The result $Q_{\mathrm{MM}}{}^*$ obtained by previous investigators is the sum of Q_1 and the first term of Q_2. (Note that $Q_{\mathrm{MM}}=Q_1+Q_2$ reduces to $Q_{\mathrm{MM}}{}^*$ in the classical limit $\hbar\rightarrow 0$.) When μ, C, and/or v are small, the higher-order terms in Eq. (3) become important. For the purpose of illustrating the importance of these terms we consider $s=6$. For this case, $Q_{\mathrm{MM}}=7.596(C/\hbar v)^{2/5}(1+25.480X+2.114X^2+10.031X^3+\cdots)$, where $X=(\hbar^2/\mu C)(C/\hbar v)^{4/5}$ and $7.596(C/\hbar v)^{2/5}=Q_{\mathrm{MM}}{}^*$. The calculated values for ^{6}Li–Xe and ^{7}Li–Kr are plotted in Fig. 1 along with the result of the partial wave analysis, Q_{PW}, of Rothe, Rol, and Bernstein[2] as a function of v. In these two systems $X=1.151\times 10^2/v^{4/5}$ and $1.138\times 10^2/v^{4/5}$, respectively; therefore, the correction terms in Q_{MM} resulting from the inclusion of the terms in $\eta(l, E)$ with $n\geq 2$ play an important role in controlling the over-all value of the cross sections. For example, when $v=10^5$ and 4×10^5 cm/sec, $Q_{\mathrm{MM}}/Q_{\mathrm{MM}}{}^*=1.293$ and 1.096, respectively, in ^{6}Li–Xe and 1.290 and 1.095 in ^{7}Li–Kr. The ratio is insensitively dependent on the nature of the collision partners of the present type. In Fig. 1 it may be interesting to note that in the "intermediate" velocity range Q_{MM} and $Q_{\mathrm{MM}}{}^*$ vary as if they are the upper and lower bounds of the undulatory results of Q_{PW}. The deviation of Q_{PW} from Q_{MM} decreases with increasing v: $Q_{\mathrm{PW}}\simeq Q_{\mathrm{MM}}$ for $v>3\times 10^5$ cm/sec in ^{6}Li–Xe and for $v>2\times 10^5$ cm/sec in ^{7}Li–Kr in the velocity range considered here.

Although it is important to consider the quantum interference[6,7] at low v, the MM method can still give us valuable information about the magnitude of Q and its velocity dependence, if we include the higher-order terms of $\eta(l, E)$. The results obtained in the past[2–4] in terms of $Q_{\mathrm{MM}}{}^*$ must be corrected by the additional important terms shown in Eq. (3).

The Landau–Lifshitz (LL) method[8] also considers the leading term of $\eta(l, E)$ only, i.e., $Q_{\mathrm{LL}}{}^*$. Although Bernstein and Kramer[9] showed that $Q_{\mathrm{LL}}{}^*$ is superior to $Q_{\mathrm{MM}}{}^*$, it is not possible to compare these two methods unless we explicitly include the higher-order terms. While we are able to calculate Q_{MM} including all important higher-order terms, Q_{LL} is very difficult to calculate due to the mathematical complexity involved in the integration of

$$\int_0^\infty l\sin^2\eta(l, E)\,dl,$$

with $\eta(l, E)$ given by Eq. (2). Still another approximate formula is that of Schiff[10] but it becomes identical to Q_{LL} for a spherically symmetric potential, when we introduce the small angle approximation.

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[*] This work was supported by the Petroleum Research Fund of the American Chemical Society.

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Conjecture on Resonant Transfer of Vibrational Energy and Radiationless Transitions in the Solid Phase: The Lifetime of Triplet Anthracene

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(Received 18 November 1965)

The currently accepted description of radiationless processes in the solid state at low temperatures is as follows[1,2]: a molecule in an excited vibronic state loses vibrational energy, thereby dropping to the zeroth vibrational level of the excited electronic state. From this state there is a transition, by tunneling between the potential-energy surfaces of the excited and ground electronic states, to a vibrationally excited state of the ground electronic state. Finally, the excess vibrational energy of the ground electronic state is removed by the surrounding medium. It is usually also assumed that the loss of vibrational energy is very rapid, so that the rate of radiationless transition is determined by the tunneling step which, in turn, is related to the product β_n of the matrix element of the perturbation which mixes the two states, β_{el}, and the Franck–Condon factor $F^{1/2}$. Except under unusual circumstances, involving strong solute–solvent interaction, it is a consequence of this last assumption that the rate of radiationless transition will be independent of the nature of the surrounding (dense) medium.

However, recent studies of laser excitation of crystalline anthracene[3,4] and naphthalene[5] show that the lifetime of the lowest triplet state is much shorter in the crystal than in an EPA glass. (Anthracene $\tau_{\mathrm{xtal}}=0.01$ sec,[3] $\tau_{\mathrm{glass}}=0.1$ sec,[4] naphthalene $\tau_{\mathrm{xtal}}=0.02$ sec,[5] $\tau_{\mathrm{glass}}=2$ sec.) Assuming these data to be correct, it is clear that a pronounced medium effect exists and that the existence of this effect requires re-examination of the accepted theory.

In this note, we conjecture that the origin of the medium effect on the triplet lifetime arises from the difficulty of removing vibrational energy from the "hot" molecule in a glass. That is, we examine the possibility that the rate of transfer of vibrational energy is not rapid relative to the rate of intersystem crossing. It is assumed herein that in the pure crystal intermolecular vibrations are coupled via resonance interactions involving vibrational transition multipole moments. Because the vibrational exciton bandwidth is expected to be of the order of 1 cm^{-1}, an efficient channel for vibrational relaxation in the crystal is available. Anharmonicity effects in large polyatomic aromatic molecules, where many atoms are involved in the normal vibrations, are usually extremely small[6] and will not lead to a mismatch of the energy levels.

Consider the case of crystalline anthracene. Provided that the vibrational exciton bandwidth I is large relative to β_n, the rate of transfer of vibrational energy may be shown to be[2,7] $\mathcal{R}=\beta_{\text{el}}F/\hbar I$. The necessary Franck–Condon factors may be computed after the vibrational overlaps for skeletal stretching, CH stretching, and carbon-atom and CH out-of-plane bending motions are evaluated. Using $\beta_{\text{el}}\approx 0.01\ \text{cm}^{-1}$, and computing $I\approx 0.2\ \text{cm}^{-1}$ for the quadrupole coupled vibrational exciton band, we find[8]

$$\mathcal{R}\approx 10^{2}\ \text{sec}^{-1}$$

which leads to a predicted triplet lifetime of 10 msec, in fortuitous agreement with experiment. The quoted value of $\mathcal{R}$ is uncertain to an order of magnitude (possibly two), but is still reliable enough, in our opinion, to show that the nature of the coupling of the hot molecule to the medium may play an important role in determining the rate of a radiationless transition.[9]

Putting aside quantitative details, what qualitative predictions can be made? First, the coupling of a vibrationally hot molecule to a glassy medium is smaller than the corresponding coupling in the pure crystal because, when the matrix is of different species from the hot molecule, resonant transfer of energy does not occur. Second, it is important that the vibrational energy be removed by free-running excitons because (a) a lattice deformation tends to decrease I greatly, (b) in the new quasistationary state of molecule plus deformed medium, β_{el} may be altered by mixing in of new states, (c) when I is not much greater than β_n, the analysis leading to the rate equation cited is no longer valid with the result that a single vibronic state is not coupled to a band of host vibrational states.

In view of the preceding comments, it would be interesting to know if the lifetime of the triplet of 2,2-paracyclophane differs much between EPA glass and pure crystal. Our analysis leads to the prediction that it should not, since this compound forms an internal triplet excimer[10] and the crystal structure is such that there ought to be a very small vibrational bandwidth. Indeed, we are led to suggest, on the same grounds, that the triplet of crystalline [2,2-] paracyclophane may be long lived relative to the triplet of crystalline benzene.

We conclude that the assumption that I is always sufficiently large that the rate-determining step in a radiationless transition is the tunneling between potential-energy surfaces is not, *a priori*, justified. Indeed, there seem to be cases where the experimental data require a different interpretation.

It is, of course, possible that β_{el} is not independent of the surrounding medium, and that the approximation of writing β_n as a product is not sufficiently accurate because of changes in coupling in the highly excited vibrational states. The magnitudes of these effects remain to be explored.

We wish to thank the Directorate of Chemical Sciences, Air Force Office of Scientific Research, and the U. S. Public Health Service for financial support. We have also benefited from the use of facilities provided by the Advanced Research Projects Agency for materials research at the University of Chicago.

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Cross Section for Atom Exchange with Charge Transfer in a Molecular Collision*

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(Received 17 November 1965)

A MOLECULAR beam has been used to study the exchange reaction

$$N_2+CO\rightarrow NO^{+}+CN^{-}, \qquad (1)$$

from threshold (11.9 eV) to 60 eV. The absolute cross section was determined by total negative-ion collection, and a mass spectrometer was used to monitor the NO^{+} ions.