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P. P. Schmidt [a] [b] [c]

[a] William Ramsay and Ralph Forster Laboratories, University College London, England
[b] Research School of Chemistry, The Australian National University, Canberra, A.C.T., Australia
[c] Department of Chemistry, University of Georgia, Athens, Georgia, U.S.A.

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A Quantum Theory of Energy Dissipation in Molecular Crystals

by P. P. SCHMIDT†

William Ramsay and Ralph Forster Laboratories,
University College London, England
and
Research School of Chemistry,
The Australian National University,
Canberra, A.C.T., Australia‡

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Abstract—The problem of the damping of molecular exciton states in a crystal is considered with respect to the trapping of the exciton at a particular site, and the subsequent radiationless transition within a molecule at the site. Damping considered in this manner has a close connection with the proposals concerning radiationless transitions put forward by Robinson and Frosch. In this paper we make use of the Robinson and Frosch proposals together with the harmonic oscillator representation of the exciton problem to show that damping at a particular site leads to damping of the exciton.

The problem we consider is analogous to the damping of the electromagnetic field in a cavity which has been considered by Senitzky. The success of the analogy in this case suggests its further extention to more complicated damping and rate problems.

Introduction

A recurring problem in the study of the optical properties of molecular crystalline solids is the question of the fate of the excitation energy which is not re-emitted as luminescence. It is generally thought that energy trapped in a molecular crystal is either converted into heat or that it becomes localized on one molecular site, gives some energy to phonon modes, i.e., to the heat bath, and employs the remaining energy in some chemical reaction such as a

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† National Science Foundation Postdoctoral Fellow.

‡ Present address. Address Sept. 1968, Department of Chemistry, University of Georgia, Athens, Georgia, U.S.A.

dimerization.[1] Energy may also become localized by interaction with traps or defects. In these cases the energy may ultimately be emitted from the crystal as light of a different wavelength. This is a common occurrence.[2] Examples are found, for instance, in the fluorescence of anthracene dissolved in naphthalene.

Suppose that there is a quantity of energy contained in a crystal. This energy content can be diminished in any of several ways. We mentioned several radiationless conversions above. However, the energy can also be converted to photon energy. This conversion process determines the radiative lifetime of an excited energy mode of the crystal.[3] The total lifetime of an energy mode is the sum of all the individual radiative and non-radiative lifetimes.

In this paper we shall not consider the radiative lifetime of an exciton mode of the crystal. We are interested, instead, in the lifetime of an exciton mode with respect to the conversion to thermal energy. We are in fact interested in the conversion to thermal energy by any and all interactions including chemical reactions. However, to consider all reasonable radiationless conversions would be an extremely formidable task, and one well outside the scope and intent of this paper. We elect instead to consider the energy conversion in a thermodynamic sense; that is, we shall attempt to assign to the crystal system energies, coupling constants, and arbitrary operators which stipulate the overall energy loss process without revealing individual loss mechanisms.

Damping Model

In recent years attempts have been made to understand the radiationless transition problem, [4, 5] but so far a systematic development of the theory has not been given. Essentially the problem is this: It is known that transitions between states of the same multiplicity (internal conversion) or between different multiplicity (intersystem crossing) can occur without emitting radiation in the free molecule.[2, 5] The effect of the local environment, particularly in the case of a molecular crystal, is merely to act as a perturbation of the individual molecular species.[5] The environment taken as a whole acts as a thermal bath.[5] Some time ago Gouterman proposed that the radiationless transitions could occur only through coupling to an environment,[4] but this has been strongly criticized by Robinson and Frosch,[5] and has not found any general acceptance. Robinson and Frosch[5] contend, on the other hand, that the environment merely acts to broaden the molecular vibrational levels and to provide a vibrational continuum ensuring irreversibility in radiationless transitions. They further assert that the rate-determining step in any radiationless transition process involves some inter- or intramolecular interaction.

The fact that an intramolecular interaction should be rate-determining in a radiationless transition brings up the interesting question of the radiationless transition in a free molecule. Robinson, in a recent publication,[6] has discussed this point in detail. He points out that a crystal system in a very true sense is a giant molecule. The interaction between electronic and vibrational motion in crystals determines, to a large degree, the lifetime of any particular electronic state. To see this fact we need go no further than the case of a metal as an example. Metallic resistivity is certainly a clear example of the pervasive importance of "vibronic" interactions. On a smaller scale it is well known that large organic molecules do not exhibit resonance fluorescence. One presumes a significant vibronic interaction as being responsible for the lack of fluorescence.[6]

On the strength of these arguments and observations one feels confident of the accuracy of the Robinson-Frosch assertion that the environment acts only to broaden the molecular vibrational levels.

An alternate dynamic way of looking at the effect of the environment is to note that the coupling between molecular and lattice vibrations in a molecular crystal is adiabatic, or strong. Consequently, molecular vibrational states relax much more rapidly than molecular electronic states (that is with respect to the conversion of electronic energy to molecular vibrational energy). The rate-determining step for the energy conversion in a crystal, as well as in the free molecule, is the intramolecular vibronic coupling.[5]

However, in a molecular crystal another relaxation possibility exists. It is the possibility of a non-resonant transition between dissimilar molecules.[5] In this case the energy of one molecule may be transferred to an excited vibronic state of a nonidentical neighbor. Vibrational relaxation then leads to an irreversible conversion of the original energy.

The basic observations listed above are sufficient to establish damping of molecular exciton modes. We can show that damping occurs if we can establish an analogy between exciton damping and the damping of the electromagnetic field which has been treated by Senitzky.[7] In order to build the analogy we examine the basic dynamic process in a molecular crystal, i.e., the energy transfer process, propose a simplified model system, which we expect reasonably represents physical reality, and list some definitions of terms which will be useful in this discussion.

The basic dynamic process associated with the exciton is the free propagation, without loss of energy, of a molecular excitation through a crystal lattice. We assume that the energy contained in an exciton mode is unavailable for the activation of any secondary process until that energy becomes localized by a trap or some defect in the crystal. This energy, in line with our previous observations, may be converted to thermal energy, i.e., activate phonon modes in the crystal, or it may initiate a chemical reaction. The most important feature is the nature of the trapping, or localization, and not the subsequent process. These subsequent processes are important, but their nature is such that they are amenable to a thermodynamic-like treatment; for phonon modes, as an example, the energy levels form, or at least nearly form a continuum,[5] and this continuum acts as a heat reservoir in the usual thermodynamic sense. It is thus the trapping rate which determines the damping of a molecular exciton.

Schematic representations of exciton propagation and trapping are shown in Figs. 1 and 2. The trapping in Fig. 1 is due to an intramolecular interaction in one of the substituent host lattice molecules. For this trapping to be a rate-determining mechanism in the damping process, the lifetime of a molecular state with respect to the conversion of electronic energy to vibrational excitation energy (the intramolecular vibronic interaction) must be longer than the resonant transfer time for the excitation; $t_v > t_r$ where t_v is the vibronic lifetime, and t_r is the resonance transfer interaction lifetime. The vibronic lifetime must be greater than the resonant transfer time otherwise resonant transfer is the only effective dynamic process. On the other hand, the vibronic lifetime must not be so great as to be ineffective in comparison to all the other dissipative processes.

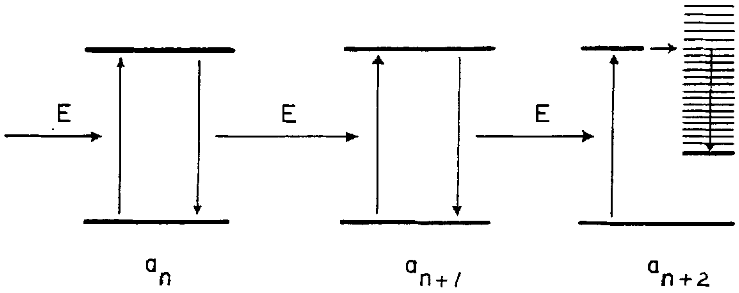

Figure 1. Schematic representation of trapping by internal conversion or intersystem crossing at a particular site.

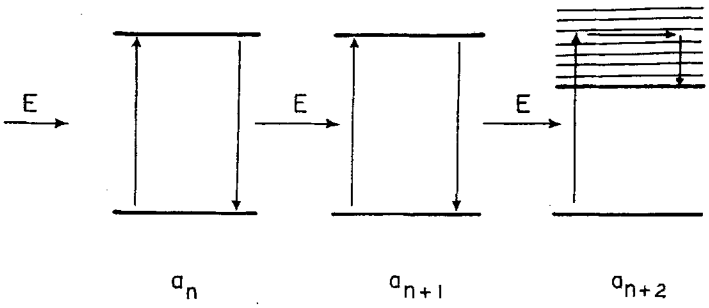

Figure 2. Schematic representation of trapping by a guest molecule in the host lattice.

Figure 2 shows trapping due to the inelastic scattering of an exciton state by an impurity. The trapping site is nonpropagating.

In this case, if we signify the times involved by t'_v and t'_r the condition for effective trapping leading to a dissipation rate is that $t'_v < t'_r$. As a result, the rate-determining interaction for damping is the intermolecular nonresonant electronic energy transfer interaction; i.e., the damping rate is limited by the rate of arrival of the exciton at the impurity site.

The Hamiltonian of a pure crystal containing one molecule per unit cell is made up of the sum of the individual free molecule Hamiltonians together with the interaction potential between molecules. The lowest order effective interaction potential between molecules is the van der Waals interaction; i.e., the dipole–dipole interaction. Thus, one can write[8]

$$H = H_0 + V \tag{1}$$

where

$$H_0 = \sum_i H_i$$

$$V = \sum_{j>i} V_{ij}; \tag{2}$$

H_i is the free molecule Hamiltonian, and V_{ij} is the interaction between molecules i and j.

The ground state wavefunction is a product of ground state free molecule wavefunctions:

$$\Phi = \prod_i \phi_i. \tag{3}$$

However, the excited state crystal wavefunction must be a particular linear combination of wavefunctions of the form

$$\Phi_i^r = \phi_i^r \prod_{i \neq j} \phi_j \tag{4}$$

due to the translational degeneracy of the crystal. The proper excited state wavefunction is a Bloch function given by

$$\Psi^r(\mathbf{k}) = N^{-1/2} \sum_i \exp(i\mathbf{k}.\mathbf{r}_i)\Phi_i^r \tag{5}$$

where **k** is the wave vector.

From eqs. (1), (3), and (5) the energy of the **k**-th level of the exciton band is found to be[8]

$$e^r(\mathbf{k}) = \Delta\,\omega^r + D^r + I^r(\mathbf{k}) \tag{6}$$

where D^r is a correction to the free molecule excitation energy, and $I^r(\mathbf{k})$ is given by

$$I^r(\mathbf{k}) = \sum_{i\neq j} \exp(i\mathbf{k}.\mathbf{r}_i - \mathbf{r}_j)\,\langle j^r i|\,V_{ij}|j i^r\rangle \tag{7}$$

which is an energy exchange term.

We now consider the types of interaction which can lead to trapping of the exciton. If the exciton becomes trapped due to an intramolecular interaction occurring at one lattice site, the trapping rate will be a function of the vibronic coupling matrix elements at that one site.[8]

The individual molecular wavefunctions are assumed to be separable in the Born-Oppenheimer approximation, and, consequently, have the form[8]

$$\phi^r = \phi^r(q, Q)\,\chi^{rn}(Q) \tag{8}$$

where $\phi^r(q, Q)$ is the electronic wavefunction which is a function of the electron coordinates q, and of the molecular vibration normal coordinates Q, and $\chi^{rn}(Q)$ is the vibrational wavefunction which is a function of Q alone. The quantum index r characterizes the electronic state, while n is the vibrational quantum number.

The individual molecular free molecule Hamiltonians depend on dynamical operators for both the electronic and vibrational motion. Thus,

$$H_i = T_e + V(q, Q) + T_v \tag{9}$$

where T_e is the kinetic operator for all the electrons,

$$T_e = -\frac{\hbar^2}{2m}\sum_p \Delta_p$$

$V(q, Q)$ is the potential energy operator including electron–electron, electron–nuclear, and nuclear–nuclear interactions, and T_v is the kinetic energy operator of the nuclear displacements.

In the Born–Oppenheimer separation one assumes the solution to the problem

$$H_e\phi = (T_e + V(q, Q))\phi = w(Q)\phi \tag{10}$$

is known. Wavefunctions, Ψ, which are solutions to the total problem

$$H_i\Psi = E\Psi \tag{11}$$

are linear combinations of (8):

$$\Psi = \sum_{rn} \phi^r \chi^{rn}. \tag{12}$$

The expectation value of a single vibronic state with respect to the manifold of vibronic states is of the form

$$e_i^{rn} + \sum_{sm} V_{rn,\,sm} \tag{13}$$

where

$$\begin{aligned} V_{rn,\,sm} = {} & \langle \phi^r(q, Q)\,\chi^{rn}(Q)|T_v|\phi^s(q, Q)\,\chi^{sm}(Q)\rangle \\ & -\hbar^2/M\langle \phi^r(q, Q)\,\chi^{rn}|\mathrm{grad}_v\phi^s(q, Q)\,\mathrm{grad}_v\,\chi^{sm}\rangle. \end{aligned} \tag{14}$$

We conclude, thus, that the exciton band energies take on the form

$$e^r(\mathbf{k}) = \Delta\omega^r + D^r + I^r(\mathbf{k}) + \sum_{sm} v_{rn,\,sm} \tag{15}$$

where the $V_{rn,\,sm}$ are single site matrix elements.

The operator T_v operating on the electronic wavefunction represents the perturbation which takes the molecule from one vibronic state to another. We assume that a particular vibronic state is propagating. This means that the energy transfer between molecules is resonant for the states Φ_i^{rn} and Φ_j^{rn}. The damping rate, when dependent on an intramolecular interaction of the type outlined above, will be specifically determined by the matrix elements $V_{rn,\,sm}$.

Another form of trapping, which is similar to that just discussed above, has been treated by Philpott.[9] An exciton can be trapped by the interaction of a vibronic and a vibrational exciton. The basis functions are formed from the double excitation functions[9]

$$\Phi^{rnm} = \phi_i^{rn}\phi_j^{m} \prod_{l\neq i\,j,} \phi_l. \tag{16}$$

The energy transfer matrix elements are then modified by the Franck–Condon integrals[9]

$$\langle \chi_{rn} | \chi_{m} \rangle .$$

Trapping in this case is governed by the Franck–Condon modified resonance exchange integrals.

Isotopically substituted guest molecules can trap excitations in a manner similar to that described above for the trapping in the host lattice through an intramolecular interaction.[8] For the isotopic guest trap problem the pure crystal Hamiltonian becomes modified by the one site operator[8]

$$H' = H + v(p) \tag{17}$$

where

$$v(p) = -\tfrac{1}{2}\hbar^2 \left(\frac{1}{m'} - \frac{1}{m}\right) \sum_{x} \partial^2/\partial Q_x^2 . \tag{18}$$

In (17) H is the pure crystal Hamiltonian, and $v(p)$ is the single site operator. In (18) m' is the mass of the isotope and x runs over all the coordinates of the substituted nuclei. Matrix elements of the operator (18) are essential to the consideration of exciton trapping in the shallow trap limit. Details of the use of (18) for the trap problem are given by Craig and Philpott.[8]

An alternate treatment of the same problem[8] makes use of the basis functions

$$\psi'(\mathbf{k}) = N^{-1/2} \sum_{i} \exp(i\mathbf{k}\,.\,\mathbf{r}_i)\, \Phi_i'^{r} \tag{19}$$

in which

$$\Phi_i'^{r} = \phi_i^r \zeta_j^s \prod_{l \neq i,j} \phi_l \tag{20}$$

where ζ_j^s is the wavefunction of the guest molecule occupying the site j. As before, one can further expand the wavefunctions ζ and ϕ in terms of Born–Oppenheimer vibronic wavefunctions, from which one can write[8]

$$\Phi_i'^{r} = \phi_i^r(q_i, Q_i)\, \zeta_j^s(q_j, Q_j)\, \chi_i^{rn}(Q_i)\, \chi_j^{sm}(Q_j) \prod_{l \neq i,j} \phi_l . \tag{21}$$

The matrix elements of the interaction operator V_{ij} between the host molecule at site i and the guest molecule at site j, in the harmonic approximation, are modified by the Franck–Condon vibrational overlap integrals:[8]

$$\langle \chi_i^{rn} | \chi_i^{r'n'} \rangle \langle \chi_j^{sm} | \chi_j^{s'm'} \rangle \langle \phi_i^{r} \, \zeta_j^{s} | V_{ij} | \phi_i^{r'} \, \zeta_j^{s'} \rangle . \tag{22}$$

The first two integrals are the Franck–Condon overlap integrals, and the last integral is the interaction matrix element. The energy conservation condition

$$rn + sm = r'n' + s'm'$$

must hold. This means simply that the vibronic energy of a host site is transferred to a guest site producing a higher excited vibronic state of that guest site. Generally, s and r' are zero signifying the electronic ground state.

We find that this same formalism can be applied to the case of a nonidentical, nonisotopically substituted guest molecule. Unlike the shallow trap problem, in which the trapping rate is primarily a function of the Franck–Condon factors (the electronic matrix elements are assumed the same between a host and an isotopically substituted guest molecule as between two host molecules), the deep trap problem places greater emphasis on the electronic matrix elements. The Franck–Condon integrals are also significant in this case.

We have now mentioned several different means of trapping the exciton in a molecular crystal. As indicated before, the subsequent relaxation of the trapped excitation is assumed much faster than the original trapping process. The system composed of traps, trapping mechanisms (vis. the intramolecular conversion) and any other means of converting energy in a crystal is considered as a system of loss points. That is, the loss point is a defect, an impurity, or a dynamic process which occurs at a particular site at which energy is irreversibly converted to vibrational energy. There is, of course, a different damping rate associated with each possible trapping process. However, as will become clear later in this paper, all these different rates are additive as the argument of an exponential function. It thus suffices merely to indicate a general matrix element associated with any arbitrary energy loss route. Figure 3 gives a block diagrammatic representation of the exciton damping process.

We now consider the formulation of the basic Hamiltonian of the exciton problem from which we can demonstrate a damping. We employ the harmonic oscillator (or second quantization) representation of the exciton problem together with the theory of a damped quantum mechanical oscillator developed by Senitzky[7] to obtain the basic Hamiltonian needed to study the damping.

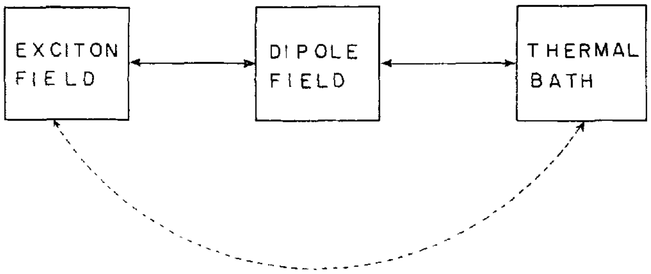

Figure 3. Block diagram of the interacting systems and the effective interaction between the exciton field and the reservoir on elimination of the intermediate system coordinates.

Suppose we have two molecules, one of which is in an excited state. If, for the sake of argument, we do not allow the excited molecule to loose energy to the radiation field, then after a period of time the excitation can be found on the other molecule. Still later, the first molecule is again found in the excited state. If now we add to this system another unexcited molecule, the excited molecule can pass its energy to either of the unexcited ones. The time it takes the excitation energy to return to the original molecule is characteristically longer than the time required in the first system with two molecules. As the number of molecules in the system increases, the time necessary for the excitation energy to again be found on the original molecule becomes greater. For a large system this time becomes so great that the time characteristic of some experimental measuring device falls well within the range of the time it takes an excitation to return to the original molecule. In this case then the conclusion one reaches analysing data from the experiment is that the energy loss from the original molecule is irreversible. This is the general picture of a dissipative system. In order to obtain damping, one must work within a time limit.

As indicated in our introductory remarks, there are a number of sites in a crystal at which an exciton may be trapped. Now, if the coupling between the trapping centers and thermal bath is strong, then the exciton trapped there decays rapidly losing its energy to thermal modes. If, on the other hand, the coupling is weak between the trap center and the bath, significant damping can only occur in the case that there is a large number of trap centers. These two possibilities dictate two ways of treating the damping problem.

First, when the coupling to the thermal bath is strong, the damping rate is determined primarily by the coupling of the exciton to the loss point; i.e., we have a problem of inelastic scattering. If we know the manner in which the loss point decays, we can demonstrate the effect of the decay mechanism on the exciton system by means of a diagonalization of the Hamiltonian which eliminates the coordinates of the loss points.

Second, when the coupling to the thermal bath is weak, damping depends on the presence of a large number of loss points.[7] The reason for this is the following: The initial states of these loss points are determined by the temperature. By using a large number of loss points the damping problem can be treated in the same manner as one would treat the decay of one excited molecule into the aggregate of a large number of unexcited molecules. In this manner the coupling between the loss points and the thermal bath can be ignored. One does not, however, ignore the thermal bath.

In order to have a better idea of how to treat the exciton damping problem the case of the damping of the electromagnetic field is first considered; this is a brief review of Senitzky's problem.[7] If ξ_m is a dipole moment operator for the m-th dipole in a system of dipoles, then the interaction of that dipole with the electromagnetic field is given by

$$\boldsymbol{\xi}_m . \mathbf{E}. \tag{23}$$

The interaction of the electromagnetic field with all the dipoles of the system is given as the sum of (23) over m. With $\mathbf{E}$ given by[10]

$$\mathbf{E} = -4\pi c p(t)\,\mathbf{u}(r), \tag{24}$$

where $p(t)$ is the conjugate momentum of the field, the total energy of interaction of the electromagnetic field with the system of dipoles is given by

$$\sum_m \boldsymbol{\xi}_m . \mathbf{E} = -4\pi c p(t) \sum_m \boldsymbol{\xi}_m . \mathbf{u}(\mathbf{r}). \tag{25}$$

It can be shown that the transformation from the conjugate momentum to the occupation number operators is given by[10]

$$p_{\mathbf{k}} = -i\frac{\omega}{4\pi c^2}(a_{\mathbf{k}}(t) - a_{\mathbf{k}}^+(t)) \tag{26}$$

which when substituted back into the expression for the interaction of the field with the dipole, eq. (26), gives

$$H_{\text{int}} = -i\frac{\omega}{c}\sum_{\mathbf{k}}(a_{\mathbf{k}} - a_{\mathbf{k}}^+)\sum_m \boldsymbol{\xi}_m . \mathbf{u}. \tag{27}$$

In line with our previous discussion we do not include any interaction between the dipoles and the thermal bath—it is unnecessary. We must, however, not neglect the thermal bath; consequently, we include in the total Hamiltonian the particular Hamiltonian of the thermal bath, H_l. Thus, the total Hamiltonian for the damping problem becomes

$$\mathscr{H} = \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} a_{\mathbf{k}}^+ a_{\mathbf{k}} + H_l - i\sum_{\mathbf{k}}\frac{\omega_{\mathbf{k}}}{c}(a_{\mathbf{k}} - a_{\mathbf{k}}^+)\sum_m \boldsymbol{\xi}_m . \mathbf{u}. \tag{28}$$

This Hamiltonian, except for the use of the second quantization representation, is the same Hamiltonian used by Senitzky[7] to study the damping of the electromagnetic field in a cavity.

In order to carry out his analysis of the loss problem Senitzky observed that the loss mechanism must be irreversible, and that the state of the loss mechanism must be determined by its temperature. The irreversible condition is ensured by coupling each mode of the electromagnetic field to a large number of dipoles. The system of dipoles is capable of absorbing energy from the electromagnetic modes over a continuous energy range.

If, instead of the Hamiltonian (28), a more general Hamiltonian is written which makes use of an arbitrary coupling constant and an operator which is specified to be a coordinate of the loss mechanism, then

$$\mathscr{H} = \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} a_{\mathbf{k}}^{+} a_{\mathbf{k}} + H_l - i\alpha \sum_{\mathbf{k}} (a_{\mathbf{k}} - a_{\mathbf{k}}^{+}) \sum_{m} \xi. \tag{29}$$

Here the only assumption essential to the analysis is that of closely spaced frequencies of the loss mechanism.[7] The thermal dependence of the system is found by taking the expectation values of various operators according to the prescription, in the energy representation,[7]

$$\rho_{nm} = \delta_{nm} Z^{-1} \mathrm{e}^{-E_n/kT} \tag{30}$$

with

$$Z = \sum_{i} \mathrm{e}^{-E_i/kT} \tag{31}$$

which gives for the expectation value of an operator O

$$\langle O \rangle = tr\, O\rho = \sum_{n} O_{nn}\, \rho_{nn}. \tag{32}$$

Before applying these ideas to the exciton problem it is necessary to note the importance of fluctuations.[7] An oscillating mode of the electromagnetic field, or for that matter any oscillator, excites the loss mechanism which in turn reacts to the oscillating mode causing dissipation. However, due to its own zero-point fluctuations the loss mechanism can act directly on the oscillator. The coupling between the loss mechanism and oscillator affords a two-way interaction. This in no way contravenes the requirement of irreversibility. In a sense the fluctuations of the loss mechanism lead to an induced and a spontaneous damping. For a more complete analysis the reader is referred to the original work.[7]

Exciton Damping

For the exciton problem the Hamiltonian obtained is similar to, but not always identical to (29). Thus, it is necessary to carry through enough of the analysis of the damping problem for the exciton case to demonstrate that a damping is found in this case which is of the same form as that considered by Senitzky.[7]

The basic Hamiltonian of the exciton problem is characterized by a sum of individual molecular Hamiltonians together with an interaction operator which yields the force law responsible for the binding in a molecular crystal. In the lowest order, and at short distances, that force law is a dipole–dipole force. The operator is characterized by

$$\frac{1}{R^3}\left[\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2 - 3\frac{(\boldsymbol{\mu}_1\cdot\mathbf{R})(\boldsymbol{\mu}_2\cdot\mathbf{R})}{R^2}\right] \tag{33}$$

$$\mathbf{R} = \mathbf{r}_1 - \mathbf{r}_2 \qquad \boldsymbol{\mu} = e\mathbf{q}.$$

A number of authors have considered the second quantization of the exciton Hamiltonian.[11,12] The object is to take the Hamiltonian in the form

$$\mathscr{H} = \sum_n H_n + H_{int} \tag{34}$$

where H_{int} is given by (33) and H_n, the individual molecular site Hamiltonian, is given by

$$H_n = \sum_i \left[\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{r_i - r_j}\right] \tag{35}$$

to a Hamiltonian of the form

$$\sum_{\mathbf{k}} e(\mathbf{k}) a_{\mathbf{k}}^{+} a_{\mathbf{k}} \tag{36}$$

which is the second quantization representation of a collection of uncoupled oscillators. Hopfield[11] has shown that (34) becomes

$$\mathscr{H} = \sum_{\mathbf{k},t} E_t a_{\mathbf{k}t}^{+} a_{\mathbf{k}t} + \frac{4\pi}{3}\frac{Ne^2}{V}\sum_{\mathbf{k},t,t'}\left[3\frac{(\boldsymbol{\mu}_t\cdot\mathbf{k})(\boldsymbol{\mu}_{t'}\cdot\mathbf{k})}{k^2} - \boldsymbol{\mu}_t\cdot\boldsymbol{\mu}_{t'}\right]$$

$$\times\,(a_{\mathbf{k}t}^{+} a_{-\mathbf{k}t'}^{+} + a_{\mathbf{k}t} a_{-\mathbf{k}t'} + a_{\mathbf{k}t} a_{\mathbf{k}t'}^{+} + a_{\mathbf{k}t}^{+} a_{\mathbf{k}t'}) \tag{37}$$

where the operators $a_{\mathbf{k}t}$ and $a^+_{\mathbf{k}t}$ satisfy the commutation relations

$$\begin{aligned}[][a_{\mathbf{k}'t'}, a_{\mathbf{k}t}] &= [a^+_{\mathbf{k}'t'}, a^+_{\mathbf{k}t}] = 0 \\ [a_{\mathbf{k}t}, a^+_{\mathbf{k}'t'}] &= \delta_{\mathbf{k}\mathbf{k}'}\,\delta_{tt'} \end{aligned} \tag{38}$$

and where the index t labels the atomic or molecular state of a particular site which contributes to the exciton band. The Hamiltonian (37) can be diagonalized by a Bogoluibov–Tyablikov transformation[12] yielding a Hamiltonian of the form (36).

The above considerations hold for the pure exciton problem; i.e., they hold for the case in which every molecule is the same. On the other hand, if there are impurity molecules in the lattice, new terms appear in the total Hamiltonian which relate to these impurities. If the transition dipole moment of the impurity is signified by $\boldsymbol{\mu}'$, then an interaction term of the form

$$\begin{aligned} \frac{4\pi}{3}\frac{Ne^2}{V}\left[3\frac{(\boldsymbol{\mu}.\mathbf{k})(\boldsymbol{\mu}'.\mathbf{k})}{k^2} - \boldsymbol{\mu}'.\boldsymbol{\mu}\right] & (a_{\mathbf{k}}e^{i\mathbf{k}.\mathbf{r}} + a^+_{\mathbf{k}}e^{-i\mathbf{k}.\mathbf{r}} \\ & + a_{-\mathbf{k}}e^{-i\mathbf{k}.\mathbf{r}} + a^+_{-\mathbf{k}}e^{i\mathbf{k}.\mathbf{r}})F \end{aligned} \tag{39}$$

can be written where $\mathbf{r}$ is the coordinate of the guest molecule in the lattice, and F is the relevant Franck–Condon factor.

In (39) the product $\boldsymbol{\mu}'.F$ serves to characterize the state of the loss point—the impurity site. Let us write instead $\boldsymbol{\mu}'.\xi$, where ξ is a new operator, the expectation value of which reveals the vibronic state of the loss system. The expression (39) is altered only by the introduction of a new term, ξ. The operator ξ is an unspecified linear combination of creation and destruction operators which specify the vibronic state of the loss point. We assume for simplicity that there are only two electronic levels of the loss point: the ground and excited level. The thermal average does not further affect the pure electronic matrix elements of the dipole–dipole interaction in (39); only the operator ξ yields thermal expectation values. Thus, we can write the interaction between the exciton modes and the thermally coupled dipoles as

$$\sum_{\mathbf{k}} C(a_{\mathbf{k}}\,e^{i\mathbf{k}.\mathbf{r}} + a^+_{\mathbf{k}}\,e^{-i\mathbf{k}.\mathbf{r}})\,\xi \tag{40}$$

where

$$C = \frac{4\pi}{3}\frac{Ne^2}{V}\left[3\frac{(\boldsymbol{\mu}.\mathbf{k})(\boldsymbol{\mu}'.\mathbf{k})}{k^2} - \boldsymbol{\mu}.\boldsymbol{\mu}'\right].$$

We have considered above the form of the interaction operator coupling the exciton modes to the thermal bath for the case in which an intermolecular interaction leads to damping. We have yet to consider the form of the coupling in the case that an intramolecular vibronic coupling operator yields damping of the exciton. We can easily determine that it is of the same form; only the matrix element C differs.

We can use the raising and lowering operators to describe the molecular state at site j:[11]

$$\psi_{jt} = \mathrm{d}_t^+\psi_{jo}$$

and

$$\psi_{jo} = \mathrm{d}_{jt}\psi_{jt}.$$

At a site j an intramolecular interaction leading to a trapping internal conversion or to an intersystem crossing will have matrix elements of the form

$$\langle tn|V|t'n'\rangle \tag{41}$$

where n is the vibrational quantum number associated with the vibronic state t. We cannot ignore the fact that t or tn may be zero—the vibronic ground state—or that tn may be a state which lies lower than $t'n'$. If all these possibilities are added together, and the relations[11]

$$\begin{aligned} a_{\mathbf{k}t}^+ &= N\alpha^{-1/2}\sum_j \exp(i\mathbf{k}.\mathbf{r}_j)\,\mathrm{d}_{jt}^+ \\ a_{\mathbf{k}t} &= N^{-1/2}\sum_j \exp(-i\mathbf{k}.\mathbf{r}_j)\,\mathrm{d}_{jt} \end{aligned} \tag{42}$$

are used, then the interaction operator can be shown to be of the form (40). Now the factors C are the matrix elements of the vibronic interaction operator at the lattice site j.

We can write the basic Hamiltonian of the problem as

$$\mathscr{H} = \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} a_{\mathbf{k}}^+ a_{\mathbf{k}} + \mathrm{H}_l + \sum_{\mathbf{k}} C(a_{\mathbf{k}}\mathrm{e}^{i\mathbf{k}.\mathbf{r}} + a_{\mathbf{k}}^+\mathrm{e}^{-i\mathbf{k}.\mathbf{r}})\,\xi. \tag{43}$$

We wish to show that the interactions described in the previous discussion lead to a damping of the form $\exp(-\beta t)$. To do this we diagonalize the Hamiltonian by means of an examination of the equations of motion of the various canonical operators in (43).

The Heisenberg equation of motion for a general operator O is

$$i\hbar\dot{O} = [O, H]. \tag{44}$$

The equations of motion for the specific operators $a_{\mathbf{k}}$ and $a_{\mathbf{k}}^{+}$ are found to be

$$i\hbar\,\dot{a}_{\mathbf{k}} = \hbar\omega_{\mathbf{k}}\,a_{\mathbf{k}} + C\,\xi\,\mathrm{e}^{-i\mathbf{k}.\mathbf{r}} \tag{45}$$

and

$$i\hbar\,\dot{a}_{\mathbf{k}}^{+} = -\hbar\omega_{\mathbf{k}}\,a_{\mathbf{k}}^{+} - C\,\xi\,\mathrm{e}^{i\mathbf{k}.\mathbf{r}}. \tag{46}$$

These equations are readily converted into first order differential equations, the solutions to which are found to be

$$a_{\mathbf{k}}^{(t)} = a_{\mathbf{k}}(O)\,\mathrm{e}^{-i\omega\,\mathbf{k}t} - i\frac{C}{\hbar}\mathrm{e}^{-i\mathbf{k}.\mathbf{r}}\int_{0}^{t}\mathrm{d}t_1\,\xi(t_1)\,\mathrm{e}^{-i\omega\,\mathbf{k}(t-t_1)} \tag{47}$$

and

$$a_{\mathbf{k}}^{+}(t) = a_{\mathbf{k}}^{+}(O)\,\mathrm{e}^{i\omega\,\mathbf{k}t} + i\frac{C}{\hbar}\mathrm{e}^{i\mathbf{k}.\mathbf{r}}\int_{0}^{t}\mathrm{d}t_1\,\xi(t_1)\,\mathrm{e}^{i\omega\,\mathbf{k}(t-t_1)}. \tag{48}$$

Further evaluation of these two equations rests upon finding an explicit form of the operator $\xi(t)$. From eq. (44)

$$i\hbar\,\dot{\xi}(t) = [\xi(t), H_l] \tag{49}$$

and, further,

$$i\hbar\,\dot{H}_l = -C(a_{\mathbf{k}}\mathrm{e}^{i\mathbf{k}.\mathbf{r}} + a_{\mathbf{k}}^{+}\mathrm{e}^{-i\mathbf{k}.\mathbf{r}})\,[\xi(t), H_l(t)]. \tag{50}$$

Equation (50) is integrated to give

$$\begin{aligned} H_l(t) = {} & H_l(O) + i(C/\hbar)\int_{0}^{t}\mathrm{d}t_l\,(a_{\mathbf{k}}(t_1)\,\mathrm{e}^{i\mathbf{k}.\mathbf{r}} + a_{\mathbf{k}}^{+}(t_1) \\ & \times\mathrm{e}^{-i\mathbf{k}.\mathbf{r}})\,[\xi(t_1), H_l(t_1)]. \end{aligned} \tag{51}$$

When (51) is inserted back into (49) one gets

$$
\begin{aligned}
i\hbar\,\dot{\xi}(t) &= [\xi(t), H_l(O)] + i(C/\hbar)\int_0^t \mathrm{d}t_1 (a_{\mathbf{k}}(t_1)\,\mathrm{e}^{i\mathbf{k}.\mathbf{r}} \\
&\quad + a_{\mathbf{k}}^{+}(t_1)\,\mathrm{e}^{-i\mathbf{k}.\mathbf{r}})\,[\xi(t), [\xi(t_1), H_l(t_1)]]. \qquad (52)
\end{aligned}
$$

This equation has the integral form

$$
\begin{aligned}
\xi(t) &= \xi^{(o)}(t) + (C/\hbar^2)\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2\,\mathrm{e}^{iH_l{}^{(o)}(t-t_1)/\hbar} \\
&\quad \times (a_{\mathbf{k}}(t_2)\,\mathrm{e}^{i\mathbf{k}.\mathbf{r}} + a_{\mathbf{k}}^{+}(t_2)\,\mathrm{e}^{-i\mathbf{k}.\mathbf{r}} \\
&\quad \times [\xi(t_1), [\xi(t_2), H_l\,(t_2)]]\,\mathrm{e}^{-iH_l{}^{(o)}(t-t_1)/\hbar} \qquad (53)
\end{aligned}
$$

and when this is substituted in (47) we find

$$
\begin{aligned}
a_{\mathbf{k}}(t) &= a_{\mathbf{k}}^{(o)}(t) - iC/\hbar\,\mathrm{e}^{-i\mathbf{k}.\mathbf{r}} \int \mathrm{d}t_1\,\xi^{(o)}(t_1)\,\mathrm{e}^{-i\omega_{\mathbf{k}}(t-t_1)} \\
&\quad - iC^2/\hbar^3 \int \mathrm{d}t_1 \int \mathrm{d}t_2 \int \mathrm{d}t_3\,\mathrm{e}^{iH_l{}^{(o)}(t-t_1)/\hbar}\,(a_{\mathbf{k}}(t_3) \\
&\quad + a_{\mathbf{k}}^{+}(t_3)\,\mathrm{e}^{-2i\mathbf{k}.\mathbf{r}})\,[\xi(t_2), [\xi(t_3), H_l(t_3)]] \\
&\quad \times \mathrm{e}^{-iH_l{}^{(o)}(t-t_1)/\hbar}\,\mathrm{e}^{-i\omega_{\mathbf{k}}(t-t_1)}. \qquad (54)
\end{aligned}
$$

The operator $\xi^{(o)}(t)$ is the operator of the uncoupled loss points and it is assumed to have matrix elements of the form[7]

$$
\begin{aligned}
\xi_{ij}^{(o)}(t) &= \xi_{ij}\,\mathrm{e}^{i\omega_{ij}t} \\
\omega_{ij} &= (E_i - E_j)/\hbar. \qquad (55)
\end{aligned}
$$

From this point on it is possible to use the results of Senitzky's calculations which follow after making the substitution of[7]

$$
\langle (a_{\mathbf{k}}(t_3) + a_{\mathbf{k}}^{+}(t_3)\,\mathrm{e}^{-2i\mathbf{k}.\mathbf{r}})\,[\xi^{(o)}(t_2), [\xi^{(o)}(t_3), H_l^{(o)}]]\rangle
$$

for

$$
\begin{aligned}
&\mathrm{e}^{iH_l{}^{(o)}(t-t_1)/\hbar}(a_{\mathbf{k}}(t_3) + a_{\mathbf{k}}^{+}(t_3)\,\mathrm{e}^{-2i\mathbf{k}.\mathbf{r}}) \\
&\quad \times [\xi(t_2), [\xi(t_3), H_l\,(t_3)]]\,\mathrm{e}^{-iH_l{}^{(o)}(t-t_1)/\hbar}.
\end{aligned}
$$

On carrying through Senitzky's[7] treatment for this case, which differs only trivially from his case, one finds for $a_{\mathbf{k}}(t)$ and $a_{\mathbf{k}}^{+}(t)$ the integral equations

$$a_{\mathbf{k}}(t) = a_{\mathbf{k}}^{(o)}(t) - i(C/\hbar)\,\mathrm{e}^{-ik.r}\int_0^t \mathrm{d}t_1\,\xi^{(o)}(t_1)\,\mathrm{e}^{-i\omega_{\mathbf{k}}(t-t_1)}$$

$$-\tfrac{1}{2}\beta\int_0^t \mathrm{d}t_1(a_{\mathbf{k}}(t_1) + a_{\mathbf{k}}^{+}(t_1)\,\mathrm{e}^{2i\mathbf{k}.\mathbf{r}})\,\mathrm{e}^{-i\omega_{\mathbf{k}}(t-t_1)} \tag{56}$$

and

$$a_{\mathbf{k}}^{+}(t) = a_{\mathbf{k}}^{+(o)}(t) + i(C/\hbar)\,\mathrm{e}^{i\mathbf{k}.\mathbf{r}}\int \mathrm{d}t_1\,\xi^{(o)}(t_1)\,\mathrm{e}^{i\omega_{\mathbf{k}}(t-t_1)}$$

$$-\tfrac{1}{2}\beta\int \mathrm{d}t_1(a_{\mathbf{k}}(t_1)\,\mathrm{e}^{2i\mathbf{k}.\mathbf{r}} + a_{\mathbf{k}}^{+}(t_1)\,\mathrm{e}^{i\omega_{\mathbf{k}}(t-t_1)} \tag{57}$$

where the β are the damping coefficients. They are defined by[7]

$$\beta = \frac{2\pi Z^{-1}C^2}{\hbar}\left[1-\mathrm{e}^{-\hbar\omega_{\mathbf{k}}/kT}\right]B(\omega_{\mathbf{k}}) \tag{58}$$

with

$$B(\omega_{\mathbf{k}}) = \int_0^\infty \mathrm{d}E\,(E+\hbar\omega_{\mathbf{k}})\,\rho(E)\,\xi^2(E+\hbar\omega_{\mathbf{k}}, E)\,\mathrm{e}^{-Ek/T}. \tag{59}$$

Equation (58) clearly shows a temperature dependence.

Using the relations

$$\dot{a}_{\mathbf{k}}^{(o)} + i\omega_{\mathbf{k}}a_{\mathbf{k}}^{(o)} = 0 \tag{60}$$

and

$$\dot{a}_{\mathbf{k}}^{+(o)} - i\omega_{\mathbf{k}}a_{\mathbf{k}}^{+(o)} = 0 \tag{61}$$

the integral equations (56) and (57) can be converted into the coupled differential equations

$$\dot{a}_{\mathbf{k}} + (i\omega_{\mathbf{k}} + \tfrac{1}{2}\beta)\,a_{\mathbf{k}} = -\tfrac{1}{2}\beta\,\mathrm{e}^{-2i\mathbf{k}.\mathbf{r}}a_{\mathbf{k}}^{+} - i(C/\hbar)\,\mathrm{e}^{-i\mathbf{k}.\mathbf{r}}\,\xi^{(o)} \tag{62}$$

and

$$\dot{a}_{\mathbf{k}}^{+} - (i\omega_{\mathbf{k}} - \tfrac{1}{2}\beta)\,a_{\mathbf{k}}^{+} = -\tfrac{1}{2}\beta\,\mathrm{e}^{2i\mathbf{k}.\mathbf{r}}a_{\mathbf{k}} + i(C/\hbar)\,\mathrm{e}^{i\mathbf{k}.\mathbf{r}}\,\xi^{(o)}. \tag{63}$$

It is an easy matter to obtain the eigenfrequencies of the coupled equations by setting $a_{\mathbf{k}} = Ae^{\lambda t}$ and $a_{\mathbf{k}}^{+} = Be^{\lambda t}$. If the driving terms in (61) and (62), i.e., the terms dependent on $\xi^{(o)}(t)$, are set equal to zero, one obtains for the frequencies

$$\lambda = \pm i\omega_{\mathbf{k}}(1-(\beta/2\omega_{\mathbf{k}})^2)^{1/2} - \tfrac{1}{2}\beta \tag{64}$$

which is the result expected for the classical damped oscillator. It can be seen from (61) and (62) that the effect of ignoring the small frequency shift due to the damping, as is usually done, in (64) is equivalent to decoupling the differential equations.[13] Setting the term in $a_{\mathbf{k}}^{+}$ equal to zero in (61) and the term in $a_{\mathbf{k}}$ equal to zero in (62) gives on integration

$$a_{\mathbf{k}}(t) = a_{\mathbf{k}}^{(o)}(t)\,\mathrm{e}^{-(\beta/2)t} - i(C/\hbar)\int_0^t \mathrm{d}t_1\,\mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}}\,\xi^{(o)}(t_1) \times \mathrm{e}^{-i\omega_{\mathbf{k}}(t-t_1)}\,\mathrm{e}^{-(\beta/2)(t-t_1)} \tag{65}$$

and

$$a_{\mathbf{k}}^{+}(t) = a_{\mathbf{k}}^{+(o)}(t)\,\mathrm{e}^{-(\beta/2)t} + i(C/\hbar)\int_0^t \mathrm{d}t_1\,\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} \times \xi^{(o)}(t_1)\,\mathrm{e}^{i\omega_{\mathbf{k}}(t-t_1)}\,\mathrm{e}^{-(\beta/2)(t-t_1)}. \tag{66}$$

The Hamiltonian is now diagonalized, and is of the form

$$\sum \hbar\omega_{\mathbf{k}}\,a_{\mathbf{k}}^{+}\,a_{\mathbf{k}}$$

The expectation value of the Hamiltonian for an exciton mode k is given by

$$\langle H_{\mathbf{k}}\rangle = \langle H_{\mathbf{k}}^{(o)}\rangle\,\mathrm{e}^{-\beta t} + \hbar\omega_{\mathbf{k}}\left[\tfrac{1}{2} + \frac{1}{\mathrm{e}^{\hbar\omega_{\mathbf{k}}/kT}-1}\right](1-\mathrm{e}^{-\beta t}). \tag{67}$$

This is, of course, identical to the result obtained by Senitzky.[7] Initially, i.e., for small t, the original exciton mode k is damped exponentially. However, due to the thermal and quantum mechanical fluctuations of the reservoir, after a significant time the first term in (67) becomes negligible with respect to the second. This means simply that the reservoir has taken over and drives the exciton mode through the loss point coupling.

Connection with the Theory of the Electronic Spectra of Mixed Molecular Crystals

Craig and Philpott[8] have shown from entirely different arguments that, "The condition that an energy E must satisfy in order to correspond to a mixed crystal transition energy is..."

$$1-\frac{C}{N}\sum_{\mathbf{k}}(E-e(\mathbf{k}))^{-1} = 0. \tag{68}$$

It is a very simple matter to show that this general trap condition is contained in the expression (64).[14]

Let us write instead of (64)

$$\omega' = \pm\,\omega_{\mathbf{k}}(1-(\beta/2\omega_{\mathbf{k}})^2)^{1/2} \tag{69}$$

where we have used the substitution $e^{i\omega' t}$ instead of $e^{\lambda t}$ in (62) and (63), and we have taken only the real part of the resulting frequency as it contains the frequency shift: $\beta/2\omega_{\mathbf{k}}$. We know that $\beta/2\omega_{\mathbf{k}}$ is small, and consequently we can expand (69) as

$$\omega' \approx \omega_{\mathbf{k}}(1\pm\beta/4\omega_{\mathbf{k}}) = \omega_{\mathbf{k}}\pm\tfrac{1}{4}\beta. \tag{70}$$

This is rearranged to give

$$1 = \pm\tfrac{1}{4}\beta(\omega'-\omega_{\mathbf{k}})^{-1}, \tag{71}$$

and summing over $\mathbf{k}$ yields finally

$$1\pm\frac{C}{N}\sum_{\mathbf{k}}(\omega'-\omega_{\mathbf{k}})^{-1} = 0, C = \tfrac{1}{4}\beta \tag{72}$$

as $\sum_{\mathbf{k}}\mathbf{1} = N$. This is the Craig-Philpott result.[8]

They have also shown that this result can be used to obtain the deep trap limit.[8, 14]

The implication this result has for the previous discussion is interesting. Recall that to obtain an easy solution to the coupled differential equations, (62) and (63), we made the rotating wave approximation which was equivalent to ignoring the effect of the damping (actually the frequency shift) on the eigenfrequencies. Obviously, the tacit implication for an exciton system is that one is dealing with loss points which are in effect shallow traps. For the deep trap limit one is not so free to ignore frequency shift terms.

One can still make the rotating wave approximation, however, as that involves only the dropping of the terms coupling the two differential equations.

If the traps lie at the bottom of the exciton band, then the shallow trap limit can be ignored as it appears sufficient merely to treat the damping of the bottom-most exciton state. If, on the other hand, the loss points form a deep trap system, then the damping that occurs is really the damping of those deep trap states.

The formalism employed in this paper is somewhat too superficial to handle these questions of the relation to deep and shallow traps adequately. A more detailed discussion is the subject of a future paper.

Temperature Dependence of the Damping

The treatment of damping in this paper has been concerned with the cases in which the damping shows little or no temperature dependence. We have been interested in the total degradation of the exciton into heat by any and all means. We wish now to elaborate on this point.

We remarked earlier that eq. (58) for the damping coefficient showed a definite temperature dependence. The dependence is of the form

$$(1-e^{-\hbar\omega_{\mathbf{k}}/kT}). \tag{73}$$

The energy, $\hbar\omega_{\mathbf{k}}$, in (73) is in fact the energy of the exciton mode **k**, and it is given by (6). This energy clearly depends on the individual molecular excitation energies, and, consequently, it is much greater than the phonon energies of the crystal system. Except for very high temperatures, for most cases (73) is essentially unity.

In contrast to the above result, in cases in which light emission is observed following some internal conversion act, there can be a marked temperature dependence. These cases all involve inband dynamic processes for which the absolute energy of the exciton is not relevant. With inband damping the temperature dependence is generally important as the exciton bandwidth is at least of the order of or smaller than kT. In considering total degradation of the exciton energy we are concerned with energies far in excess of kT, and it is for this reason that the temperature dependence is small. It is for this reason also that the absolute energy of the exciton is relevant.

In contrast to our result (i.e., small temperature dependence) Gouterman[4] proposed that the damping was strongly dependent on the coupling of the molecular electronic states to the phonon modes of the environment. Although he found a similar temperature dependence, his energies were phonon energies. As a result one would expect a much more marked temperature effect on the damping. This generally has not been found, and recent publications by Robinson,[6] and by Siebrand[15] confirm this view.

Summary and Conclusion

We began our investigations by examining the connection between the Robinson–Frosch[5] ideas concerning radiationless transitions and the problem of traps in the exciton theory. Using Robinson and Frosch's predominately empirical proposals we were able to set up a model Hamiltonian which was composed of the exciton Hamiltonian, an arbitrary Hamiltonian of the reservoir, and an interaction term. By examining the equations of motion of the various operators we were able to eliminate the reservoir Hamiltonian. It was replaced by terms for the level shift, the damping, and a driving term which is better known as a noise source operator: $\xi^{(o)}(t)$.[16]

In this work we have found that it is possible to relate the damping of an exciton mode to the impurity trap problem or to the internal conversion problem by means of the same formalism used to study the damping of the electromagnetic field in a cavity. With this as a first step we are encouraged to test the applicability of the analogy to field damping and the theory of quantum noise; such tests will be the object of future publications. Lax has shown that "if $\mathbf{a} = a_1, a_2, \ldots$ is some set of system operators, and

$$\mathrm{d}\,\langle a_u\rangle/\mathrm{d}t = \langle A_u(\mathbf{a})\rangle \tag{74}$$

are the correct mean equations of motion including frequency shifts and damping, then

$$\mathrm{d}a_u/\mathrm{d}t = A_u(\mathbf{a})+F_u(\mathbf{a},t) \tag{75}$$

is a valid set of operator equations provided that the operators F_u are endowed with the correct statistical properties."[16] Analysis of these sets of equations for the exciton problem may make it possible to analyse and find the origin of frequency shifts and damping terms from the rate equations.

When studying the properties of exciton systems one is generally interested in those aspects of the problem which fall roughly within the domain of the rigid lattice approximation. To introduce deviations from this approximation in a quantitative sense is generally a formidable task. Consequently, one would wish for some approximate or parametric representation of many higher order dynamic interactions. The use of the equations (74) and (75) which include dissipation effects enables one to investigate transport and other properties in a direct way. The results of such investigations should provide semi-empirical theories which are of greater use to the experimentalist.

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14. This expression is general and holds, as Craig and Philpott have shown,[8] over all trap depths. In the deep trap limit $e(\mathbf{k})/E$ is much smaller than 1 and the denominator within the sum of (68) can be expanded in powers of $e(\mathbf{k})/E$. This leads to the expression for the deep trap limit:

$$E = e^{\tau} + C + \frac{1}{CN}\sum_{k} (I(\mathbf{k}))^2.$$

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