Absorption Spectrum versus Excitation Spectrum of Pyrazine

by

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Abstract

The first ME spectrum of pyrazine was measured as an excitation spectrum. Assuming the quantum yield to be constant over the spectrumt was considered as an absorption spectrum and de-diagonalisation led to zero order energies and coupling constants of the singlet and triplet states.

By measuring the lifetimes of eight strong ME's we have now shown that the quantum yield varies by as much as a factor of three over the spectrum. With these lifetimes the excitation spectrum can be converted into a real absorption spectrum and a new and now correct set of values for the zero order energies, their widths and the coupling constants was obtained. The most important result is the fact that the zero order singlet and triplets decay non-radiatively at different rates.

1. Introduction

In molecular beam spectroscopy one usually measures excitation spectra. A laser beam is directed towards the molecular beam and one measures the radiation emitted, which is not in the direction of the laser beam. Although this fact is, of course, well known, excitation spectra are often treated as if they were absorption spectra. In the numerical sense, that is in the derivation of coupling constants, this can lead to erroneous results. After all, the quantum yields of the various spectral lines observed may not at all be the same and thus intensities from an excitation spectrum may not at all reflect the intensities of an absorption spectrum.

A case in point is the Molecular Eigenstate (ME) spectrum of the J'=0, K'=0 rotational member of the $^1B_{3u}$ state of pyrazine. In the not too recent past (1) we have measured this excitation spectrum and assuming the quantum yield to be constant we have used these data to derive a set of zero-order energies and a set of coupling constants for the interaction of the J'=0, K'=0 rotational singlet state with the available triplet rovibronic states. (2)

Since it was still possible that the quantum yield did vary over the ME-spectrum, we have now measured a number of lifetimes of the ME's. For a limited number (eight) this allows the determination of their quantum yields, which in turn gives access to the actual absorption spectrum. This spectrum can then be used to derive a new and now correct set of the previous effort. This paper reports on the results obtained.

2. Experimental

The apparatus used in the experiment has been extensively described before (3). It basically consists of a doubly skimmed argon molecular beam into which pyrazine was seeded. The beam was obtained from a 100 μm continuous nozzle at a backing pressure of 0.5 atmosphere. The interaction with the laser field occurred 30 cm from the beam orifice, where the Doppler width was some 15 MHz. The undispersed laser induced fluorescense was focussed onto the cathode of an EMI 9863/350 QA photomultiplier.

The very narrow band laser field was obtained from an intracavity $LiIO_3$ doubled modified Spectra Physics ring laser, which yielded about 2mW of UV power (cw) with a bandwidth of less than 0.5 MHz. Its relative frequency was measured by a sealed-off, temperature stabilized, Fabry-Perot interferometer.

For lifetime measurements the laser was held at a particular frequency where an absorption occurred and the light was modulated with a Coherent Radiation electro-optic modulater in conjunction with a polarizer. "Single" frequency pulses of 40 nsec duration were obtained with an on-off ratio of about 150. The repetition rate was 12 kHz. The photons emitted were measured with a

single photon counting system equipped with a pile-up inhibitor. For the strongest lines in the spectrum about 0.1 photons per shot were detected.

3. Theory

The ME-spectrum results from the interaction of one singlet (rotational) state with a number of triplet (ro)vibronic states. In low resolution spectroscopy, or with short-time (i.e. large coherence-width) lasers this interaction does not show up in the spectrum at all. At most, it will lead to an (unresolved) broadening of the singlet spectrum.

In high resolution spectroscopy one can observe the molecular eigenstates resulting from the extensive mixing of the singlet with the triplet states. Of course, the singlet character of these states is responsible for their absorption of light, but both the singlet and the triplet character may contribute to their radiationless decay (f.i. through Cariolis interaction to the S_0 manifold). We are interested in the various decay channels, how do we pick them apart?

Calling the singlet state $|S\rangle$ and the states of the triplet manifold $\{|T\rangle\}$ we can write for the wavefunction of the i'th ME:

$$\Psi_i = C_{S_i} |S\rangle + \sum_T C_{T_i} |T\rangle \qquad (1)$$

$|S\rangle$ and $\{|T\rangle\}$ being orthogonal, we can write for the decay rate of an ME:

$$\gamma_{ME_i} = |C_{S_i}|^2 \gamma_S + \sum_T |C_{T_i}|^2 \gamma_T \qquad (2)$$

with $\gamma_S = \gamma_S^r + \gamma_S^{nr}$, consisting of a radiative and a non-radiative part. γ_T is purely non-radiative. The absorption intensity of the i'th ME is given by

$$A_i \propto |\mu_S|^2 |C_{S_i}|^2 I_1 \qquad (3)$$

where μ_S and I_1 are, respectively the transition dipole moment of the singlet state and the intensity of the laser. The excitation intensity, however, is modified by the quantum yield Q_i of the ith ME and given by the branching ratio:

$$E_i \propto A_i Q_i = A_i \frac{\gamma^r_{ME_i}}{\gamma_{ME_i}}$$

$$= \frac{|\mu_S|^2 \, |C_{S_i}|^2 \, |I_1|C_{S_i}|^2 \, \gamma_S^r}{\gamma_{ME_i}}$$

$$= \frac{|\mu_S|^2 \, |C_{S_i}|^4 \, \gamma_S^r I_1}{|C_{S_i}|^2 \, \gamma_S + \sum_T |C_{T_i}|^2 \, \gamma_T} \qquad (4)$$

From equation (4) it is immediately obvious, that if there is no decay of the triplet manifold ($\gamma_T=0$ for all T), the expression is totally equivalent to eqn. (3), and excitation spectrum and absorption spectrum are identical, except for a constant multiplication factor.
Rewriting eqn. (4), we have

$$E_i = \alpha \frac{|C_{S_i}|^4}{\gamma_{ME_i}} \qquad (5)$$

where α contains some constants and factors for the sensitivity of the apparatus. It is independent of the ME studied.
We then have $|C_{S_i}|^2 = (E_i \gamma_{ME_i}/\alpha)^{1/2}$, and since we measure E_i (the intensity of an ME in the excitation spectrum) and γ_{ME_i} the inverse lifetime of the ME, we can calculate the relative absorption spectrum as given by $|C_{S_i}|^2$. The constant $\alpha^{1/2}$ can be removed by requiring that $\sum_I |C_{S_i}|^2 = 1$, only one singlet state is distributed over the ME-spectrum.

The absorption spectrum can then be used to obtain the zero order energies, the zero order widths and the coupling constants, as has been outlined elsewhere (2,4).

4. Results

In our experiments a higher dynamic range was available than before (1). Therefore, figure 1 shows the original ME-spectrum of the P(1) transition of the $^1B_{3u}$-state of pyrazine (bottom) and in the inset the rather more detailed results we have now. Instead of the original 13 lines we now measure 36 over a larger spread of frequency. The estimate of the rovibronic density of states, however remains largely the same. Due to its symmetry pyrazine has four separate manifolds of states of different nuclear symmetry (very equivalent to H_2 having two sets: ortho and para). Interactions can only occur within a nuclear manifold. The statistical weights of the states are 17,13,9,9 for the A_g, B_{1g}, B_{2g} and B_{3g} manifolds, respectively. The J'=0, K'=0 is an A_g state. It can therefore only interact with 17/48'th of the rovibronic triplet manifold. However, these are triplets and their number should be multiplied by three.

We find a total of 35 triplet states over 7,6 GHz, yielding 140 states per cm^{-1}. Haarhoff-type calculations of the density of vibronic states in the triplet manifold around the singlet energy have yielded 100 states per cm^{-1} Of these we could maximally "see" 17/48x3x100 = 106 per cm^{-1}.
Given the fact that the vibronic states are arbitrarily distributed, the result is that we "see" all available states. This must mean that all triplet vibrations are somewhat mixed at 4000 cm^{-1} above the triplet origin, which appears to be a reasonable result. If the mixing were complete we would expect all singlet triplet coupling constants to be of about the same magnitude. To obtain these, however, we first have to discuss the lifetime measurements.

Figure 2 shows a typical result of a lifetime measurement on a strong ME. Out of a total of 36 lines, for 8 a reasonably reliable lifetime could be measured. All the experimental data are collected in table I. Using eqn 5, we can also calculate the relative absorption intensities and they are given as well. They have been normalized to one, but since there are other (weaker) lines in the excitation spectrum, this normalization is fairly arbitrary. Taking into account the effect of the other stades, of which the lifetimes have not been measured, leads to minor adjustments of the numbers obtained (5), we leave it aside for the present.

Having 8 positions of the ME's, as well as 8 lifetimes and 8 absorption intensities we can use the Green's function method of Lawrance and Knight (4) to go to the zero order situation with one singlet state, seven triplets, seven coupling constants and eight widths, one for every state. The results are given in table II.

It can be seen that the coupling constants vary between 67 and 462 MHz. There is no democratic distribution, the mixing of vibronic states in the triplet manifold is far from complete!

Although the errors in the widths are fairly high, some conclusions can be drawn. There is considerably zero-order triplet decay as evidenced by the finite widths of the zero-order triplet states, and also by the lack of proportionality between the lifetimes of the ME's and their excitation intensities. Apart from the singlet's radiative decay, yielding a width of 3,3 MHz (6), there is room for some non-radiative decay, as evidenced by other work (7).

There appears to be no regularity in the energies of the triplet states, and given the fact that we "see" them all, this is probably not surprising. It therefore does not appear to be useful to try to identify these states as to their vibrational quantum number.

The pitfalls provided by an excitation spectrum are illustrated in Table III. For the eight states measured we can calculate the quantum yields Q_i from the lifetimes and the absorption intensities. It will be clear that the quantum yields can vary by as much as a factor of three depending on which ME was excited. This should be a general warning to all who measure

excitation spectra and assume that they are proportional to absorption spectra. Only lifetime measurements can deny or corroborate this assumption!

These observations also lead to the conclusion that it is hard to speak of "the" quantum yield of pyrazine. Apparently every ME has its own! One could speak of "the" quantum yield of the J'=0, K'=0 rotational state of the $^1B_{3u}$(0-0) transition of pyrazine, but then one should be certain that one has excited all the ME's belonging to that state with the same field intensity. This would be a very hard experiment to carry out correctly, particularly since the spread of the ME's appears to be larger than we thought previously. Estimates we have made (7), however, yielded Q(J'=0, K'=0)=0,15 which, given the uncertainties, does not compare unfavorably with the value of 0,22 as estimated by Amirav and Jortner (8) from the extrapolation of their direct measurements of the quantum yield.

Conclusions

It was shown that the previously reported (1) excitation spectrum of the ME's belonging to the P(1) member of the $^1B_{3u}$ (0-0) state of pyrazine is not proportional to the absorption spectrum. The quantum yields of the ME's can vary by a factor of three, as evidenced by a measurement of their lifetimes.

After these measurements, however, the actual absorption spectrum can be derived. With the new data a new and now correct set of zero-order energies, widths and coupling constants can be obtained, which differs from the previous one (2) mainly in the distribution of the energies. All qualitative conclusions remain the same. A new feature is the occurrence of zero-order triplet decay, which could not be found previously. It is of the same order of magnitude as the zero order singlet decay and can therefore not be neglected.

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TABLE 1.

Energies[a], excitation intensities and lifetimes of the ME's belonging to the P(1) member of the $^1B_{3u}$ 0_0^0 transition of pyrazine. Also calculated relative absorption intensities are given.

energy (MHz)	excitation intensity	lifetime (nsec)	absorption intensity
-4725	18		
-4337	42		
-3849	20		
-3686	21		
-3245	81		
-2884	376		
-2530	179		
-2438	33		
-2341	22		
-1881	21		
-1770	28		
-1694	39		
-1536	28		
-1515	58		
-1456	1666	200 (50)	0.118
-1071	19		
-984	20		
-929	58		
-689	30		
-637	25		
-589	66		
-535	1278	512	0.065
-502	55		
-353	3891	443	0.122
-318	1441		
-221	8168	342	0.200
-44	1305	437	0.071
62	4031	560	0.110
593	21		
631	199		
765	10000	280	0.245
867	1503	529	0.069
1443	28		
1867	55		
2722	28		
2781	29		

[a] The M.E. energies are referred to the center of gravity of the excitation spectrum which is at ν=-12192 MHz relative to the electronic origin ν_0 of the $^1B_{3u} \leftarrow {}^1A_g$ 0_0^0 transition.

TABLE 2.

Zero order energies, widths and coupling constants (all in MHz).

energy		width	coupling
singlet	triplets		constant
	-1243	5.0	462
	- 459	1.6	119
	- 265	1.6	105
	- 55	2.7	150
0		5.0	
	+ 56	0.6	117
	+ 506	3.0	457
	+ 891	1.6	67

TABLE III.

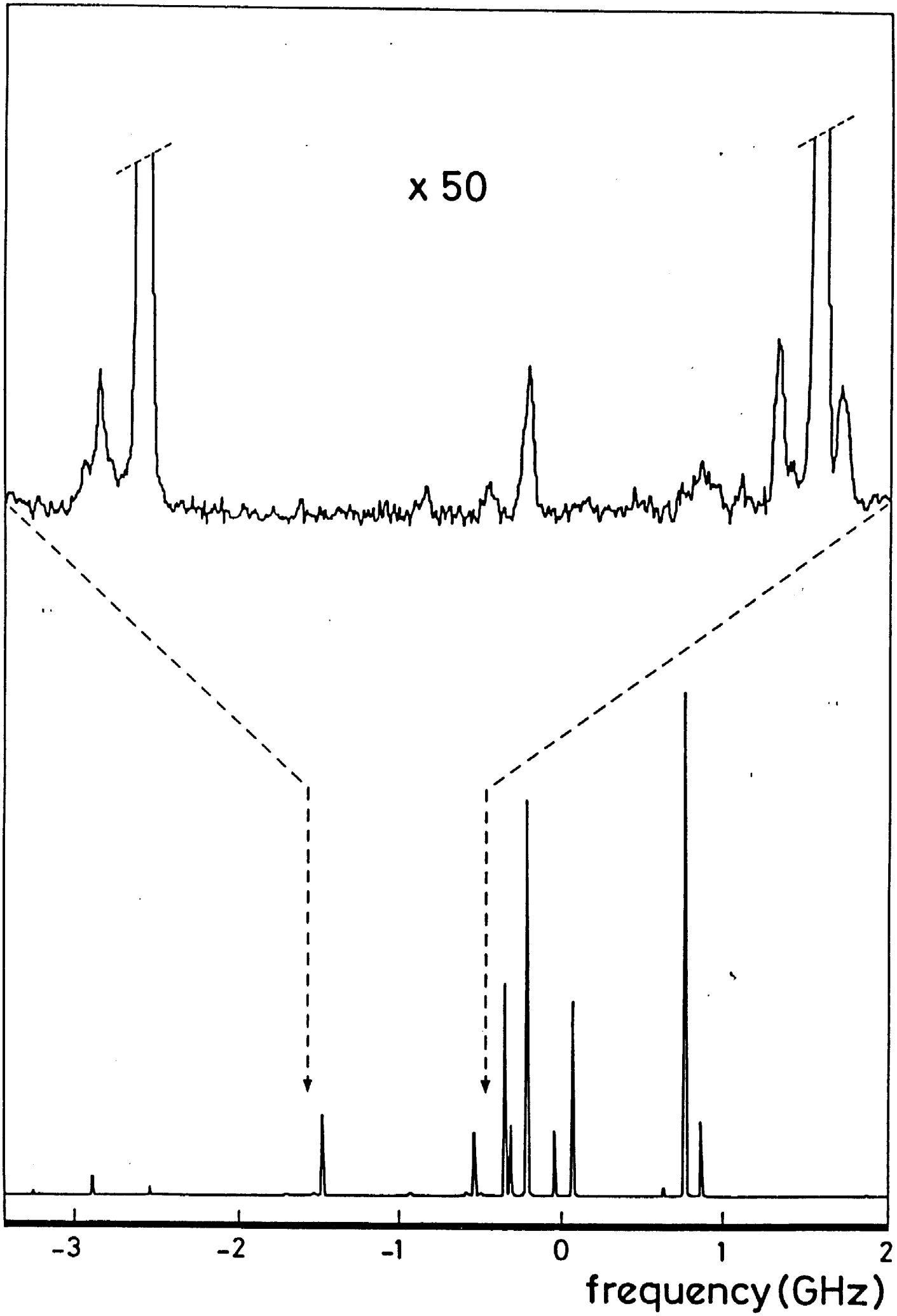
Quantum yield of ME's

ME(MHz)	Q_i
-1456	0.075
- 535	0.110
- 353	0.178
- 221	0.226
- 44	0.102
+ 44	0.203
+ 765	0.226
+ 867	0.121

Figure captions

Fig. 1 Excitation spectrum of the P(1) transition of pyrazine at ν=-12192 MHz relative to the origin of the $^1B_{3u}$ (0-0) transition

Fig. 2 Decay curve of the strongest line of the P(1) transition.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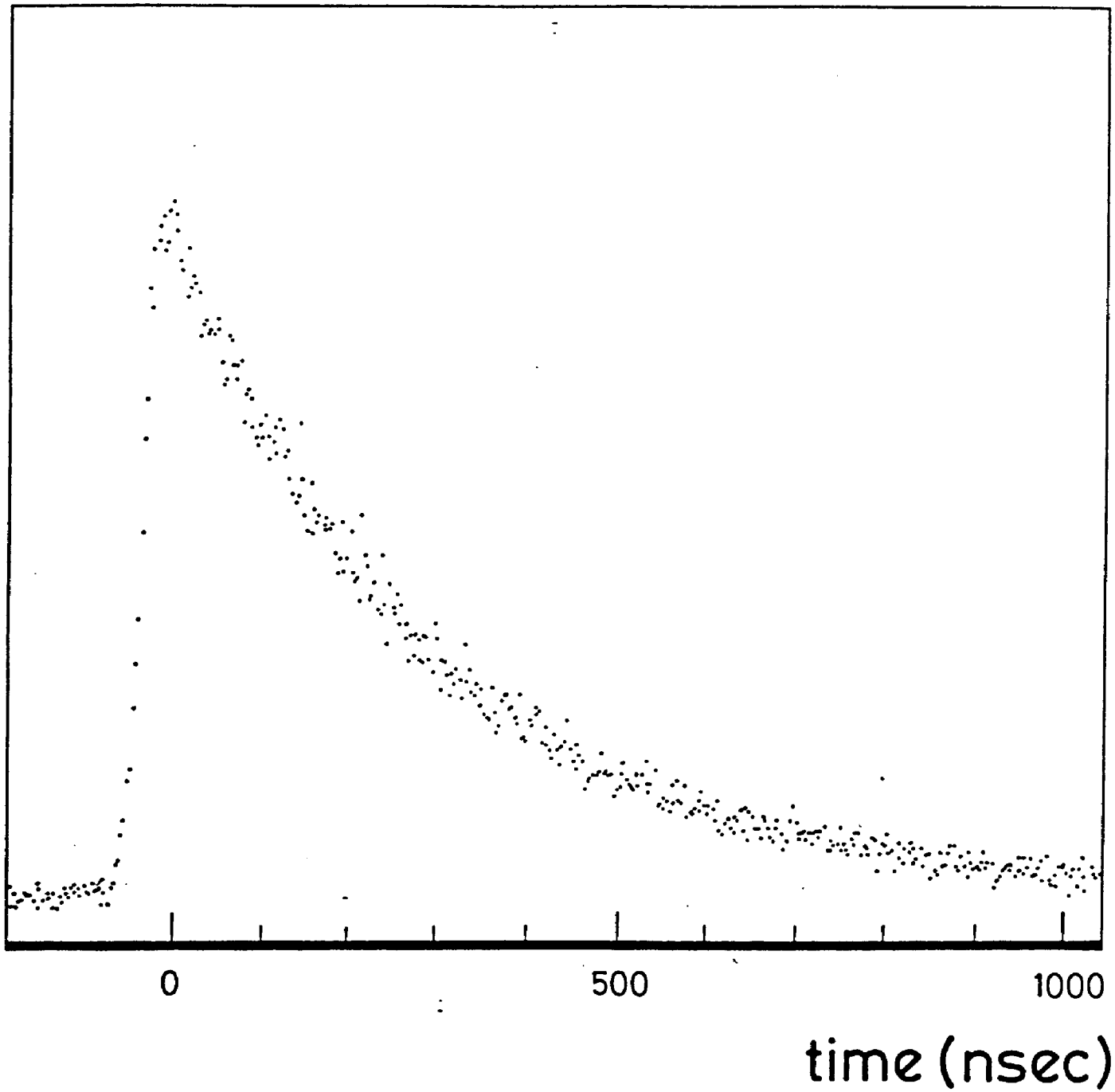
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