[7] A. M. Ponte Gonealves and C. A. Hutchison, Jr., J. Chem. Phys. **49**, 4235 (1968).

[8] G. Herzberg, Disc. Faraday Soc. **35**, 7 (1963).

[9] A. D. Walsh, J. Chem. Soc. **1953**, 2306.

[10] E. C. Lim and Y. H. Li, J. Chem. Phys. **52**, 6416 (1970).

[11] F. K. Fong, S. L. Naberhuis, and M. M. Miller, J. Chem. Phys. **56**, 4020 (1972).

[12] F. K. Fong and W. A. Wassam, J. Chem. Phys. (to be published).

[13] In the limit of low temperatures, Eq. (5) reduces to Eq. (29) of Ref. 11.

[14] A. Nitzan and J. Jortner, J. Chem. Phys. **58**, 2669 (1973). following paper.

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Comments on optical selection studies

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Recently, we have extended the multiphonon formalism of intramolecular radiationless relaxation[1,2] to treat nonradiative transitions from a single, optically selected vibronic level.[3,4] The main ingredients of our model[3,4] are: (a) A two electronic level system is considered; (b) the molecular nuclear motion is harmonic; (c) the molecular normal modes are identical in the two electronic states; (d) the molecular vibrational modes are segregated; and (e) the promoting nontotally symmetric modes were assumed to be characterized by zero origin displacements, while their frequencies may vary between the two electronic states. This highly idealized scheme was applied to study the decay of a single vibronic level and of sequence broadened superposition of initial states. These results can be also used to derive the Boltzmann averaged nonradiative decay probability, which is applicable in the case of rapid vibrational relaxation in a dense medium. Assumption (e) was challenged by Fong and Wassam[5] who derived the nonradiative decay probability of a single vibronic level and its Boltzmann average for a harmonic model (characterized by identical frequencies) where the promoting modes are characterized by finite origin displacements.

The results of Fong and Wassam are applicable, in principle, when a large configurational change between the relevant initial and the final (dissipative) electronic states is encountered. We are not aware of any spectroscopic evidence that promoting modes for electronic relaxation between two relevant electronic configurations are characterized by finite origin displacements in an "isolated" large molecule. Utilizing the powerful tool of optical spectroscopy, equilibrium configurational changes in excited states relative to the ground state will result in a normal (0-*n*) progression for a nontotally symmetric mode. This information should be sufficient, provided that the ground state acts as the dominating dissipative channel. On the other hand, electronic relaxation between two electronically excited states requires information concerning the relative origin shifts in these relevant states relative to the ground state. In spite of extensive studies only very few examples for excited state configurational changes were recorded. The lowest triplet states of crystalline *m*-dichloropyrazine[6,7] and dibromobenzene[6,7] exhibit a progression of one nontotally symmetric mode. The most detailed investigations have been performed on the benzene molecule in the solid state where EPR,[8] ENDOR,[9] and optical studies[10] demonstrate the distortion of the $^3B_{1u}$ state, while optical[11] studies indicate that the $^1B_{2u}$ state is not hexagonal. However, all these data pertain to the solid state and there is no way to separate the contributions of intramolecular effects, originating from pseudo-Jahn Teller coupling, and crystal field effects.[6] In fact, the notion of crystal field distortions is well known in ligand field theory,[12] and it is plausible (although not proven) that the sparse cases of molecular configurational distortions studied in dense phases originate predominantly from the effects of crystal forces. We thus conclude that configurational changes in excited states of large isolated molecules were not yet documented. Furthermore, even when a nontotally symmetric mode configuration is distorted, this mode will couple two closely lying states which do not provide a proper pair for electronic relaxation in a large molecule, whereupon configurational distortions provide a necessary but insufficient condition for the validity of the Fong–Wassam picture. We thus conclude that this modified scheme[5] is of limited applicability for molecular relaxation processes and may perhaps be encountered in some large molecules characterized by low symmetry. The situation is different for multiphonon electronic relaxation in impurity states in solids, where the segregation of accepting and promoting modes is inapplicable. This point was recognized a long time ago by Ryckayzen,[13] and obviously only the concept of thermally averaged decay probability applies.

Finally we would like to point out that it would be exceedingly difficult to provide a conclusive evidence for origin shifts in promoting modes. Fong and Wassam[5] have argued that this effect results in a substantial contribution of two quantum changes to the Boltzmann averaged decay probability, while in the limit of zero displacement for the promoting mode only single quantum changes are involved. This conclusion is valid only for the grossly oversimplified model where the frequencies in the relevant electronic states are equal. Frequency changes[2,4] as well as anharmonicity effects[14] in the accepting modes will result in a large contribution of two quantum jumps to the nonradiative decay probability.

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[1] R. Englman and J. Jortner, Mol. Phys. **18,** 145 (1970).

[2] K. F. Freed and J. Jortner, J. Chem. Phys. **52,** 6272 (1970).

[3] A. Nitzan and J. Jortner, J. Chem. Phys. **55,** 1355 (1971).

[4] A. Nitzan and J. Jortner, J. Chem. Phys. **56,** 2079 (1972).

[5] F. K. Fong and W. A. Wassam, J. Chem. Phys. **58,** 2667 (1973), preceding paper.

[6] R. M. Hochstrasser and D. A. Wiersman, Israel J. Chem. **10,** 517 (1972).

[7] R. M. Hochstrasser and C. A. Marzzacco, in *Molecular Luminescence*, edited by E. C. Lim (Benjamin, New York, 1969), p. 631.

[8] M. S. deGroot and J. H. Van der Waals, Mol. Phys. **6,** 545 (1963).

[9] A. M. Ponte Goncalves and C. A. Hutchinson, J. Chem. Phys. Phys. **49,** 4235 (1968).

[10] D. M. Burland, G. Castro and G. W. Robinson, J. Chem. Phys. **52,** 4100 (1970).

[11] V. L. Broude, Opt. Spectroscopy **30,** 46 (1971).

[12] J. S. Griffith, *The Theory of Transition Ions* (Cambridge U. P., Cambridge, England, 1961).

[13] G. Ryckayzen, Proc. Roy. Soc. (London) **A241,** 480 (1957).

[14] D. M. Burland and G. W. Robinson, J. Chem. Phys. **51,** 4548 (1969).

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Comment: "On a modified Rayleigh–Schrödinger perturbation expansion"*

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We wish to comment on the recent discussion by Rubinstejn and Yaris[1] (RY) of the invariance properties of MRS. (We use their notation as much as possible.)

(i) We first summarize the relevant results of RY using, however, a somewhat different line of argument: As RY show, the MRS series is the same as the RS series based on the zero order Hamiltonian

$$H_0' \equiv \sum_n |n\rangle\langle n|H|n\rangle\langle n|. \qquad (1)$$

Since H_0' and V' are uniquely specified by H and the zero order functions $|n\rangle$ it follows that the MRS series is invariant to any transformations which leaves H and the $|n\rangle$ invariant, thus to any of the transformations

$$H_0 \rightarrow AH_0+A', \qquad V \rightarrow V-AH_0+H_0-A'. \qquad (2)$$

In particular through second order the MRS series can be written

$$E^{[2]\prime} = \langle 0|H_0+V|0\rangle - \sum_n \frac{|\langle 0|H_0+V|n\rangle|^2}{\langle n|H_0+V|n\rangle - \langle 0|H_0+V|0\rangle}, \qquad (3)$$

in which form the invariance is manifest since under the transformation (2),

$$H_0+V \rightarrow H_0+V, \quad \text{and} \quad |n\rangle \rightarrow |n\rangle.$$

(ii) Consider the RS series based on the zero order Hamiltonian

$$H_0'' \equiv \sum_n |n\rangle(\langle n|H|n\rangle + \langle n|H^2|n\rangle/\langle n|H|n\rangle)\langle n|. \qquad (4)$$

Since H_0'' (and hence V'') is uniquely specified by H and the zero order functions $|n\rangle$, it follows that the RS series based on H_0'' is invariant to any transformations which leave H and $|n\rangle$ invariant, and thus to any of the transformations (2). Therefore, contrary to statements in RY, MRS is *not* unique in processing this invariance property. In particular through second order