Bixon–Jortner Revisited

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Abstract. After twenty years, the theory of radiationless transitions in molecules is reviewed. Its qualities and its strengths are discussed. It is pointed out, however, that this theory does not explain properly the quantum yield for nonresonant excitation, which should approach unity for large values of detuning. Insertion of an intermediate state remedies this situation and leaves the theory largely unaffected. The requirement of an intermediate state may explain the rather arbitrary variation of quantum yields among organic molecules and it may also be responsible for the rather too large number of interacting states observed in a high-resolution molecular eigenstate spectrum.

1. INTRODUCTION

One could argue that the subject of radiationless transitions was started with Ishikawa and Noyes[1] or with Robinson,[2] but it would seem that the first quantitative treatment was given by Bixon and Jortner.[3] It seems appropriate, on this occasion, to review their paper and its conclusions after further twenty years of experimental and theoretical efforts. This paper purports to do so for the case of pyrazine, which has probably yielded most to experimental investigation.

2. PYRAZINE

As early as 1974, Tramer and co-workers[4] observed the by now well-known fast and slow components of the fluorescence of pyrazine and published a theory[5] which, although quite similar to Bixon and Jortner's, differed in detail. They basically argued that if the background manifold was not too dense, the coherent superposition of molecular eigenstates (MEs) would — as in Bixon and Jortner's model — indeed lead to interference, but not so extensively as to completely destroy on the average the singlet amplitude present in these states, which was the supposition of Bixon and Jortner. Therefore, after an initial fast decay, which is a signature of the rapid development of the "doorway" state into the background states, a slow component remains, which can be loosely considered to be due to the independently radiating MEs.

Similar observations were made on glyoxal, methylglyoxal, and biacetyl by Van der Werf et al.,[6–8] but the interpretation was given in terms of a kinetic model called "Reversible Intersystem Crossing." Although this model leads to the same conclusions, it was wrong since it did not take into account the phases of the wave function and, therefore, it could not properly describe the interference phenomenon.

Through the development of supersonic nozzles and lasers, it later became possible to resolve the rotational structure of the pyrazine $^1B_{3u}$ spectrum, and a large number of experiments were reported[9–11] on the dependence of the quantum yield and of the ratio of fast to slow components on the overall rotational quantum number, usually called J. All these papers led to the general conclusion that the quantum yield decreased and the ratio of the fast to the slow component increased with J'.

A breakthrough occurred when Van der Meer et al.[12] reported the observation of the ME spectra of pyrazine. The use of an intracavity doubled ring laser and of a doubly skimmed molecular beam permitted the recording of excitation spectra with a resolution of about 10 MHz. This work clearly revealed, at least for the $J' = 0$, $K' = 0$, $v = 0$ $^1B_{3u}$ state, that the number of triplet states coupled to the singlet was limited to about 12. This was

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also in accordance with the earlier observations of quantum beats in the fluorescence from this state.[13,14] A similar conclusion could be drawn for the $J' = 1, K' = 0$ state, and for higher J's ($J' < 4$) it also appeared that about the same number of triplet states are coupled to a J', K' state.

Later work by Van Herpen et al.,[15] who determined the lifetime of 8 of the 12 MEs observed in the P(1) region of the spectrum, permitted reconstruction of the absorption spectrum. They could then dediagonalize this so as to find the diagonal and the off-diagonal matrix elements of the so-called Bixon–Jortner matrix depicting the interaction of a singlet with 12 triplet states. This procedure had previously been carried out erroneously for the excitation spectrum,[16] but the general conclusions remained the same: coupling elements varying between 50 and 500 MHz, apparently randomly distributed. A later analysis by Levine and co-workers[17] showed that this distribution can be viewed as a chaotic one, which is also true for the distribution of the energies of the MEs.

Recently, Siebrand, Meerts and Pratt[18] further analyzed the ME excitation spectra for $J' = 1, 2,$ and 3 and found that essentially the same results are obtained as for $J' = 0$: a limited number of triplet states (about 12) are coupled to a J', K' state.

3. THE QUANTUM YIELD OF PYRAZINE

It would seem that the situation of pyrazine is clear. Nevertheless, a few problems remain. If S_1 were coupled to the {T} manifold only, all effects would be as decribed above, but the quantum yield would be 1! However, as Amirav and Jortner[11] unequivocally showed, the quantum yield is about 0.15! Therefore, De Lange et al.[19] investigated the intensity distribution of the rotational lines and argued that this could be interpreted by a Coriolis coupling of S_1 to {S_0}. Essentially simultaneosuly, Van Herpen et al.[15] concluded from their ME lifetime measurements to finite widths of the zero-order triplet states, ranging from 1 to 5 MHz. Taking it all together,[19] a quantum yield of 0.15 is then indeed obtained from these measurements as well.

Again, the situation seemed satisfactory, but a few worries remained. Amirav[20] measured considerable absorption "between" the rotational lines, and Van Herpen et al.,[15] working towards a higher dynamic range of their experiments, found more and more little peaks in their ME spectrum, the total for P(1) finally reaching 36, instead of the 12 peaks reported earlier.

The "in-between" absorption had been discussed earlier by Drabe et al.[21] and was put down as nonresonant light scattering (NRLS), which could also be responsible for the strong variation of the ratio of the fast to slow component, when this quantity is measured, varying the exciting frequency across the rotational spectrum.[22] The ratio is high between the lines and low on top of them. The high value of this ratio (often called A^+/A^-) between the lines would be due to NRLS, where the emitted light follows the laser, and the very small slow component would be due to remanent absorption in the tails of the rotational transitions.

However, Lorincz et al.[23] and shortly later Knee et al.[24] convincingly showed that using picosecond lasers of less than 100-ps widths in time yielded fast components of about 100 ps, and the fast emission could therefore not be due to NRLS. This led to a paper of De Lange et al.[25] showing that with a picosecond laser one excites a "block" of MEs in ω space, and it is the width of this block that determines the decay rate of the fast component. Thus, the theory was back to Tramer's of 1974,[4] although the condition put forward by him (the Lorentzian distribution of S_1 over the MEs) was not fulfilled. Therefore, the numbers derived from his theory would be in error.

An interesting suggestion was made by Amirav.[20] What if the extra absorption between the rotational lines were due to yet another (dense) manifold, possibly deriving from some other triplet state? The ME spectra might not show such a manifold, since the states would not be resolved even with a 10-MHz resolution. He suggested that, in particular, the $K \neq 0$ states might be coupled to such a dense manifold, the fast component having yet another interpretation: it would be due to the $K \neq 0$ states, the $K = 0$ leading to the slow component. Such a situation seems to be manifest in benzene.[26]

By bolometric detection of the absorption of pyrazine in a beam, Van Herpen et al.[27] could, however, show that such an in-between absorption is absent under their conditions. Also, the finite widths of the $K \neq 0$ lines in the higher J' ME spectra argue strongly against a K-selective mechanism.

Therefore, in the case of pyrazine we are left with a few uncomfortable questions, such as (1) what is the "in-between" absorption which Amirav reports? (2) what are the "extra states" observed by Van Herpen et al.?[15]

4. NONRESONANT EXCITATION AND ITS RELEVANCE FOR PYRAZINE

Most spectra reported of pyrazine in beams are so-called excitation spectra, in which one observes all the light scattered by the molecules as the excitation fre-

quency is changed. As De Lange et al.[28] have pointed out, the process of fluorescence (slow scattering) should not be different, in principle, from the process of fast scattering (Rayleigh, Raman). Therefore, there should be a single mathematical formalism which accounts for both. There can be no discontinuity in the physics when we slowly change the exciting light from resonant to nonresonant excitation. One condition, however, should be fulfilled. The quantum yield on resonance may be considerably lower than unity, but as the light is detuned, it should rise to one (at least, if the quantum yield is defined as $E/\Delta I$, where E is the light scattered (fast or slow) and ΔI is the amount of light removed from the exciting beam by introducing a sample in its path). This, by the way, is the only quantity that can be observed experimentally. Clearly then at sufficient detuning, where there is no or hardly any absorption, whatever is scattered (E) is removed from the beam and $E = \Delta I$.

It appears, as De Lange et al.[28] showed, that the Bixon–Jortner formulation of the theory of radiationless transitions does not show this behavior. The quantum yield, as calculated from their theory, is independent of the frequency of the exciting light. This finds its cause in the frequency independence of their radiationless rate $\Gamma_{nr} = 2\pi < v^2 > \rho$.

One way to remedy the situation is by postulating an "intermediate state". The "doorway" state then first evolves into the intermediate state and then, through its coupling to the background states, into those. One then finds for the radiationless rate:[28]

$$\Gamma_{nr} = \frac{v_{ls}^2 \gamma_{nr}}{(\omega - \omega_s)^2 + \gamma_{nr}^2},$$

where v_{ls} denotes the coupling between the "doorway" and the intermediate state, ω_s is its frequency referred to the "doorway" state, and γ_{nr} is its width due to the coupling to the other background states. Clearly, now Γ_{nr} is frequency-dependent and as the exciting light is detuned, it goes to zero, and therefore the quantum yield goes to unity!

This conclusion has two significances for the results obtained on pyrazine:

1) It could explain the so-called in-between absorption observed by Amirav.[20] The quantum yield of pyrazine at $J' = 0$ is about 15%, and it is lower at higher J'. In-between the rotational lines, the scattering is quite strong, since it is close (on both sides!) to a number of optical transitions. Its "quantum yield" should be close to unity. Therefore, the scattered light at resonance (fluorescence) is reduced by a factor of at least 10 (more at higher J'), while the nonresonant light is enhanced compared to regular experience because of the proxim-

ity of optical transitions. In an excitation spectrum, one does not distinguish instantaneous from slow scattering, and the "in-between absorption" is explained. It would require considerable effort to show quantitatively that it can be as high as reported.

2) The presence of an intermediate state in radiationless transitions may also explain the "extra states" observed by Van Herpen et al.[15] Clearly, if a "doorway" state is coupled to a background via an intermediate state, such could also be the case for the triplet states that are coupled to the "dumping" states. In their paper, Van Herpen et al.[15] report considerable widths for the triplet states, presumably due to their coupling to the $\{S_0\}$ manifold. It is not at all unlikely that this coupling also proceeds via an intermediate state, and if such a coupling is strong enough, such a state deriving from $\{S_0\}$ might show up in the ME spectrum, since it then would get some light-absorbing amplitude from the "doorway" state. In this manner, more and more MEs would show up as the dynamic range of the experiments increases, just as observed in the pyrazine spectra.

5. THE NATURE OF THE INTERMEDIATE STATE

Since the "mediation" of an intermediate state seems to be required for having a low quantum yield at resonance, it is worth speculating on its nature.

We are considering coupling to a dense manifold, usually 2 or 3 eV above its electronic origin. The states there will consist of additions of all vibrational modes of the molecule. The state excited may have a strong coupling with one or several of the vibrational background modes. Since first-order interactions are strongest, it might be the state in which the vibrational quantum number differs by one unit. Many other quanta would have to be present to make up for the energy required. These are expected to be highly mixed, also with the "preferred" mode. Therefore, the preferred state will be strongly coupled to the others.

In this connection, it seems worthwhile to speculate about the tremendous variation in quantum yields observed in organic compounds. We have argued here that to have a really low quantum yield requires an intermediate state close to the "doorway " state and probably with one quantum of a preferred vibrational mode. Such states will occur more or less randomly in singlet or triplet manifolds of organic molecules, and this may well be the reason for the seemingly random occurrence of high and low quantum yields.

6. CONCLUSIONS

We have shown that the postulation of an intermediate state gives a proper behavior of the quantum yield in

the Bixon–Jortner formalism. It has also been argued that this postulate allows an understanding both of the "in-between" absorption as observed by Amirav[20] and of the "extra states" observed by Van Herpen et al.[15] The requirement of the intermediate state for a low quantum yield on resonance may well be an explanation for the apparently random variation of quantum yields in organic compounds.

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