FLUCTUATIONS IN INTRAMOLECULAR LINE SHAPES – RANDOM MATRIX THEORY

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Random matrix theory is used to develop a model for the distribution of energy levels and intensities in intramolecular line shapes. The effects of missing lines, either due to their weak intensity, or due to the finite spectral resolution, are quantitatively incorporated. It is shown how the information regarding spectral fluctuations in intermediate size molecules is eroded in the large molecule statistical limit. Our predictions are compared with recent experimental data on highly vibrationally excited acetylene, and the relevant statistical measures are calculated

Recent experimental studies of molecular line shapes in isolated polyatomic molecules have generated a vast interest in the statistical analysis of these spectra [1–5] The purpose of such is to indentify some *universal* features which will be of interest to a wide class of systems. This is in contrast to the traditional analysis which focuses on *specific* information on a particular molecule (i.e. level positions and dipole strengths).

Random matrices provide a natural theoretical framework for interpreting the statitsics of energy levels, as well as their widths, in complicated quantum systems [6,7]. The model which has been most extensively studied, is Wigner's gaussian orthogonal ensemble (GOE) of asymptotically large, real, symmetric random matrices. Its main predictions are level repulsion (Wigner [8]) long-range order in the level sequence (Dyson–Mehta [9]) and a χ_1^2, distribution for the widths or intensities (Porter–Thomas [10]). These results were proposed originally for nuclear spectra but are expected to be valid much more generally. A remarkably close agreement between the

GOE predictions and nuclear data have been found [11], and there are indications that the same may be true for atomic [12] and molecular [1,2,13,14] spectra as well. Recent arguments [15,16] and calculations [17] may indicate that GOE-type fluctuations are characteristic of quantum mechanical spectra of chaotic hamiltonians

In this paper, we shall make use of random matrix theory, and develop a systematic method for the analysis of molecular spectra We shall consider a prototype molecular level scheme and analyze its statistical features and the information content of the spectral line shapes for intermediate size and large molecules. Our model molecular hamiltonian (fig. 1) is:

$$H = |g\rangle\epsilon_g\langle g| + |s\rangle\epsilon_s\langle s|$$
$$+ \sum_{l=1}^{N} |l\rangle\epsilon_l\langle l| + \sum_{l=1}^{N} V_{sl}(|s\rangle\langle l| + |l\rangle\langle s|), \tag{1}$$

and the radiation–matter interaction is

$$M = \bar{\mu}_{gs}(|g\rangle\langle s| + |s\rangle\langle g|)$$
$$+ \sum_{l=1}^{N} \mu_{gl}(|g\rangle\langle l| + |l\rangle\langle g|). \tag{2}$$

[*] Alfred P. Sloan fellow, Camille and Henry Dreyfus teacher-scholar.

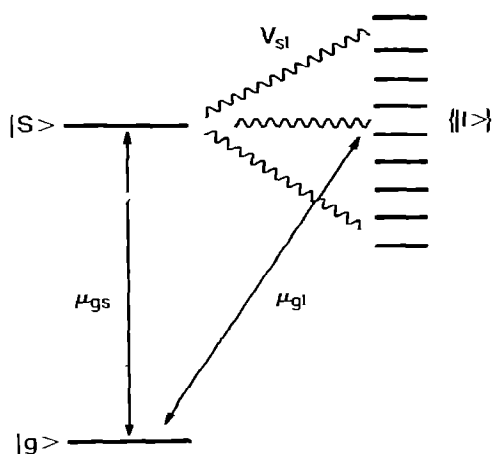Fig 1. The molecular level scheme of our ensemble. μ_{gl}, V_{sl} and ϵ_l are random variables.

Here $|g\rangle$ is the ground state (we shall take $\epsilon_g = 0$) which is radiatively coupled to a single doorway state $|s\rangle$ which, in turn, is coupled by some intramolecular coupling V_{sl} to a background manifold $\{|l\rangle\}$. This is the fundamental model in molecular radiationless transitions whereby $|s\rangle$ is a singlet and $|l\rangle$ is a manifold of vibrational states belonging to another electronic state [18]. It also applies to intramolecular vibrational redistribution whereby $|s\rangle$ and $\{|l\rangle\}$ belong to the same electronic state and V_{sl} is an anharmonic coupling [19]. We have also allowed the quasicontinuum states $|l\rangle$ to carry oscillator strength via μ_{gl} (the Fano level scheme) [20]. For this model, the absorption line shape, given that the molecule is initially in the ground state $|g\rangle$ is

$$I(\omega) = \sum_j |\langle g|M|j\rangle|^2 \delta(E_j - \omega) \equiv \sum_j I_j \delta(E_j - \omega), \quad (3)$$

where E_j are the eigenvalues of H:

$$H|j\rangle = E_j|j\rangle. \quad (4)$$

Our statistical assumption concerns the manifold $\{|l\rangle\}$ in eq. (1). We assume that ϵ_l are centered around the doorway ϵ_s, with a constant average spacing D, and the fluctuations around the average are those of GOE. Furthermore, the states $|l\rangle$ are, except for the orthonormality conditions, completely random vectors (independent of the ϵ_l distribution) in the $N \times N$ "statistical space" [‡]. It follows [6] from the ran-

domness of the vectors $|l\rangle$ that, for large N, all the V_{sl} and μ_{gl} are independent gaussian variables; the only correlations allowed are for $l = l'$ in which case V_{sl} and μ_{gl} have a bivariate gaussian distribution. We specify the first two moments as follows (where the bar denotes ensemble averaging):

$$\overline{V_{sl}} = 0, \quad \overline{V_{sl}^2} = v^2,$$

$$\overline{\mu_{gl}} = 0, \quad \overline{\mu_{gl}^2} = \mu^2, \quad \overline{V_{sl}\mu_{gl}} = rv\mu, \quad (5)$$

where r is the correlation coefficient of V_{sl} and μ_{gl} $(0 < r < 1)$. We have analyzed the statistics of the energy levels and the line shape function for this ensemble, for $N \to \infty$. The statistical properties of the E_j are little different from those of ϵ_l, i.e. the level density is still $1/D$ and the fluctuations are those characteristic of GOE. The ensemble average of $I(\omega)$ is given by:

$$\overline{I}(\omega) = (\mu^2/D)[(\omega - \epsilon_s + \Delta)^2 + \phi^2]/[(\omega - \epsilon_s)^2 + \tfrac{1}{4}\Gamma^2], \quad (6)$$

where

$$\Gamma = 2\pi v^2/D, \quad \Delta = rv\mu_{gs}/\mu,$$

$$\phi^2 = (1 - r^2)(v^2\mu_{gs}^2/\mu^2 + \tfrac{1}{4}\Gamma^2). \quad (7)$$

Eq. (6) is a well-known result when ϵ_l form a continuum and was proposed, without proof, for all values of Γ/D, by Lane et al [21–23]. In the absence of radiative coupling to the quasicontinuum ($\mu_{gl} = 0$) it reduces to a simple lorentzian profile

$$\overline{I}(\omega) = \pi^{-1}\mu_{gs}^2 \tfrac{1}{2}\Gamma/[(\omega - \epsilon_s)^2 + \tfrac{1}{4}\Gamma^2] \quad (8)$$

The Fano line shape [20] corresponding to our model whereby μ_{gl} and V_{sl} are fixed and independent of l, may be obtained from eq. (6) by setting $r = 1$.

Eq (6) gives the ensemble averaged line shape. The actual line shape, however, in a given experiment, corresponds to a particular realization of the random variables (ϵ_l, V_{sl}, μ_{gl}) and will have fluctuations around $\overline{I}$. These fluctuations are observable in intermediate size molecules. In large molecules, as we shall shortly see, they are suppressed and the only information content of the spectral line will be $\overline{I}(\omega)$. In order to analyze these fluctuations, let us recall an elementary result of

[‡] In other words, the ensemble of the operators $\sum_l |l\rangle \epsilon_l \langle l|$ is a one to one map of the GOE such that the average level density is a constant instead of a semicircle.

statistics. Suppose we have ν independent random gaussian variables x_i, each having a zero mean and a variance $1/\nu$. If we consider the sum of their squares $y \equiv \Sigma_{i=1}^{\nu} x_i^2$, its distribution called χ_ν^2 (i.e. χ square with ν degrees of freedom) is given by [10]:

$$P(y)\,dy = [\Gamma(\rho)]^{-1}(\rho y)^{\rho-1}\exp(-\rho y)\,\rho\,dy, \qquad (9)$$

where $\rho = \frac{1}{2}\nu$ and Γ is the gamma function. This distribution is characterized by the mean $\bar{y} = 1$ and the variance $\overline{y^2} - \bar{y}^2 = 2/\nu$.

From eq. (3) we see that each component of the spectrum I_j is the square of the overlap of the molecular eigenstate $|j\rangle$ with the "doorway state" $M|g\rangle$. These overlaps are expected to have a gaussian distribution and therefore $I_j/\overline{I_j}$ should have a χ_1^2 (Porter–Thomas) distribution given by $P(y)$ with $\nu = 1$. We thus expect [‡‡] that if we measure the intensities in a small frequency interval ($\Delta\omega \ll \Gamma$) they will follow χ_1^2. This will not be the case for the entire distribution of intensities I_j since the mean intensity $\bar{I}(\omega)$ depends on ω. We shall therefore define new scaled variables

$$J_j \equiv I_j/\bar{I}(\omega_j). \qquad (10)$$

By construction $\bar{J}_j = 1$ regardless of ω_j. We thus expect that the distribution of J_j will obey the χ_1^2 law, i.e.

$$P(J)\,dJ = (2\pi J)^{-1/2}\exp(-\tfrac{1}{2}J)\,dJ. \qquad (11)$$

What happens as the molecular size increases? If the experimental spectral resolution is R, each experimentally observed intensity will be on the average the sum of $\nu = R/D$ lines and the experimental distribution of J will become χ_ν^2 (i.e. eq. (9) with $\nu > 1$). As $\nu \to \infty$ have [10] [$\chi_\nu^2(J) \to \delta(J-1)$]. This implies that as the density of states increases, we shall gradually lose the information about fluctuation and $I(\omega)$ will turn into $\bar{I}(\omega)$!

We next turn to the energy level fluctuations (i.e. deviations of the level positions from a regular "picket fence" spectrum). We briefly review the GOE predictions [6,11,24]. To begin with, one may deal with the spacing distributions. For example, the nearest neighbour spacing distribution is well-approximated for GOE by the Wigner surmise,

$$P_0(x)\,dx = \tfrac{1}{2}\pi x\exp(-\tfrac{1}{4}\pi x^2), \quad x_j = (E_{j+1}-E_j)/D. \qquad (12)$$

‡‡ This result holds when $\Gamma/D > 1$.

This should be compared with $\exp(-x)$ for the Poisson ensemble of completely random levels. A systematic way of analysis was developed recently [11]. It starts with the hierarchy of Dyson's k-level cluster functions [25], of which the two-level function Y_2 is the most important. $[1 - Y_2(r)]$ dr gives the probability of observing a level in an infinitesimal interval D dr at a distance rD from another given level, irrespective of where the other levels are. Y_2 is zero for Poisson for all r, whereas for GOE its value is 1 at $r = 0$ (implying level repulsion), it falls off as $1/\pi^2 r^2$ for $r \gtrsim 1$, and its integral ($0 < r < \infty$) is 0.5 (the latter two implying a long-range order in the spectrum). One may test the data directly for Y_2, or for better accuracy, may calculate $\Sigma^2(r)$ and $\bar{\Delta}_3(r)$ defined below.

Consider an interval of fixed length rD. The average number of levels in the interval is r. The variance of the number of levels is

$$\Sigma^2(r) \equiv r - 2\int_0^r (r-t)\,Y_2(t)\,dt, \qquad (13)$$

which is simply r for Poisson, and for GOE approaches [6,9] $2/\pi^2 \log r + 0.44$ for $r \gtrsim 1$. This implies a long-range order in the GOE (e.g. for $r \approx 10^4$, $\Sigma^2(\text{GOE}) \approx 1$ whereas Σ^2 (Poisson) $\approx 10^4$). The GOE is therefore characterized by much smaller fluctuations than the Poisson, and due to its "ordered nature" will be much more sensitive to missing levels than the Poisson ensemble, $\bar{\Delta}_3$, introduced by Dyson and Mehta [9], is another measure for level fluctuations. For an interval $(-L, L)$ of the spectrum centered at zero, we define

$$\Delta_3(r) \equiv (1/2L)\int_{-L}^{L} [N(E) - AE - B]^2\,dE. \qquad (14)$$

Here $N(E)$ is the number of levels below E in that interval, $r = 2L/D$, and $AE + B$ is the "least-squares fit" straight line to the staircase function $N(E)$. The ensemble average of Δ_3 is related to Σ^2, and hence to Y_2 [26],

$$\bar{\Delta}_3(r) = (2/r^4)\int_0^r (r^3 - 2r^2 t + t^3)\,\Sigma^2(t)\,dt. \qquad (15)$$

$\bar{\Delta}_3(r) = \frac{1}{15}r$ for Poisson whereas for GOE it approaches $1/\pi^2 \log r - 0.007$ for $r \gtrsim 10$. One may study $\Sigma^2(r)$ or $\bar{\Delta}_3(r)$ as a function of r. It should be noted that the

sample errors (i.e. the variances of Σ^2 and Δ_3) associated in the analysis of data are also now fully understood [11] and Σ^2 and Δ_3 are among the "sharpest" measures available.

In order to illustrate how these ideas may be utilized to extract useful information from molecular spectra, we shall consider now one "clump" observed recently in acetylene by Field, Kinsey and co-workers [1]. Our first goal is to determine $\overline{I}(\omega)$. To that end we define the intergrated intensity,

$$S(\omega) \equiv \int_{-\infty}^{\omega} I(\omega_1) \, d\omega_1 . \tag{16}$$

In fig. 2, we show a three-parameter fit of $S(\omega)$ obtained by substituting $\overline{I}(\omega)$ [eq. (8)] in eq. (16) and making a least-squares fit of Γ, ϵ_s and μ_{gs}. The fit is remarkably good. A five-parameter fit using eq. (6)
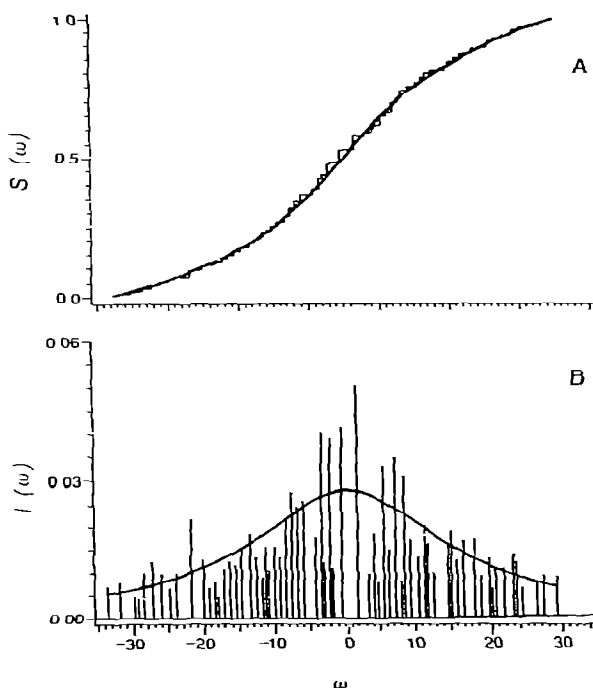

Fig. 2. The ensemble averaged line shape $\overline{I}(\omega)$. (A) The staircase function is the integrated intensity $S(\omega)$ of the experimental results [1]. The curve is the least-squares fit using eqs. (8) and (16). $D = 1$, $\Gamma = 33$. ϵ_s was obtained from the fit and was set $\epsilon_s = 0$. (B) The experimental [1] I_j and the best fit $\overline{I}(\omega)$ of (A).

[Instead of (8)] showed very little improvement so that we chose $\mu = 0$. $\overline{I}(\omega)$ calculated using these parameters is also shown in fig. 2. Once $\overline{I}(\omega)$ is determined, we can calculate $J_j \equiv I_j/\overline{I}(\omega_j)$ and consider their distribution, $P(J)$. There are several problems in comparing $P(J)$ directly with χ_1^2 [eq. (11)]. We first have to assume that the experimental results are "pure" with no spurious levels (i.e. all levels have the same set of good quantum numbers). Another problem arises from the finite experimental resolution which implies that closely lying levels may not be resolved. This, as shown earlier, will change χ_1^2 into χ_ν^2, ν being the number of unresolved transitions in each of the observed spectral lines. In general we can have a mixture of χ_ν^2 with various values of ν. A third problem arises since as is clearly seen in fig. 2B, there is a lower bound I^* for the experimentally observed intensities such that all levels with $I < I^*$ are missing. The effect of I^* can be easily incorporated into the theory by proper integrations. In fig. 3 we show the experimental [1] histogram of $P(J)$ together with the χ_1^2 distribution (broken line). The solid curve represents a distribution calculated from χ_1^2 by taking $I^* = 6 \times 10^{-3}$ and omitting all lines with $I < I^*$. It is evident that the later is at least in qualitative agreement with the histogram. The missing levels have thus a dramatic effect on the observed distribution $P(J)$. The fraction f of randomly missing levels $(N_T - N)/N_T$ (N_T being the total number of levels in the observed range and N is the number of lines actually observed) is estimated from this curve to be ≈ 0.7.

The statistics of level positions as reflected in Σ^2 and $\overline{\Delta}_3$ is also consistent with this picture of missing
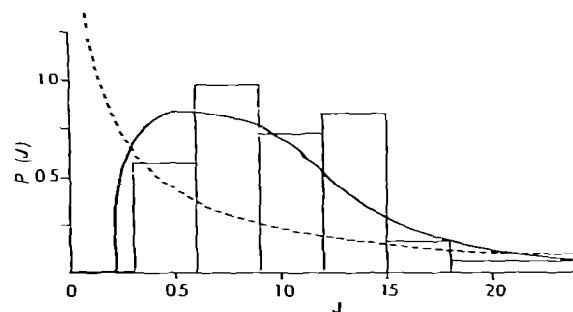

Fig. 3. Histograms of the experimental distribution $P(J)$. The broken curve is a χ_1^2 distribution and the solid curve is a modified χ_1^2, with missing levels, $I^* = 6 \times 10^{-3}$.
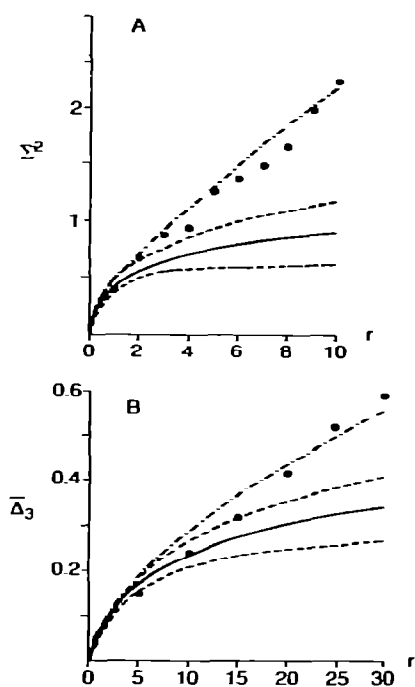
Fig 4. Measures of energy level fluctuations. (A) Σ^2 versus r. The dots represent the experimental data [1]. Shown are the calculations for GOE (solid line) and for GOE with $f = 0.15$ (dotted line). We also show the sample errors for the GOE (broken lines). When f is finite the sample errors increase. (B) $\bar{\Delta}_3$ versus r. The curves are as in (A). Δ_3 (65) was calculated to be 0.42 ± 0.11 for GOE and 0.96 for GOE with $f = 0.15$ (with a larger sample error), compared with the experimental $\Delta_3(65) = 0.85$.

levels. In fig 4 we show $\Sigma^2(r)$ and $\bar{\Delta}_3(r)$ as calculated from the experimental data. It is clear that the simple GOE predictions are not in good agreement with these curves. Assuming however, a fraction f of randomly missing levels we calculate Σ^2 and $\bar{\Delta}_3$ using the following expressions:

$$\Sigma^2(r) = fr + (1-f)^2 \Sigma^2_{GOE}(r/(1-f)) \qquad (17)$$

and

$$\bar{\Delta}_3(r) = \tfrac{1}{15}fr + (1-f)^2 \bar{\Delta}_{3,GOE}(r/(1-f)). \qquad (18)$$

The curves with $f = 0.15$ shown in fig. 4 are certainly consistent with the experimental data. It should be noted that the sample errors associated with Σ^2 and Δ_3 measures increase with f so that the estimates of

f from the fluctuations in intensities and in level positions are not inconsistent.

In conclusion we have shown how the statistical analysis the line shape parameters Γ, ϵ_s, μ_{gs} together with the fraction f of missing levels. It should be noted that by "missing" we mean levels that do interact with the doorway state but are not resolved in the spectrum due to experimental resolution or dynamic range. In addition, there may exist, of course, many more levels which do not interact at all with the doorway state and therefore do not affect the spectrum. The number of lines in the experiment (65) is relatively small (although excellent agreement with GOE predictions had been obtained in some nuclear data for 70 levels [27]). We expect that this type of analysis will become even more useful and quantitative when more data with larger numbers of levels, improved spectral resolution, and fewer missing levels will become available.

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