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This Week's Citation Classic

Bixon M & Jortner J. Intramolecular radiationless transitions. *J. Chem. Phys.* **48**:715-26, 1968. [Dept. Chemistry, Tel-Aviv University, Tel-Aviv, Israel]

A theory for intramolecular radiationless transitions in an isolated molecule is presented. Molecular eigenstates are evaluated for a model in which a zero order excited state is coupled to the quasicontinuum of the vibrational states. The optically excited state is described as a superposition of those eigenstates; the resulting wavefunction exhibits an exponential nonradiative decay. [The *SCI*® indicates that this paper has been cited over 345 times since 1968.]

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"After finishing my PhD thesis work in 1966, I joined the faculty of the chemistry department at Tel-Aviv University. As my main field of interest was statistical mechanics, I looked for interesting problems in this field. Jortner suggested the subject of electronic radiationless transitions in polyatomic molecules. At that time it was usually assumed that a coupling between the excited molecule and the surroundings is essential in order for the transition to take place. Therefore this subject could be classified as a problem in statistical mechanics.

"At the same period more and more experimental evidence had been accumulated indicating that there are cases in which radiationless transitions occur in isolated molecules. Perhaps the most influential evidence has been the observation[1] that the fluorescence yield of benzene in the gas phase becomes independent of pressure at low enough pressures. As a result of such evidence we had to change direction and look for an explanation of radiationless transitions as an intramolecular phenomenon.

"The main obstacle in the route towards a reasonable theory was the customary belief that in order for an irreversible transition to occur, one needs a continuous spectrum. In an isolated molecule such spectra exist in cases of dissociation and ionization. On the other hand, no such continuum exist in a bound molecule. As we looked at the problem we soon enough realized that the demand for strict irreversibility is unfounded. The theory has to explain irreversibility only on time scales long compared to the observation time of an isolated molecule. The understanding of this fact was the impetus to our work. The continuous spectrum is not needed anymore; it is sufficient to have a density of states p, big enough (quasicontinuum) so that h/p is longer than any observation time. Such a quasicontinuum is provided, in polyatomic molecules, by the vibrational excited states. All that remained to be done was to construct a convincing model and show that its behavior corresponds to the physical situation.

"From the physical point of view the construction of the model was straightforward. A short optical excitation results in an excited vibronic state, which is not a molecular stationary state because the vibronic interactions couple it to the background vibrational states. The initial state may therefore be described as the proper linear combination of exact eigenstates which is equivalent to the excited vibronic state. The time development of such state is given by the phase development of its components, and the overall development may be described as dephasing. By choosing the simplest mathematical description for such a model it was fairly simple to solve it, especially as it was treated a long time ago in an approximate description of predissociation.[2]

"I believe that the paper has been highly cited for two main reasons: the first one is that it appeared exactly at the proper time, as the first reasonable explanation of intramolecular processes. The second is due to its simplicity; a simple understandable model describes the basic physics of intramolecular radiationless transitions. For a review of recent developments in the field, see W. Rhodes and P. Avouris et al."[34]

1. Kistiakowsky GM and Parmenter CS. Effects of pressure on fluorescence and intersystem crossing in benzene vapor. *J. Chem. Phys.* **42:2942-8, 1965**.
2. **Rice OK. Perturbations in molecules and the theory of predissociation and diffuse spectrum.** . Phys. Rev. 33:748-59, 1929..
3. **Rhodes W. Molecular excited state relaxation processes. J. Chem. Educ. 56:562-7, 1979**
4. **Avouris P. Gelbart WM and El Sayed MA. Nonradiative electronic relaxation under collision** free conditions. Chem. Rev. 77:793-833, 1977.