is the spectral average:

$$\langle \Delta_3(\alpha, L) \rangle = \overline{\Delta}_3(L). \tag{12}$$

For analytical purposes sums are used instead of the integral in Eq. (12), such formulae are found in Bohigas and Giannoni [16] and Feingold and Fishman [40]. Spacing distributions and the  $\Delta_3(L)$  statistics are independent fluctuation measures and are complementary information; spacing distribution measures short range correlations, while  $\Delta_3(L)$  characterizes long-range ones. For a Poissonian level  $\overline{\Delta}_3(L) = L/15$ , whereas for a GOE sequence:

$$\overline{\Delta}_3(L) = (1/\pi^2)(\ln L - 0.0687). \tag{13}$$

The meaning of these two limiting expressions is that for a random set of levels the variance of deviations from the mean behaviour is proportional to the number of levels, whereas for the strongly correlated case the increase is only logarithmical. It is quite possible to find cases where spacing distributions indicate strong correlations, while spectral rigidity is low. It is often found that for actual level systems (theoretically computed or experimentally determined) the increase of  $\overline{\Delta}_3(L)$  with  $L$  is slower than indicated by the GOE limit in Eq. (13), and saturation is observed (see e.g. Zimmermann et al [116]). It is possible to relate  $\overline{\Delta}_3(L)$  to the sum over classical periodic orbits and find the general criterion for the saturation of spectral rigidity. This occurs when  $L \gg L_{\max}$ , where  $L_{\max}$  is given by semiclassical considerations (Berry [12]) as

$$L_{\max} = h\langle d \rangle / T_{\min} \simeq \hbar^{-(N-1)}, \quad (14)$$

where  $\langle d \rangle$  is the mean level spacing:  $\langle d \rangle^{-1} \simeq \hbar^N$ , and  $N$  is the number of freedoms in the semiclassical system.  $T_{\min}$  in Eq. (14) is the period of the shortest classical closed orbit.

In addition to these two most important statistical measures, there are a number of others. One of these is the "number statistic";  $n(L)$ , which is a discrete variable counting the number of levels contained in the interval  $L$ . Provided the spectral sequence is unfolded, the average of  $n(L)$  is  $L$ . The useful measures derived from this quantity are its higher moments, its variance  $\sum^2(L)$ , its skewness  $\gamma_1(L)$  and its excess  $\gamma_2(L)$  (Pandey [90]).

All of these (and previous fluctuation measures) are derivable from the level correlation functions. The  $k$ -level correlation function is defined as (Bohigas-Giannoni [17]):

$$\tilde{R}(E_1, \dots, E_k) = (N! / (N - k)!) \int \dots \int P_N(E_1, \dots, E_N) dE_{k+1} \dots dE_N, \quad (15)$$

where  $P_N$  is the joint probability density of the energy level  $E_i$ :

$$P_N(E_1, E_2, \dots, E_N) = C_N \exp(-(1/4\sigma^2) \sum_i E_i^2) \prod_i |E_i - E_j|, \quad (16)$$

where  $C_N$  is a normalization constant, and  $\sigma^2$  is the variance of the eigenvalue  $E_i$ .

In Eq. (16)  $P_N(E_1 \dots E_N) dE_1 \dots dE_N$  gives the probability of having one level at  $E_1$ , another at  $E_2 \dots$  and another at  $E_N$  within the intervals  $\{E_j, E_j + dE_j\}$ .

When we unfold the energies  $E_i \rightarrow \tilde{E}_i$  (see earlier) a new set of  $k$ -level correlation functions is obtained:

$$R_k(\tilde{E}_1, \tilde{E}_2 \dots \tilde{E}_N) = \lim_{N \rightarrow \infty} \frac{\tilde{R}_k(E_1, \dots, E_k)}{\tilde{R}_1(E_1) \dots \tilde{R}_1(E_k)}. \quad (17)$$



The functions  $R_k$  characterize the fluctuation properties of levels completely. Of central importance are the  $k$ -level cluster functions

$$Y_k(\tilde{E}_1 \dots \tilde{E}_k) = \sum_G (-1)^{k-m} (m-1)! \prod_{j=1}^m R_{G_j}(\tilde{E}_t, \text{ with } t \text{ in } G_j), \quad (18)$$

where  $G$  stands for division of the indices  $1, 2 \dots k$  into subgroups  $[G_1, G_2, \dots, G_m]$ . The most significant of the cluster functions is the two-level one:  $k = 2$ , when there are two subgroups:  $m = 1 [(1,2)]$  and  $m = 2 [(1),(2)]$ :

$$Y_2(\tilde{E}_1, \tilde{E}_2) = -R_2(\tilde{E}_1, \tilde{E}_2) + R_1(\tilde{E}_1)R_1(\tilde{E}_2). \quad (19)$$

Another possibility is to use the probability that in a sequence of unfolded levels  $\{\tilde{E}_i\}$  of mean spacing unity, a length  $L$  contains exactly  $k$  levels. This is given by

$$E(k; L) = \lim_{N \rightarrow \infty} (N! / (N-k)!) \int \dots \int_{\text{in}} d\tilde{E}_1 \dots d\tilde{E}_k \int \dots \int_{\text{out}} d\tilde{E}_{k+1} \dots d\tilde{E}_N P_N(E_1 \dots E_N), \quad (20)$$

where the first group of integrals is performed on the variables inside the interval  $[\alpha, \alpha + L]$  and the other group is an outside integral. The probability  $E(k; L)$  in Eq. (20) is simply related to various fluctuation measures, e.g. the nearest neighbour spacing distribution  $p(\tilde{E})$  in Eq. (8):

$$p(\tilde{E}) \equiv p(0, \tilde{E}) = (d^2 / d\tilde{E}^2) E(0, \tilde{E}). \quad (21)$$

Practically it is better to use integrated quantities:

$$y_k(L) = \int_0^L \dots \int_0^L Y_k(\tilde{E}_1 \dots \tilde{E}_k) d\tilde{E}_1 \dots d\tilde{E}_k. \quad (22)$$

Using  $y_k$  quantities the various number statistics can be easily given as, e.g. the average number of levels in an interval  $L$ :

$$\overline{n(L)} = y_1(L) = L. \quad (23)$$

The variance of this number is:

$$\Sigma^2(L) = \overline{(n(L) - L)^2} = y_1(L) - y_2(L). \quad (24)$$

Particularly important are the quantities related to the two-level cluster function  $Y_2(\tilde{E}_1, \tilde{E}_2)$  in Eq. (19) which will be called two-point measures. E.g.:

$$1 - Y_2(\tilde{E}) = \sum_{k=0}^{\infty} p(k, \tilde{E}), \quad (25)$$

so that all orders of spacing distributions are two-point measures. Using  $Y_2(\tilde{E})$  we may write the variance of the number statistic  $\sum^2(L)$  as

$$\sum^2(L) = L - \int_0^L (L-r)Y_2(r)dr \quad (26)$$

and establish a relationship between  $\bar{\Delta}_3(L)$  and  $\sum^2(L)$ :

$$\bar{\Delta}_3(L) = (2/L^4) \int_0^L (L^3 - 2L^2r + r^3) \sum^2(r)dr. \quad (27)$$

For a Poissonian spectrum of energy levels the relationships for the various fluctuation measures are simple: For spacing distributions:

$$p(k, L) = (L^k/k!) \exp(-L). \quad (28)$$

For  $k$ -level cluster functions:

$$Y_1(\tilde{E}) = 1; \quad Y_k(\tilde{E}_1, \tilde{E}_k) = 0; \quad k \geq 2 \quad (29)$$

and also:

$$\sum^2(L) = L \quad \text{and} \quad \bar{\Delta}_3(L) = L/15. \quad (30)$$

In the GOE limit these formulae are considerably more complicated. Analytical forms for the different cluster functions (Eq. (18)) were derived on the basis of Mehta's work [83]. Mehta and Pandey [85] gave relationships among functions related to spacing distributions, on the one hand, and the  $k$ -level correlation and cluster functions, on the other.

The two-level cluster function  $Y_2(r)$  is given for the limiting cases of small and large  $r$  values:

$$Y_2(r)_{r \rightarrow 0} \rightarrow 1 - (1/6)\pi^2 r + (1/60)\pi^4 r^3 + \dots \quad (31a)$$

and

$$Y_2(r)_{r \rightarrow \infty} \rightarrow (1/\pi^2 r^2) - (1 + \cos^2 \pi r)/\pi^4 r^4 + \dots \quad (31b)$$

The quantity  $1 - Y_2(r)$  is 1 for the Poissonian case (see Eq. (29)), while it increases from zero asymptotically to unity for the GOE limit.

The  $\bar{\Delta}_3(L)$  formula was already given in Eq. (13) while

$$\sum^2(L) = (1/\pi^2) \ln L + 0.44 \quad (32)$$

for the GOE case.

4.2. The power spectrum statistics

In addition to the above statistical tests in recent years another important fluctuation measure has been added to the arsenal; the statistical Fourier-transform (FT) technique. In their first paper on this topic Leviandier et al [78] introduced this robust method to detect long-range correlations in optical spectra. The method consists simply of taking the Fourier-transform of a set of energy levels, or directly spectroscopic data. There have been a number of theoretical papers describing the properties of this method (Coy and Lehmann [26]; Coy, Hernandez and Lehmann [27], Jost and Lombardi [69], Levine and Kinsey [79], Lombardi, Labastie, Bordas and Broyer [81]; Pique, Chen, Field and Kinsey [94,95], Pique, Joyeux, Manners and Sitja [98]; Remacle and Levine [106]).

The Fourier-transform of energy levels or spectral lines is denoted in many different ways, let us adopt here  $C(t)$ , where  $t$  refers to time, and the abscissa may be given in dimensionless ( $t/\varrho$ ) units ( $\varrho$  is energy density measured per frequency interval). The quantity examined is the square modulus of the Fourier-transform  $|C(t)|^2$ , or as it is usually denoted in signal processing: the power spectrum. This has to be spectrally or ensemble averaged prior to use. The power spectrum contains two main components, a fast and a slow component. The fast component, whose amplitude is proportional to the square of the number of lines or energy levels, is the Fourier-transform of the overall spectral envelope, whereas the more significant slow component is the Fourier-transform of the shape of the spectral lines, and its amplitude is proportional to  $N$  only:

$$\begin{aligned} \langle |C(t)|^2 \rangle = & N^2 A_E^2(t) \langle y \rangle^2 \langle L(t, \Gamma) \rangle^2 + N \langle y^2 \rangle \langle L^2(t, \Gamma) \rangle \cdot \\ & \cdot [1 - G(t) b_2(t)] \otimes A_E^2(t), \end{aligned} \tag{33}$$

where  $\otimes$  denotes the convolution operation (see: Pique et al [94]), and  $N$  is the number of lines in the spectrum,  $A_E(t)$  is the Fourier-transform of the spectral envelope,  $L(t, \Gamma)$  is the FT of the normalized line-shape of individual lines (of width  $\Gamma$ ),  $y$  is the integrated line intensity, and the angle bracket  $\langle, \rangle$  denotes averaging over all spectral features. The quantity  $G(t)$  is related to the distribution of line intensity  $y$  and line width  $\Gamma$  in the spectrum. For a Lorentzian line shape  $G(t = 0) = \langle y \rangle^2 \langle \Gamma \rangle^2 / \langle y^2 \rangle \langle \Gamma^2 \rangle$ .

When there are correlations in the spectrum (or within a set of energy levels) a "correlation hole" appears between the fast and the slow components of the power spectrum. The fast component that depends on level density and not level spacing, is not important for the study of level statistics. In the case of a theoretical spectrum of unfolded energy levels represented by sticks of equal amplitude, the fast component reduces to a very narrow channel. It is the slow component of the square modulus that is proportional to  $1 - b_2(t)$ , where  $b_2(t)$ , the two-level form factor is the Fourier-transform of the two-point correlation function  $Y_2(E)$  in Eq. (25):

$$b_2(t) = \int_{-\infty}^{+\infty} Y_2(\tau) \exp(2\pi i \tau t) d\tau. \tag{34}$$

When correlations exist among levels or spectral features ( $Y_2 \neq 0$ ), the amplitude of the slow component is multiplied by  $1 - b_2(t)$ , and since the latter difference is zero for the GOE limiting case for  $t/\rho = 0$ , and rises approximately to unity for  $t > \rho$  (average level density), a correlation hole is displayed. The correlation hole is "filled" for an uneven distribution of line intensities, as  $G(t) < 1$  for such a case, and this reduces the observability of the hole. Extensive noise of the spectrum leads also to the filling of the correlation hole.

An enormous advantage of the power spectrum method is that the correlation hole persists (but becomes narrower) when several pure sequences are superimposed, as it happens in transforming actual spectral details. So the technique is capable of detecting correlations in any mixture of levels or different stretches of spectra.

All this is true only for spectral or ensemble averages, or smoothed FT spectra. Individual level sequences or single lengths of spectra lead to total modulation, "speckle noise" is observed. This is analogous to diffraction of laser light from a rough surface. In the modulation there is a lot of information on the spectral fine structure, that is, however, not needed for correlation analysis.

Through the two-level cluster function  $Y_2(\tilde{E}_1, \tilde{E}_2)$  in Eq. (19) the power spectrum is related to the spectral rigidity statistics (Lombardi et al [81]):

$$\Delta_3(r) = \int [1 - b_2(t)] K(r, t) dt, \quad (35)$$

where  $K(r, t)$  is a kernel function:

$$K(r, t) = (1/(2\pi t)^2) [1 - F(y)^2 - 3F'(y)^2], \quad (36)$$

where, in turn

$$F(y) = (\sin(y)/y); \quad y = \pi r t.$$

Equations (35) and (36) can be derived from Eqs (27) and (33) by inverting the order of integrations. It is then also seen that  $|C(t)|^2$ ,  $\Delta_3(r)$  and  $\Sigma^2(r)$  are all closely related and therefore all convey information on second order correlations between the location of two levels. The disadvantage of the power spectrum, viz. that it is very noisy, as opposed to the relatively smooth behaviour of the spectral rigidity  $\Delta_3(r)$  and  $\Sigma^2(r)$  statistics, may be turned into an advantage, since one is then free to handle this noisy appearance by any noise reducing method chosen at will.<sup>2</sup>

Depending on the nature of the quantum system to which the statistical Fourier-transform method is applied we have four well defined examples (see Lombardi et al [81]), these are shown in Fig. 2 containing sketches of smoothed power spectra.

<sup>2</sup>The author is grateful to Professor Rémi Jost, CNRS Service National des Champs Intenses, Grenoble, France, for pointing out this property.

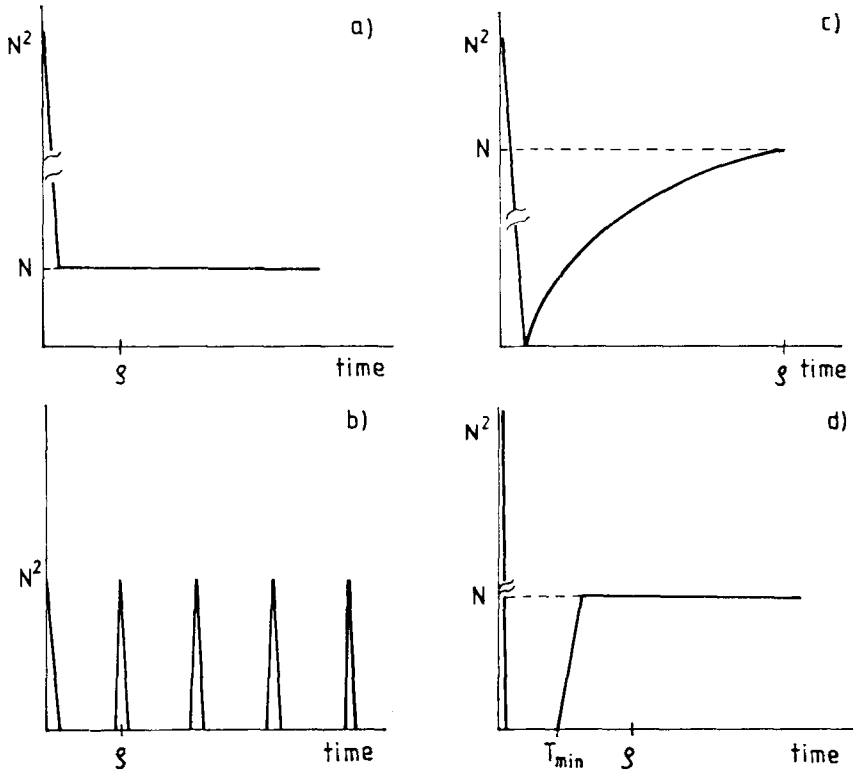


Fig. 2. Power spectral behaviour

Cases a, b, c and d correspond to a Poissonian (random) spectrum, a GOE spectrum, the harmonic oscillator and finally a set of uncoupled anharmonic oscillators. To understand the four typical forms in Fig. 2 we can apply the simple recipe in Lombardi et al [81] (based on Balian and Bloch [7,8], Berry [12]; Gutzwiller [48,49,50,51,53,54]).

An understanding of the behaviour of  $|C(t)|^2$  may be obtained by a thought experiment. Let us start classical orbits from a phase space point  $(p, q)$  for the problem. At every time such an orbit closes upon itself (returns to  $(p, q)$ ) enter a peak into the power spectrum. Then the harmonic oscillator yields regular peaks separated by the oscillator period  $T$ , whereas a set of anharmonic oscillators shows up a flat hole, as nothing is found in the spectrum prior to the closing of the shortest orbit ( $T_{\min}$ ). In strongly correlated systems the number of closed orbits decreases with time and that gives rise to the correlation hole.

Before leaving the subject of the power spectrum fluctuation measure, it is very important to point out another approach or philosophy of power spectra. The calculation of the constant amplitude stick spectrum of energy levels is equivalent to the estimation of the time evolution of a molecular wavefunction. There is therefore a strong connection between the theory of statistical Fourier-transformation and the

theory of radiationless relaxation processes (Bixon and Jortner [15], Lahmani et al [74], Delory and Tric [31]). Another way of stating this is to point out that the square modulus of the FT yields the survival probability of an initially prepared state  $|\psi(0)\rangle$  after a duration of time  $t$ ;

$$|C(t)|^2 = |\langle\psi(0)|\psi(t)\rangle|^2 \quad (37)$$

(see Levine and Kinsey [79], Pique et al [94]).

Therefore the power spectrum may also be regarded as the spectral autocorrelation function (see also: a maximum entropy formalism of the autocorrelation function by Remacle and Levine [106], and the relationship to the rate of exploration of the phase space (Lorquet, Engel and Levine [82]). The connection between mode selective chemistry — a centrally important aspect of laser-induced chemistry — and the application of the power spectrum method described above was given by Levine and Jortner [80].

## 5. Examples from high-resolution spectroscopy

In spite of the obvious lack of molecular spectroscopic analyses about ten years ago (Bohigas and Giannoni [17], Brody et al [20]), in recent times there has been a surge of efforts to extend such analyses to high-resolution molecular spectra, as already mentioned in the Introduction. The greatest problem in applying the usual fluctuation measures to molecular spectra is the extraction of a statistically significant sample size of line or level sequences of definite symmetry and good quantum numbers from the very complicated structure of highly excited molecular spectra. It is characteristic of such studies that when complete ro-vibronic (electronic excited state) or ro-vibrational (electronic ground state) analyses are available usually only levels with  $J = 0$  (no rotation) are included. This is meant to simplify the construction of symmetry-wise pure sets, and to reduce the number of features to a manageable size. However, when high vibrational excitation occurs assignment of the spectral features is frequently not possible, and, of course, this is exactly why one would like to use the statistical method described here.

In such cases special experimental techniques are sought that lead to spectral simplification, or the power spectrum method is used that, as pointed out before, is comparatively insensitive to symmetry mixtures and spectroscopic resolution. In the following a number of recent examples shall be quoted. Special attention is devoted to the SEP (stimulated emission pumping) method developed in 1981 and applied since then.

In their seminal paper Leviandier et al [78] applied the newly proposed method to the highly excited acetylene ( $C_2H_2$ ) vibrational levels, and to singlet-triplet anti-crossing (ac) spectra of methyl-glyoxal. Acetylene vibrational spectra were obtained by the SEP method (to be described later). This was the first example of using the Fourier-transform method to a highly excited vibrational spectrum (at about

27900  $\text{cm}^{-1}$ ) and it gave an independent proof (relative to earlier statistical examinations) of strong correlations. The ac spectra of methyl-glyoxal were only taken at a vibrational excitation level of 3000  $\text{cm}^{-1}$  and couplings in those spectra were known to be very small.

Jost and Lombardi [69] used the optical-microwave double resonance data of Lehmann and Coy [75] to show the lack of level correlations in those spectra, and the SEP spectra of acetylene, taken by Abramson et al [2], to demonstrate strong correlations objectively (objectivity being provided by the independent power spectrum method). Their own singlet-triplet anticrossing spectra of methyl-glyoxal ( $\text{CH}_3\text{-CO-CHO}$ ) displayed strong correlations in the  $T_1$  electronic state. One of their main conclusions was that only two-step, state-to-state processes, such as optical-optical or microwave-optical double resonance, or the optical anticrossing technique can provide spectra with sufficient spectral purity for statistical correlation studies. Molecular beam techniques may also help reducing spectral congestion prior to such an analysis.

Among molecular studies one of the most interesting cases is that of nitrogen dioxide ( $\text{NO}_2$ ). This molecule has a very complicated vibronic spectrum between 12000 and 25000  $\text{cm}^{-1}$  (Hsu et al [66]). In this spectral region there are four electronic states potentially interacting with one another (Jackels and Davidson [67,68]; Gillispie and Khan [44,45]). The assignment and interpretation of the observed spectra have not yet been achieved. The molecule has been the subject of many statistical approaches (Haller, Koppel and Cederbaum [56,57]; Hardwick [59]; Lehmann and Coy [75,76]; Persch et al [92]; Smalley et al [108]; Zimmermann, Koppel and Cederbaum [116,117]). Hardwick conjectured in 1985 [59] that all selection rules based upon the rotational quantum numbers are broken, and the spectrum is an ideal example of total ergodicity. Lehmann and Coy [76], however, found in their microwave-optical double resonance experiments that although the intensity distribution of the spectral lines indicate perfect ergodicity (Heller's  $F$  parameter approaches 1/3, see: Heller [60]), the first neighbour separations and the  $\Delta_3$  spectral rigidity tests show regular classical dynamics (Poissonian behaviour). Their study involved not only vibronic band origins ( $J = 0$ ) but rotational branches of known  $J$  value as well. A similar study by Jost and Lombardi [69], using the power spectrum method indicated no correlation hole in the  $\text{NO}_2$  spectra. So, in spite of the fact that many more rotational transitions were found than expected with strict rotational selection rules, the statistical behaviour of levels did not display classical chaoticity signs.

Many such problems may be approached, as we have already noted, by stimulated emission pumping, and before looking at further examples a short characterization of the SEP method is given.

## 6. Experimental studies of level correlations by SEP spectroscopy

There are several methods in spectroscopy to access high vibrational levels with great specificity and resolution. One of these is direct overtone pumping and

another important tool is stimulated emission pumping.

Direct overtone pumping utilizes lasers of appropriate fundamental frequency or harmonics. An early example of this method was reported by Swofford et al [111]. A modern laser system for this purpose is the  $\text{Ti}^{3+}$ : sapphire laser that allows one to excite the range between 700 and 1100 nm (9000 and 15000  $\text{cm}^{-1}$ , resp.). Coy et al [28] reported the use of this laser in double resonance studies on ammonia. The measurement of overtones at high energy requires very sensitive modulation detection techniques, such as optoacoustic spectroscopy, as overtone intensities are usually very low.

In 1981 Kittrell et al [70] devised a double resonance method to obtain simplified spectra of highly excited vibrational states (between about 8000 and 30000  $\text{cm}^{-1}$ ). The technique is capable of accessing specific vibrationally excited levels of the electronic ground state. Figure 3 is a simple sketch of this folded variant of optical-optical double resonance (OODR).

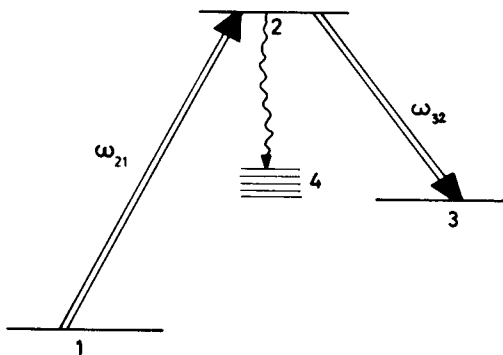


Fig. 3. The scheme for the SEP experiment  $\omega_{21}$ : pumping;  $\omega_{32}$ : dumping;  $\rightarrow$  4 fluorescence

A laser is used to pump population from level 1 (of the electronic ground state) to level 2 (of an excited electronic state), and a second laser is used to force population from level 2 into a high excited vibrational state in the ground electronic state (3). Both lasers are narrow bandwidth tunable pulsed lasers in the visible range that are frequency multiplied when necessary. The process may be monitored by using fluorescence (spontaneous side fluorescence or induced one by a third laser) to the ground state (indicated by levels 4 in Fig. 3) so the obvious requirement is that there should be an observable fluorescence from level 2. The two lasers involved in the experiment may be time shifted and used in antipropagating arrangement so that Doppler broadening can also be eliminated resulting in highly resolved spectra.

The selection of levels involved is controlled by Franck-Condon factors between the two electronic states so an additional requirement for good SEP spectra



is that the two potential surfaces should be sufficiently different. This is automatically satisfied when electronic excitation results in major changes in geometry. The method was originally applied to the  $B \leftarrow X$  system of iodine ( $I_2$ ).

Other versions of the SEP experiment are also known with different detection methods, such as polarization-labelling (Brand et al [18]). For a review see: Hamilton et al [58].

The SEP method has been used extensively on the acetylene ( $C_2H_2$ ) molecule, and many statistical tests were performed (Abramson et al [1,2,3]; Engel and Levine [37]; Farantos [39]; Holme and Levine [63,64,65]; Pique et al [94,95,96]; Sumpter and Thompson [109]; Sundberg et al [110]).

Acetylene has vibronic transitions  $\tilde{A}(^1A_u) \leftarrow \tilde{X}(^1\Sigma_g^+)$  that were sampled both at about  $9550 \text{ cm}^{-1}$  above the vibrationless level of the  $S_0(\tilde{X} \ ^1\Sigma_g^+)$  state and about  $28000 \text{ cm}^{-1}$  above the vibrational origin. In the high energy region very unusual spectral features were observed; "clumps" of lines, with a clump width of about  $1.5 \text{ cm}^{-1}$ , containing, in high resolution, about 70 individual components. An analysis of these features showed that they all belong to the same  $J$  quantum number, and vibrational angular momentum quantum number  $l = 0$  ( $\sigma_g^+$ ). All clumps have very similar structure. The intensity distribution within and among the clumps showed a convincingly ergodic behaviour. As all other quantum numbers cease to be "good" at this high level of excitation, symmetry is completely defined by  $J$ ,  $l$  and parity so that appropriate statistical tests could be made.

Pique et al [95], used the FT technique to detect strong correlations among  $1500 \text{ cm}^{-1}$  long pure vibrational sequences in the SEP spectrum around  $26500 \text{ cm}^{-1}$ . In another work on the same SEP spectra of acetylene Sundberg et al [110] carried out both intensity distribution studies and applied static fluctuation measures (such as  $P(S)$  and  $\Delta_3(L)$ ). All these measures suggested a near GOE behaviour for highly vibrationally excited  $\tilde{X}$  levels, in accordance with the results of Abramson et al [3].

Pique et al [94] reported a more detailed analysis of the  $26000 \text{ cm}^{-1}$  range SEP spectra. The smoothed power spectra had time dependent features corresponding to the correlation hole, the recovery time from it, and recurrences. The width of the spectral clumps and that of their fine structure lines define two time scales ( $t_\varrho = 20 \text{ ps}$  and  $267 \text{ ps}$ , resp.) that could be related to the recovery time from the correlation hole ( $t_{\text{corr}}$ ) (3 ps for a single spectral stretch, 45 ps for a spectral average). For a GOE-like spectrum the theoretical expectation is that  $t_{\text{corr}} = t_\varrho$ , whereas for the HCCH spectra  $t_{\text{corr}} \simeq t_\varrho/6$  from which the conclusion was drawn that several symmetry species or good quantum numbers exist even in this high excitation regime. However, about  $1400 \text{ cm}^{-1}$  higher (at  $27900 \text{ cm}^{-1}$ , see: Abramson et al [3]) the power spectra suggest fully chaotic dynamics. The works of Pique et al [94,95] showed that the power spectrum provides more dynamical characterization of the statistical behaviour than the single number fluctuation measures (e.g. spacing and spectral rigidity).

One more study on acetylene should be mentioned (Chen et al [25]) via the SEP technique in the  $11400\text{--}15700 \text{ cm}^{-1}$  range above zero-point level. These spectra were rotationally resolved and allowed the examination of the coupling

of rotation and vibration. There are five vibrational normal modes for acetylene ( $\nu_1, \nu_2(\Sigma_g^+), \nu_3(\Sigma_u^+), \nu_4(\pi_g), \nu_5(\pi_u)$ ). The  $\tilde{A} \leftarrow \tilde{X}$  electronic excitation involves a large change of geometry (the CCH bond angle changes from  $180^\circ$  in the  $\tilde{X}$  state to  $120^\circ$  in the  $\tilde{A}$  state, and the C-C bond length increases from 0.1208 nm to 0.138 nm) so the strongest vibrational progressions are those of  $\nu_4$  (trans-bending mode) and its combination with the C-C stretch ( $\nu_2$ ) mode. Reduced term value plots showed a significant difference between  $l = 0$  and  $l = 2$  levels. (The  $l$  quantum number measures vibrational angular momentum from the two degenerate modes:  $l = |l_4 \pm l_5|$ ). It was found that while the  $l = 0$  levels were unperturbed, the  $l = 2$  levels are strongly affected by vibration-rotation interactions.

In spite of these strong perturbations the two-point correlation statistics did not exhibit level repulsion, the fluctuation measures were all close to Poissonian behaviour. The authors drew the conclusion that the separation of vibrational and rotational degrees of freedom persists even at this high excitation regime.

The SEP technique has become quite widespread in the study of near dissociation vibrational behaviour, that is so important for chemistry, and has enabled a number of very interesting molecular dynamic studies. Another well studied example is that of formaldehyde ( $\text{CH}_2\text{O}$ ), from the George Harrison Spectroscopy Laboratory at the Massachusetts Institute of Technology, Cambridge, USA.

In a series of papers (Dai et al [29,30]; Reisner et al [104,105]; Vaccaro et al [114]) very careful and extensive vibrational-rotational analyses were reported for the range  $4500\text{--}9300\text{ cm}^{-1}$ . In formaldehyde there are strong Coriolis and Fermi perturbations that increase in strength with rising vibrational energy and level density. The SEP technique allowed a major simplification of the emission spectra and by its use it has become possible to state that molecular rotation is important in intramolecular vibrational dynamics. The interactions destroy the goodness of vibrational and  $K$  rotational quantum numbers, leading to an increase of vibrational density over the usual anharmonic level counts (for such estimates see e.g. Toselli et al [113]). Such studies (Dai et al [30]) have, however, led to a surprising conclusion, viz., that the increasing complexity of the spectrum with increasing  $J$  value (angular momentum) results in diminishing chaotic behaviour. This is an explicable but intriguing finding.

Among SEP studies on more exotic molecules the case of the Na trimer ( $\text{Na}_3$ ) (Broyer et al [21]) may be mentioned. A theoretical discussion of the SEP spectrum was given by Gomez Llorente et al [46] who concluded that the SEP spectra may be fully interpreted, regarding vibrational dynamics, using a classical Hamiltonian.

## 7. Conclusion and outlook

This overview paper strived to summarize, perhaps in a rather selective and superficial way, the modern use of statistical methods in the analysis of molecular spectra. Contrary to the original pessimistic predictions in one of the fundamental works in this field, in the review by Brody et al [20]: *“Parenthetically it should be*

clear that, because of the limited amount of information contained in the fluctuations, highly detailed level-to-level calculations, as often carried out especially for nuclei, should in many cases not be worth the great labor involved in making them" (see: p. 469 in [20]), the past ten or so years have displayed steadily growing activity in statistical spectroscopy. (To be correct it should be mentioned that Brody et al modified their previous conclusion for cases of interesting symmetry effects!) One of the most promising mathematical techniques appears to be the power spectrum method, already casting contemporary studies into a framework much more interesting for the chemist who aspires to selective laser chemistry and therefore appreciates the connection between the methods of static spectroscopy and dynamical phenomena on the picosecond time scale extractable from the former via Fourier-transformation. Let us quote here R. D. Levine in "Mode Selective Chemistry" ([80]): *"The exploration of phase correlation can be conveniently discussed in terms of time correlation functions. The simplest is the autocorrelation function of the initially excited region., This can be obtained from the experimental spectrum by taking its Fourier-transform. Dynamical computations can, of course, directly yield the correlation functions. Obtaining the information from experiment is however of obvious interest"* (p. 549 in [80]).

There is a close link between studies of classical chaos on simple systems relevant to molecular spectroscopy, and the type of statistical studies reviewed here. One aspect is especially interesting and could perhaps contribute to further developments: the role of molecular rotation. Although it is not simple to extract molecular levels of known rotational (and overall) symmetry from spectroscopy, the interest in such aspects is obvious. Most of the attention so far has been centered on vibrational behaviour with rotations eliminated. We know notwithstanding that molecular rotation has a very important effect, some of its recognitions stemming already from its contributions to classical chaos (Fahrer and Schlier [38]). An even more significant aspect is the involvement of rotational dynamics in intramolecular energy redistribution (Knight [71]). Intramolecular state mixing is decisively important for the unravelling of intramolecular photochemical and photophysical processes and it has become evident that it is not enough to consider solely the vibrational Hamiltonian in accounting for time-averaged and time-resolved spectroscopic experiments. Intramolecular energy flow is central to the understanding of the breaking of molecular bonds, so it is central in efforts to understand chemical processes both on the traditional level and induced with the help of lasers.

The field of statistical spectroscopy is undergoing maturation but perhaps it has not yet won the battle among spectroscopists who still believe in completely assignable spectra, and any failure in obtaining such a full analysis is thought to be curable by more exacting studies. It is the hope of the present author that with an increase of statistical activity on difficult assignment cases molecular spectroscopy will benefit from such approaches.

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