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The fast component in the decay of the $^1B_{3u}$ state of pyrazine has long been an enigma. It was originally interpreted to be due to intermediate level structure[1] and the theory for the latter led to the simple result that the ratio of the amplitudes of the fast and slow component (A^+/A^-) measured the number of states coupled to the doorway state.[2] This result was used by many authors[3–5] to "count" the number of states as a function of the rotational quantum number J. This pretty picture was upset by the actual measurement of the molecular eigenstates,[6] which clearly showed that the number of coupled states was about 10–12 and at least for low J (< 4) independent of J.[7]

In addition, with a nanosecond laser exciting the $P(1)$ component of the rotational spectrum quantum beats *were*, but a fast component was *not* observed.[4,8] On the other hand, with a picosecond laser Rice[9] and Zewail[10] unequivocally established that a fast component with a decay of about 100 ps *was* present. The question then arises, what is the fast component due to? The answer appears to be quite simple. In the first place it should be realized that the molecular eigenstate (ME) spectrum is very "empty." In the bottom of the J manifold the separation between rotational singlet (doorway) states is about 0.4 cm^{-1}, or 12 GHz. The singlet states have an interaction width of about 2–5 GHz, which means that the ME spectrum spreads over only one third of the total frequency range. In addition the ME spectrum does not show any signs of a Lorentzian distribution of amplitudes, the matrix elements for the singlet triplet coupling vary widely, and the background triplet states are irregularly spaced.

In a very rough approximation, to a broad laser the ME spectrum looks like "blocks" of absorption of widths of about $\Delta\nu = 3.5$ GHz spaced by typically 8.5 GHz. The Fourier transform of the product of a broad ($\gg 2$ GHz) laser amplitude distribution and one such block looks like $\sin(2\pi\Delta\nu t)/t$.

To obtain the time-dependent emission characteristics this quantity should be squared, and it should be noted that for a considerable part of its time range it can be fitted very nicely with an exponential. The fit is improved, when it is realized that the blocks are built from some 10–14 individual narrow Lorentzians, which at longer times lead to exponential decay, which for the short times considered here looks like a constant. Finally, in the experiments so far undertaken the excitation was not of one block, but of many. These blocks are not all of the same width, neither are they centered around the same frequency. Therefore, considerable averaging takes place, since the observed decays result from an incoherent superposition of a number of coherently decaying blocks. Even in the experiments of Rice *et al.*, who carefully selected the J-number excited the minimum number of

blocks was three for $P(2)$ and $R(1)$, deriving from the three possible $\Delta K = 0$ transitions.

The proof of the pudding is in the eating. It appeared therefore worthwhile to Fourier transform the actual ME spectrum, particularly the Q branch, which probably has been studied most. An ME spectrum of the Q branch is not known, since all rotational transitions pile up there. We know, however, the appropriate widths of the many blocks in the Q branch, since the $P(1)$ and $R(0)$ ME spectra, both deriving from single rotational lines are approximately 4000 and 2500 MHz wide, respectively. We therefore took the Q branch as being composed of 12 blocks with widths varying randomly between 2000 and 5500 MHz. Within these blocks 12 ME's were randomly generated and each ME was "dressed" with a complex Lorentzian. The integrated intensities and the centers of the blocks were taken from a conventional symmetric top calculation for the various J states at a temperature of 4 K.

The real and imaginary amplitudes of the states in the blocks were then multiplied by the laser amplitude of a Gaussian envelope with a width of 30.000 MHz (10ps). The resulting "excitation amplitudes" were Fourier transformed for each block independently. The amplitudes in time were squared and the resulting decays were added. In an equation:

$$S(t) = \sum_n \{FT \sum_i [A_i(\omega_{in}) \cdot L(\omega_{in})]\}^2, \tag{1}$$

where S is the decay, n numbers the block, i the states within a block, $A_i(\omega_{in})$ is the amplitude of the ith ME and $L(\omega_{in})$ the amplitude of the laser at the frequencies ω_{in}.

The final result for $S(t)$ is shown in Fig. 1. A rather nice fit to an exponential with a time constant of 100 ps is found, very similar to what is observed in experiment.[9,10] Nonre-
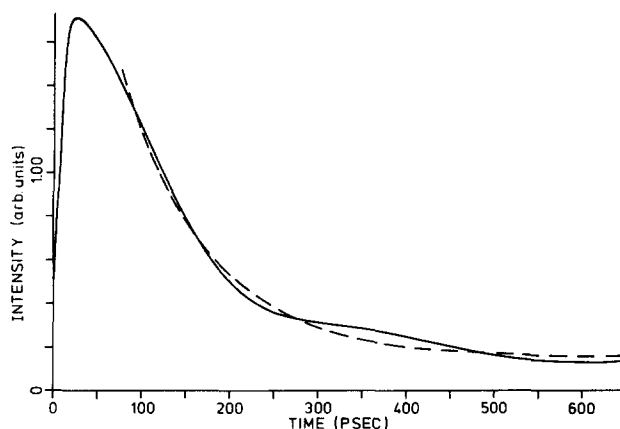

FIG. 1. Decay reconstructed from ME's of Q branch (drawn line). Dotted line: best exponential fit ($\tau = 100$ ps).

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sonant excitation of R (0) and P (1) did not alter the result, because of the relatively low intensities in these transitions.

It should be realized that the present interpretation (at least for low J) is very close to Tramer's original one,[2] the main difference being the fact that the intensities of the ME's show a very non-Lorentzian distribution and therefore the numbers obtained from the decays are misleading.

A final point deserves mentioning. The "dephasing" which leads to the fast component is a very rapid process, it lasts in the order of 100–200 ps. The collision free quantum yield of pyrazine is about 1%.[11] With a radiative life time of 300 ns, the radiationless lifetime is about 3 ns, considerably longer than the dephasing time. The A^+/A^- ratio is usually determined by dividing the peak of the emission by the emission observed at longer times. This later emission is affected by the radiationless process, the dephasing is not. It may therefore well be that the rise of A^+/A^- is totally determined by the strong drop in the quantum yield, as was observed by Baba[12] and Amirav.[11] Indeed, A^+/A^- appears to go as $(2J + 1)^{3.9}$ and the quantum yield as $(2J + 1)^{-1}$.

[1] A. Frad, F. Lahmani, A. Tramer, and C. Tric, J. Chem. Phys. 60, 4419 (1974).
[2] F. Lahmani, A. Tramer, and C. Tric, J. Chem. Phys. 60, 4431 (1974).
[3] H. Saigusa and E. C. Lim, J. Chem. Phys. 78, 91 (1983).
[4] Y. Matsumoto, L. H. Spangler, and D. W. Pratt, J. Chem. Phys. 80, 5539 (1984).
[5] P. M. Felker, Wm. R. Lambert, and A. H. Zewail, Chem. Phys. Lett. 89, 309 (1982).
[6] B. J. van der Meer, H.Th. Jonkman, J. Kommandeur, W. L. Meerts, and W. A. Majewski, Chem. Phys. Lett. 92, 565 (1982).
[7] B. J. van der Meer, H. Th. Jonkman, and J. Kommandeur, Laser Chem. 2, 77 (1983).
[8] B. J. van der Meer, H.Th. Jonkman, G. M. ter Horst, and J. Kommandeur, J. Chem. Phys. 76, 2099 (1982).
[9] A. Lorincz, F. A. Novak, D. D. Smith, and S. A. Rice, in Ultrafast Phenomena IV, Springer Series in Chemical Physics 38, edited by D. H. Anston and K. B. Eisenthal (Springer, Berlin). p. 362; A. Lorincz, D. D. Smith, F. Novak, R. Kosloff, D. J. Tannor, and S. A. Rice, J. Chem. Phys. 82, 1067 (1985).
[10] J. L. Knee, F. E. Doany, and A. H. Zewail, J. Chem. Phys. 82, 1042 (1985).
[11] A. Amiraw and J. Jortner (to be published).
[12] H. Baba, N. Ohta, O. Sekiguchi, M. Fruita, and K. Uchida, J. Phys. Chem. 87, 943 (1983).

Crossover behavior for Brownian motion

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In this study, the Brownian motions of polystyrene latex and bacteriophage T4 were observed with phase contrast and epifluorescence microscopes. Their trajectories were recorded in a video system for numerical analysis.

In random motions, the trajectory length L (r) is defined by the step-length (r) multiplied by the number of steps when a given trajectory in the random motion is successively divided with r. If the trajectory is a "fractal", L (r) is generally expressed by L (r) $\propto r^{1-D}$, where D is called the fractal dimension. This D is exactly given by $D = 2$ for the mathematical Brownian motion.[1]

Experimentally, the motions within a certain time interval are unable to be detected due to the instrumental limitation in video recording. (In our present experiments this limit was 1/30 s.) Therefore, it follows that the motion in a finer time-division is approximated by a finite, straight line segment. This means that the mean segment length (m.s.l.) takes a nonzero value.

The plots, $\log L$ (r) vs $\log r$, obtained from our experimental data are shown in Fig. 1, for the cases of latex motion (a), T4 motion (b), and T4 adsorption process to its host $E.$ coli B cells [(c) and (d)]. The case (a) is regarded as a simple diffusion process. These plots do not exhibit any ideal fractal behavior as expressed by the above relation, L (r) $\propto r^{1-D}$, in which D must be a constant. Instead, the figure shows a transition-like behavior from the fractal state

$D = 1 (r \ll \text{m.s.l.})$ to the state $D = 2 (r \gg \text{m.s.l.})$ as r increases.[2,3] This implies that the intermediate range of r is a crossover range between the above two limiting fractals. This means that when we define D *(r) by

$$1 - D^*(r) = \frac{d \log L (r)}{d \log r},\qquad(1)$$

$D^*(r)$ changes from 1 to 2 in the crossover range.

Now let us construct an experimental formula of $D^*(r)$. First, since D^* is a dimensionless quantity, D^* should be expressed as a function of r/r_0 with a distance parameter r_0. Next, in order to express the sharpness of the transition, it is reasonable to write $D^* = D^*[(r/r_0)^n]$ with a sharpness parameter n. A suitable function covering the limiting cases $r = 0$ and $r = \infty$ may be written in the form

$$D^*(r) = 2 - \frac{1}{1 + (r/r_0)^n}\qquad(2)$$

Equation (2) in the case of $n = 1$ was first theoretically derived by Takayasu for a one-dimensional Markovian random walk model, in which r_0 was a finite mean-free-path length.[4] Substituting Eq. (2) into Eq. (1) and integrating, we have the following expression of L (r);

$$L (r) \propto \frac{1}{[1 + (r/r_0)^n]^{1/n}}\qquad(3)$$

Since, r_0 is experimentally determined from the relation,