The analysis of intensity fluctuations for a fully resolved spectrum: Pyrazine

J. Kommandeur

Laboratory for Physical Chemistry, University of Groningen, 9747 AG Groningen, The Netherlands

W. L. Meerts

Lab. voor Experimentele Natuurkunde, Katholieke Universiteit, Nijmegen, 6525 ED Nijmegen, The Netherlands

Y. M. Engel and R. D. Levine

The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University, Jerusalem 91904, Israel

Intensity fluctuations in the recently published fluorescence excitation spectrum of pyrazine in the $^1B_{3u} \leftarrow {}^1A_g$ 0_0^0 band are analyzed. A numerical study of a model Hamiltonian of a bright state coupled to a manifold of dark states is performed as an aid to the interpretation of the results. The distribution of fluctuations in the intensities computed for the model Hamiltonian is near to that expected in the chaotic limit.

I. INTRODUCTION

The possible manifestations of chaotic classical dynamics in the observed spectra of molecules in a topic of considerable current interest. One aspect is the variation in the intensity of adjacent lines. In the classically regular regime one expects the quantal (optical) spectrum to be governed by strong selection rules. Nearby transitions will then differ markedly in their intensity. As the excitation energy is increased, the classical dynamics, for trajectories at the energy of the upper state, will become increasingly more chaotic. Adjacent molecular eigenstates will then be much more "similar" and the fluctuations in intensity will be reduced. The random matrix theory,[1] the "statistical wave function" approach,[2–4] and the maximum entropy formalism[5,6] indicate that the fluctuations do not die out but approach a universal limit. The signature of classical chaos is then a, so-called Thomas Porter,[1] distribution of fluctuations.

Computational studies[7,8] show that the limiting distribution of fluctuations can indeed be achieved for realistic molecular Hamiltonians and that even en route to this limit, the distribution of fluctuations has a universal form but with a system-dependent parameter. The open question is whether an experimental example of a spectrum with a distribution of fluctuations at the chaotic limit is available.[9]

The analysis of intensity fluctuations in the absorption spectra of molecules requires resolved lines and a wide dynamic range with special reference to weaker transitions. Failure to resolve nearly overlapping lines and/or failure to discern very weak transitions both tend to reduce the extent of apparent fluctuations.

The recently measured[10] excitation spectrum of the $J' = 0$ levels in the $^1B_{3u} \leftarrow {}^1A_g$ 0_0^0 band of pyrazine[11,12] provides data of the required quality. Thirty-six molecular eigenstates have been resolved and the decay of eight of these states has been directly measured. It was thereby found possible (as discussed in detail in Ref. 10; see also Refs. 11–13) to convert the directly measured excitation spectrum to an approximation for the absorption spectrum.

The observed multiline spectrum has been interpreted as being due to a singlet–triplet coupling (V_{ST}) that couples a single zero-order "bright" singlet state with many (N in number) zero-order triplet states ($T_j, j = 1,...,N$), leading to a dense manifold of many molecular eigenstates. The absorption intensities $|C_{Si}|^2$ are then the weights of the bright state in the different molecular eigenstates. We have analyzed the fluctuations in these computed absorption intensities using the procedure of Ref. 6 with additional details as given below. The conclusion is that the extent of state mixing which is required to reproduce the well-resolved experimental excitation spectrum of pyrazine provides an example of intensity fluctuations near the chaotic limit. The fluctuations in the singlet–triplet couplings and in the excitation spectrum were also analyzed and lend further support to our conclusion.

In concluding the introduction we wish to reiterate our basic premise, namely that extensive vibrational state mixing does not imply that the "weight" $|C_{si}|^2$ of the zero-order bright state in the ith molecular eigenstate should vary uniformly as a function of energy. Rather, it can fluctuate (about a smooth envelope) and the extent of these fluctuations is used here (in Sec. III) as a characterization of the extent of state mixing. The theoretical background is discussed, *interalia*, in Ref. 6 which also contains a "handbook" providing details for implementing the statistical analysis, including the estimation of standard deviations on the computed measures due to the finite number of lines. Section II is an outline of the computation of the weights $|C_{si}|^2$. These computations, which follow Ref. 10, are meant to reproduce the observed excitation spectrum. We do not, however, claim that this reproduction is unique.

II. THE ABSORPTION SPECTRUM

The absorption spectrum

$$S(E) = \sum_{i=1}^{N} y_i \delta(E - E_i) \tag{1}$$

is defined in terms of the weights $y_i \equiv |C_{si}|^2$ of the bright singlet state in the i molecular eigenstates. To determine these weights one needs the matrix representation of the Hamiltonian in the uncoupled zero-order basis. The recon-

struction of the zero-order basis has been discussed in Ref. 10 and is as follows: From the measured excitation spectrum and the lifetimes of eight molecular eigenstates and using a dediagonalization procedure,[14] one determines the zero-order energies of the bright singlet ($|S\rangle$) state and of the N triplets ($|T_j\rangle$), $j = 1,..,N$), the coupling elements V_{ST_j}, and the decay rates (γ_S, γ_{T_j}). The eight measured lifetimes suffice to uniquely determine only eight triplet decay rates. While the eight molecular eigenstates whose lifetimes have been determined contain the major part of the total excitation intensity, it was suggested in Ref. 10 that the resulting zero-order basis is not large enough. Hence, a second dediagonalization procedure (using assumed lifetimes for those states whose decay was not monitored), was performed that included 36 triplet states. This led to a redistribution of the singlet amplitudes C_{Si}. Our conclusion (as discussed below) is that while the redistribution is not large it is significant and that the absorption spectrum using 36 states is the more realistic one.

In the present paper we start from the dediagonalized Hamiltonian matrix of Ref. 10, except that we multiply the off-diagonal elements (the V_{ST_j}'s) by a coupling constant η. $\eta = 1$ corresponds to the Hamiltonian matrix of Ref. 10.

It is only for $\eta = 1$ that the computation is meant to agree with the observed spectrum. We report results for other values of η in order to demonstrate two points of theoretical interest. (1) $\eta < 1$ corresponds to reduced state mixing. We wish to show that this leads to more extensive fluctuations (i.e., to a lower value of the parameter ν discussed in Sec. III). (2) $\eta > 1$ corresponds to even stronger mixing, hence we expect that as η increases the fluctuations will settle down to a universal limit. This will not, however, be the case if the basis size is too small for convergence. The behavior for $\eta \geqslant 1$ serves therefore to examine whether the basis size (N) is large enough (at the realistic value $\eta = 1$).

The diagonal elements of the Hamiltonian matrix ϵ_i ($i = 1,..,N$, $N = 8$ or 36) are given (in MHz) in Table II of Ref. 10 with respect to the energy ϵ_0 of the zero-order singlet state which is taken as zero. The only off-diagonal elements of the Hamiltonian are along one row and one column, those coupling the zero-order singlet to the triplets, $H_{0j} = \eta V_{ST_j}$, with values for V_{ST_j} also from Table II of Ref. 10. Diagonalizing such a Hamiltonian is well known to be analytical. The eigenvalues E (the molecular energy levels) are the solutions of

$$E = \epsilon_0 - \sum_j H_{0j}^2/(\epsilon_j - E). \tag{2}$$

There is one unperturbed triplet level between every two molecular eigenstates. The (normalized) weight of the singlet state in the ith molecular eigenstate is given by

$$|C_{Si}|^{-2} = 1 + \sum_j H_{0j}^2/(\epsilon_j - E_i)^2. \tag{3}$$

The absorption spectrum is now given by Eq. (1). Computations were performed for $0 < \eta \leqslant 4$. The fluctuations in the $|C_{Si}|^2$'s (at a given value of η) are then analyzed by the method of Sec. III with the results discussed in Sec. IV. The main findings are: (i) As η increases from zero towards uni-

ty, the extent of fluctuations does diminish. (ii) By $\eta \approx 0.4$, the results computed for the two basis sizes ($N = 8$ and 36) differ by more than the range allowed (cf. Sec. III) due to the use of a finite sample. Hence, the $N = 8$ basis is not large enough for convergence at $\eta = 1$ while the $N = 36$ basis appears to suffice up to $\eta \approx 2$. (iii) For $\eta = 1$ and $N = 36$, the fluctuations are quite near to those expected for the chaotic limit.

A dediagonalized Hamiltonian of the same or very similar structure has been used in many other model studies of the optical spectrum due to a single bright state. The one point that requires emphasis is that the magnitude of the matrix elements of the Hamiltonian (for $\eta = 1$) is that found in Ref. 10 to reproduce the excitation spectrum. We reiterate that this does not imply that the dediagonalized Hamiltonian is unique.

III. ANALYSIS

The analysis is based on the following premise: En route to classical chaos, the distribution of (squares of) quantal matrix elements should be that distribution known as χ^2 with ν degrees of freedom. $\nu = 1$ is the signature of classical chaos. Further details are provided in the reviews in Refs. 1, 2, and 6. Previous computational results[7,8] show that $\nu < 1$ in the regular regime and $\nu \to 1$ as the system becomes more classically chaotic. The present dediagonalized matrix Hamiltonian has not been derived from a geometrical Hamiltonian and hence the classical limit cannot be discussed. What can be done is to examine weaker and weaker state mixing which corresponds to $\eta \to 0$. We indeed find that in the range $0 < \eta \leqslant 1$, ν is higher for higher values of η.

Given a set of (squares) of matrix elements $y_i \equiv |C_{Si}|^2$ we compute ν as the implicit solution of [Eq. (2.33) of Ref. 6]

$$\langle \ln(y/\langle y \rangle) \rangle = \Psi\left(\frac{\nu}{2}\right) - \ln\left(\frac{\nu}{2}\right). \tag{4}$$

Here $\Psi(x)$ is the Ψ function,[14] $\Psi(x) = d \ln \Gamma(x)/dx$. The averages in Eq. (4) are over the distribution of values,

$$\langle y \rangle \equiv N^{-1} \sum_{i=1}^{N} y_i, \tag{5}$$

and similarly for $\langle \ln y \rangle$. The uncertainty $\delta\nu$ in ν is computed using Eq. (2.40) of Ref. 6 with $s^2 = 1/N$ since the statistical uncertainty in our results is only due to the finite size of the basis. Many practical details regarding the determination of ν will be found in Ref. 6.

In principle, ν characterizes the fluctuation of y_i about a smooth envelope. In the present problem the *smooth* spectral envelope is,[6] cf. Eq. (1),

$$S^0(E) = \sum_i y_i A(E - E_i), \tag{6}$$

where $A(E - E_i)$ is a normalized window function of finite width. To achieve a degree of smoothing, the width of the window function need be at least equal to the average spacing between eigenstates.[7,15] We have verified that at that window width, $S^0(E)$ in the present problem is so slowly varying that within the uncertainty of ν (i.e., to within $\pm \delta\nu$), $S^0(E)$ can be taken as flat.

	$\nu \pm \delta\nu$	
y_i	8 states	36 states
V^2_{ST}	1.3 ± 0.6	1.5 ± 0.3
$|C_{Si}|^2$	9.3 ± 1.5	1.8 ± 0.3
I_i	3.5 ± 0.9	0.6 ± 0.2
γ_{ME_i}	4.8 ± 1.0	11.9 ± 0.9

IV. RESULTS

The extent of fluctuations was determined for four distinct types of amplitudes with the results reported in Table I. The four distributions were: (i) The distribution of zero-order singlet–triplet coupling elements $y_j = |V_{ST_j}|^2$. The purpose here is to examine whether these matrix elements have a chaotic distribution, (ii) the distribution of the (computed) absorption intensities $y_i = |C_{Si}|^2$, (iii) the distribution of the observed[10] excitation intensities $y_i = I_i$, and (iv) the distribution of lifetimes $y_i = \gamma_{ME_i}$.

For the distribution of the singlet–triplet coupling strengths, as used in Ref. 10, we find that it is essentially chaotic ($\nu = 1.3 \pm 0.6$ and $\nu = 1.5 \pm 0.3$ for $N = 8$ and 36, respectively). This serves as a probe of the coupling within the manifold of zero-order triplet states. It implies that the observed excitation spectrum is consistent with extensive state mixing within the manifold of zero-order triplet states.

Next ν was determined for the absorption intensities of Ref. 10 (i.e., $\eta = 1$ for the present problem). For $N = 8$ we obtained $\nu = 9.3 \pm 1.5$ which implies far less fluctuations than the chaotic limit. Repeating the analysis for $N = 36$ led to $\nu = 1.8 \pm 0.3$ which is reasonable on the basis of the strong chaotic coupling.
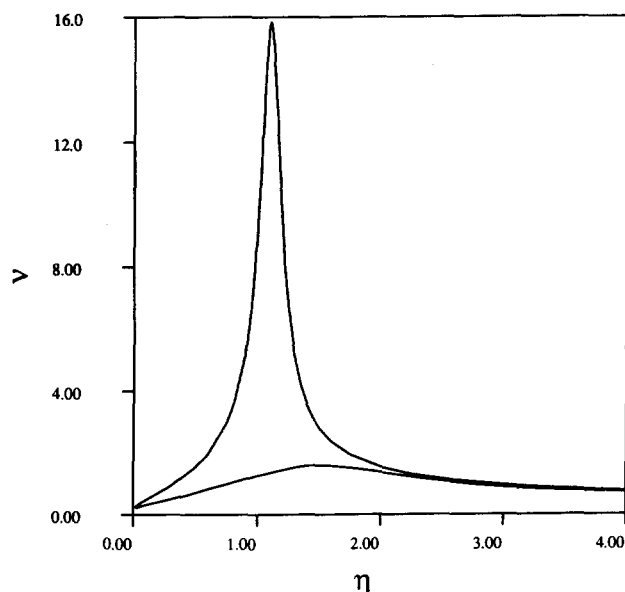
Whether the absorption spectrum is chaotic or not depends not only on the chaotic nature of the coupling but also on its overall magnitude η. For that reason we have computed the absorption spectrum for η values in the range 0 to 4, as discussed in Sec. II, and analyzed the fluctuations for $N = 8$ and 36. The values of ν vs η for the two bases are shown in Fig. 1. Very clearly, the smaller ($N = 8$) zero-order basis is too small at all but the lowest value of η. In particular, the rise of ν to 16 must be considered unphysical. The reason is that the fluctuation distribution is very sensitive to the smaller values of the intensity [note that it is $\langle \ln y \rangle$ which determines ν, cf. Eq. (4)]. If the basis size is too small, and the coupling is strong, there is a tendency for the zero-order state to be uniformly distributed (hence high ν), contrary to the true physics of the problem.

For $N = 36$ it appears that for $\eta = 1$ the basis size is sufficient. Figure 2 shows $\nu + \delta\nu$ vs η for $N = 36$. It is our conclusion that beyond $\eta \approx 2$ this basis is also too small as is judged by the decline of ν.

Figure 3 shows an actual histogram of $y_i \equiv |C_{Si}|^2$ for $N = 36$ and $\eta = 1$ and the theoretical distribution for $\nu = 1.5$.

Also given in Table I are the results for ν for the distribution of fluctuations in the directly observed excitation spectrum (I_i) and for the distribution of lifetimes. The latter distribution is too narrow. That is not unexpected for a number of reasons. For $N = 8$, the distribution is derived from the measured lifetimes of typically the eigenstates of shorter lifetimes. Hence, there is a built-in bias against the longer lifetimes. For $N = 36$, the authors of Ref. 10 *assumed* a lifetime of 500 ns for *all* of the unknown values. This will further tend to reduce the fluctuations in the lifetimes of zero-order states. The high value of ν (≈ 12) is simply a reflection of the assumption made about the unknown lifetimes of the eigenstates and not a result about the physics. We quote the results for the lifetimes only as a demonstration that the range of values of ν does serve as a useful diagnostic of the input.
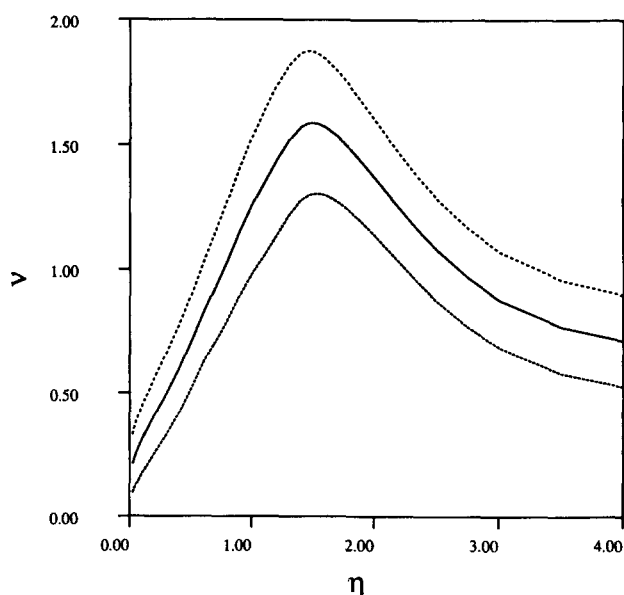

FIG. 1. The value of the parameter ν (for the χ^2 distribution) determined for the computed absorption spectrum at various values of the singlet–triplet coupling constant η. The value for pyrazine as used in Ref. 10 is $\eta = 1$. Upper curve: using $N = 8$ triplet states; lower curve: using $N = 36$ triplet states. Both computations assume a single bright singlet state.

FIG. 2. The range, $\nu \pm \delta\nu$, of ν values vs η for the computed absorption spectrum for $N = 36$. The value of ν is shown as a solid line and the dashed lines show the range.
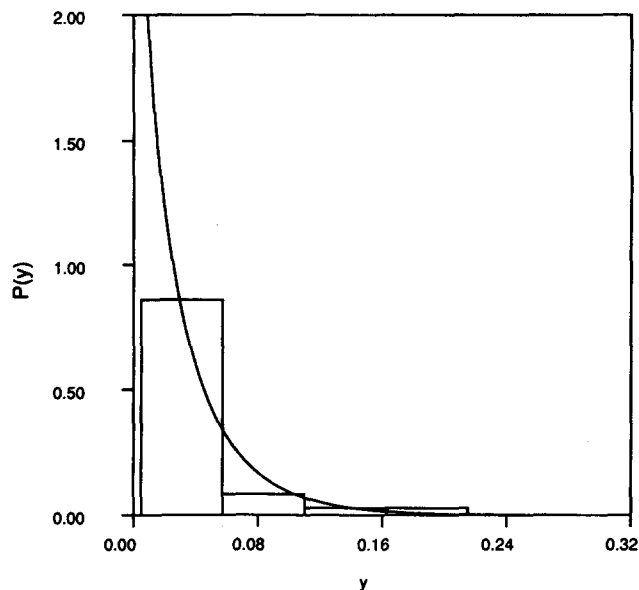
FIG. 3. A histogram for the distribution of the (normalized) absorption intensity $y \equiv |C_{si}|^2$ for pyrazine and the fit (continuous line) by a χ^2 distribution with $\nu = 1.5$.

V. CONCLUSIONS

Analysis of a computed absorption spectrum which has been chosen to reproduce the fluorescence excitation spectrum of pyrazine of the $^1B_{3u} \leftarrow {}^1A_g$ 0_0^0 transition band indicates that the distribution of intensities is near to that expected for the fully chaotic regime. It was further demonstrated that by artificially lowering the strength of the singlet–triplet coupling, the computed intensities show wider fluctuations.

[1] T. A. Brody, J. Flores, J. B. French, P. A. Mello, A. Pandey, and S. S. M. Wong, Rev. Mod. Phys. **53**, 385 (1981).

[2] E. J. Heller and R. L. Sundberg, in *Chaotic Behavior in Quantum Systems*, edited by G. Casati (Plenum, New York, 1985).

[3] M. V. Berry, J. Phys. A **10**, 2083 (1977).

[4] V. Buch, R. B. Gerber, and M. A. Ratner, J. Chem. Phys. **81**, 3393 (1984).

[5] Y. Alhassid and R. D. Levine, Phys. Rev. Lett. **57**, 2879 (1986).

[6] R. D. Levine, Adv. Chem. Phys. **70**, 53 (1987).

[7] J. Brickmann, Y. M. Engel, and R. D. Levine, Chem. Phys. Lett. **137**, 441 (1987).

[8] J. G. Leopold, R. D. Levine, and D. Richards (to be published).

[9] The observed [K. K. Lehmann and S. L. Coy, J. Chem. Phys. **83**, 3290 (1985) and private communication] intensity fluctuations in NO_2 do appear to be near the chaotic limit [J. P. Pique, R. D. Levine, J. L. Kinsey, and R. W. Field (to be published)]. The fluctuations in the fluorescence *lifetimes* of rovibronic levels in SiH_2 [Y. M. Engel, R. D. Levine, J. W. Thoman, J. I. Steinfeld, and R. McKay, J. Chem. Phys. **86**, 6561 (1987)] provide the only example of the chaotic limit.

[10] W. M. van Herpen, W. L. Meerts, K. E. Drabe, and J. Kommandeur, J. Chem. Phys. **86**, 4396 (1987).

[11] J. Kommandeur, W. A. Majewski, W. L. Meerts, and D. W. Pratt, Annu. Rev. Phys. Chem. **38**, 433 (1987).

[12] J. Kommandeur, Adv. Chem. Phys. **70**, 133 (1987).

[13] K. W. Holtzclaw and D. W. Pratt, Chem. Phys. Lett. **118**, 375 (1985).

[14] W. D. Lawrance and A. E. W. Knight, J. Phys. Chem. **89**, 917 (1985).

[15] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965), Chap. 6.

[16] M. Feingold and Y. Alhassid (to be published).