Some Comments on a Formal Theory of Photochemical Dissociation Reactions

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(Received 29 April 1968)

In this paper we present a formal theory of photochemical fragmentation reactions for the case that intramolecular energy transfer is of importance. The zero-order spectrum of the molecule is assumed to consist of a discrete level in resonance with a dense set of levels belonging to another electric manifold, which in turn is in resonance with a translational continuum representing molecular fragmentation. The exact eigenstates of the system are computed formally and shown to be resonant scattering states. Explicit formulas are derived for the probability of the system being in a nonstationary state represented by a wave packet localized in the discrete state, or the dense set of states resonant with the discrete state. In the case that the resonant scattering state may be approximated by a quasistationary bound state, an explicit formula relating the rate of unimolecular photochemical decomposition to the coupling matrix elements and densities of eigenstates of the system is derived. The general relationship between translational motion and internal molecular motion is discussed, as are some aspects of the dissociative decay process, the nature of the excited states, and the possible role of interference phenomena involving coherently excited states.

I. INTRODUCTION

When an isolated molecule absorbs a photon it may:

(a) be excited to a bound upper electronic state with only small change in geometry,

(b) undergo a radical change of geometry to form a new molecule, but without loss of atoms,

(c) ionize,

(d) decompose into two or more molecular fragments,

(e) undergo some combination of processes (a)–(d).

Photochemical processes, which are normally classified under (b) and (d) and their consequents, have been studied for many years.[1] From these studies there has emerged a taxonomy of possible reaction pathways. By this statement we mean that interest in photochemical reactions has been focused primarily on the problems of delineating mechanisms of sequential reactions, of discovering whether or not specific Born–Oppenheimer electronic states are involved in a reaction, and of deducing relationships between stereochemical factors and reaction products. That this taxonomy is successful is testified to by the increasing use of photochemical methods for synthesis of compounds, and by the accuracy with which one may predict the products of a photochemical reaction.[1]

Similarly, an elaborate taxonomy of fragmentation reactions has been built up for the case of electron-impact excitation,[2] as studied by mass spectrometry. This taxonomy is accurately enough known to permit determination of the structures of complex organic molecules.[2]

Fragmentation and rearrangement reactions, whether excitation occurs via absorption of a photon or via electron impact, involve highly excited molecular states which are not adequately described by the set of Born–Oppenheimer states used to describe the ground state and low-lying excited states of a molecule. Thus, despite the successes cited above, we still have little understanding of the fundamental molecular processes underlying photochemical and related reactions. For example, we do not know how the electronic, vibrational, rotational, and translational degrees of freedom of a molecule are coupled so as to favor some specific mode of rearrangement or fragmentation, we do not know the relative importance of the many possible electronic states in influencing reaction pathways, and we do not have a clear and physically incisive picture of the nature of the states of the excited molecule before reaction occurs. It is the purpose of this paper to present a simplified description of the photochemical act. In so far as we are now able to do so, we have designed our analysis to elucidate the nature of the electronic states of the photoexcited molecule and their relationship with the mode of reaction.

An interesting and important qualitative theory of photochemical reactions has been developed by Peters and applied to the analysis of the photolytic decomposition of methane and ethane.[3] The ideas employed by him are the following: it is supposed that the excited state in which the decomposition occurs is formed by populating an excited molecular orbital and that there is just one well-defined molecular state in which the decomposition occurs. It is also supposed that the products of the reaction are formed in their electronic ground states. In essence, this supposition is equivalent to the condition that the electronic energy of the excited molecule is lost in the form of vibrational and

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[1] See, for example, N. Turro, *Molecular Photochemistry* (W. Benjamin and Co., New York, 1965); J. Calvert and J. N. Pitts, *Photochemistry* (John Wiley & Sons, Inc., New York, 1966).

[2] See, for example, K. Biemann, *Mass Spectrometry* (McGraw-Hill Book Co., New York, 1962); *Mass Spectrometry of Organic Ions*, F. W. McLafferty, Ed. (Academic Press Inc., New York, 1963); J. H. Benyon, *Mass Spectrometry* (Elsevier Publ. Co., Amsterdam, 1960).

[3] D. Peters, J. Chem. Phys. **41**, 1046 (1964).

translational energy of the reaction products. An obvious corollary of this condition is that vibrational energy first turns up in the bonds which are formed or seriously modified in the reaction. The vibrational energy may then, later, be redistributed in many different ways.

More recently Mies and Kraus have presented a quantum-mechanical theory of the unimolecular decay of activated molecules.[4] Because of the similarity between this process and autoionization they used the Fano theory of resonant scattering.[5] Their theory provides a detailed description of the relationships between level widths, matrix elements coupling discrete levels to the translational continuum, and the rate of fragmentation of the molecule.

It is our opinion that the contributions of Peters and of Mies and Kraus represent important advances in the development of a theory of photochemical reactions. However, these theories must be extended to include interpretation of the following phenomena:

(i) It is often possible to describe the photoexcitation of a molecule in terms of a localized excitation, e.g., excitation of the C-O group of a ketone. In most photochemical decompositions the bond that breaks and leads to fragmentation is not the same as the site of localized excitation.[1] Therefore, it is necessary to consider the mechanism of intramolecular energy transfer as part of the photochemical reaction.

(ii) As a bond stretches and breaks, there is established a continuous connection between the translational coordinate along which fragment separation occurs and the vibrational motions of the molecule. Since the bond stretching motion is not, in general, a normal mode of vibration, it is necessary to understand how the vibrational modes can be combined to give the decomposition mode.

In the theory of Mies and Kraus, and also in the theory of Peters, a reaction coordinate is identified but its coupling to other modes of motion is not studied. Also, in the theories mentioned it is supposed that the molecule can be prepared in the state that will decompose, thereby avoiding discussion of intramolecular energy transfer. Thus, in the theory of Mies and Kraus, it is supposed that the true molecular state describing the system is a mixed state of prediagonalized blocks of states. One block consists of the excited molecular states, and these states overlap the continuum which describes the resulting dissociated fragments. Using our previously published theory of radiationless processes,[6–8] we take a different point of view. In this paper, we suppose that the mixed state representing an excited molecule has components consisting of the molecular excited state(s), a dense manifold of vibrational states of some other electronic state(s), and the translational continuum of the molecular fragments. The dense manifold of vibrational states acts as an intermediary between the molecular state(s) which can be excited directly and the translational states of the continuum. In particular, we assume that there is no direct coupling between the components of the mixed state representing the discrete molecular states which can be excited directly and the components representing continua. Thus, if a nonstationary wave packet concentrates energy in the components corresponding to discrete molecular states, this energy must "flow through" the vibrational manifold in order to cause molecular fragmentation. In setting up this formal representation we are unavoidably confronted with problems (i) and (ii). We shall show how the breakdown of the Born–Oppenheimer approximation is intimately related to the mechanism of the reaction and how an understanding of the energy-flow pattern leads to at least partial understanding of the phenomena cited under (i) and (ii).

II. GENERAL CONSIDERATIONS

In the upper excited states of a molecule, it is often found that the vibrational levels corresponding to one Born–Oppenheimer manifold overlap the dense set of vibrational levels corresponding to some lower electronic Born–Oppenheimer state. If the energy separation between the overlapping levels is comparable with or less than the off-diagonal matrix elements of the nuclear kinetic-energy operator in the basis of Born–Oppenheimer states, the Born–Oppenheimer representation of the states of the molecule is no longer adequate. In this limiting case the true molecular eigenstate can be thought of as mixtures of Born–Oppenheimer states.

In what follows we shall, as in our previous studies of the theory of radiationless processes,[6–8] assume that the set of molecular Born–Oppenheimer states is complete. It is then possible to represent any eigenstate of the molecule as a linear superposition of Born–Oppenheimer states, with coefficients determined by the overlaps of each of the Born–Oppenheimer states and the true eigenstate. Of course, in the absence of knowledge of the true eigenstate this expansion cannot be used. However, there are situations when this exact representation is useful. Consider, for example, the case that the ground state is adequately represented as a Born–Oppenheimer state, and that a dipole transition from the ground state is allowed to only one of the set of B–O states. Then, by absorption of a photon, the molecule can be prepared in a nonstationary state which is a time-dependent superposition of exact

[4] F. H. Mies and M. Kraus, J. Chem. Phys. **45**, 4455 (1966).
[5] U. Fano, Phys. Rev. **124**, 1866 (1966).
[6] M. Bixon and J. Jortner, J. Chem. Phys. **48**, 715 (1968).
[7] J. Jortner and R. S. Berry, J. Chem. Phys. **48**, 2757 (1968).
[8] D. P. Chock, J. Jortner, and S. A. Rice, J. Chem. Phys. **49**, 610 (1968).

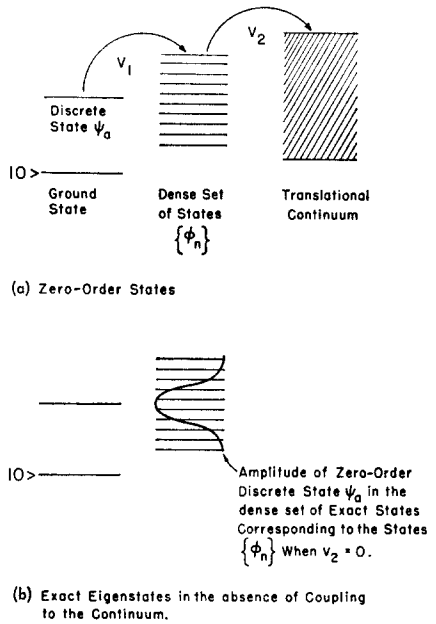

FIG. 1. Schematic energy-level diagram of (a) the zero-order states and (b) the exact eigenstates in the absence of coupling to the continuum.

eigenstates, each of which is itself a time-independent superposition of B–O states. By following the evolution in time of a system prepared in this way we can learn much about energy redistribution in the molecule, radiative and radiationless decay processes, etc. Of course, assuming that both the B–O states and the exact states form complete sets, a B–O state may be represented in terms of a superposition of exact states. Then, the procedure described is equivalent to preparing the system in a B–O state, but that state is not to be thought of as stationary.

We now apply the same expansion technique to the description of photochemical decomposition. Suppose that the set of molecular states has the following characteristics:

(i) In the zeroth approximation, in the energy region of interest, the spectrum of states consists of one discrete state overlapping a dense but discrete set of vibrational levels belonging to a different electronic state, the dense set of vibrational states in turn overlapping the translational continua corresponding to molecular fragmentation. The zero-order states need not be B–O states, although it will sometimes be convenient to assume that they are. What is important is that the existence of a zero-order localized excitation implies the existence of a zero-order separable Hamiltonian. Our zero-order states are the eigenstates of that separable Hamiltonian.

(ii) The discrete level is coupled to the dense set of vibrational levels, and the vibrational levels are coupled to the continuum, but the discrete level is not directly coupled to the translational continua (see Fig. 1).

The energy-level scheme hypothesized can be thought of as corresponding to the existence of a localized electronic excitation coupled to electronic ground-state vibrations which in turn are coupled to a fragmentation continuum. Examples of this behavior are found in many carbonyl compounds and in methyl-substituted benzenes.[1,9] In both classes of compounds, localized excitation of a chromophore may lead to fragmentation (often H-atom dissociation) at a distant bond.

Consider the excitation of a molecule with the energy-level scheme described. Let Ψ_E be an eigenfunction of the complete Hamiltonian, $\mathcal{H}$, and ψ_a, $\{\phi_n\}$, ξ_E be the eigenfunctions of the zeroth-order Hamiltonian, $\mathcal{H}_0$, corresponding to the single discrete state, the set of vibronic states of another electronic state, and the fragmentation continuum, respectively. We write

$$\begin{aligned}\mathcal{H}&=\mathcal{H}_0+(\mathcal{H}-\mathcal{H}_0)\\&=\mathcal{H}_0+\mathrm{V}\end{aligned}\tag{1}$$

and

$$\Psi_E=a(E)\psi_a+\sum_n b_n(E)\phi_n+\int dE' c_{E'}(E)\xi_{E'}.\tag{2}$$

We shall later assume, in Sec. III, that the zero-order states are B–O states, that the ground state is adequately represented as a B–O state, and that the ground state is connected, via dipole transition matrix element, only to the state ψ_a and *not* to the states $\{\phi_n\}$ or ξ_E. Absorption of a photon by a molecule will then lead to the creation of the nonstationary state ψ_a (see Fig. 2).

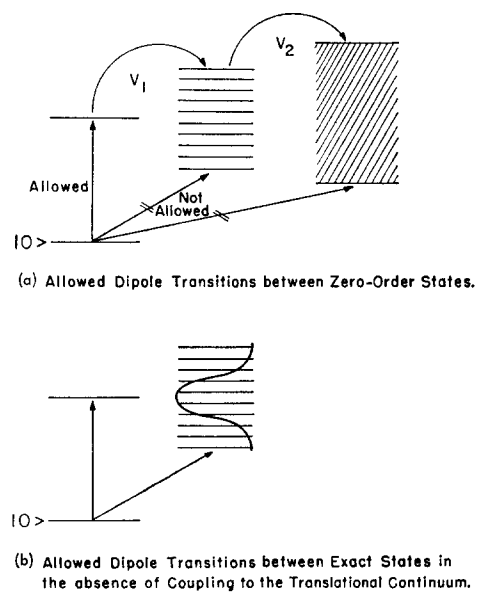

FIG. 2. Schematic diagram showing transitions between the sets of levels of the hypothetical spectrum. (a) Allowed dipole transitions between zero-order states. (b) Allowed dipole transitions between exact states in the absence of coupling to the translational continuum.

[9] P. Johnson and S. A. Rice, Chem. Phys. Letters **1**, 709 (1968).

Before Eq. (2) can be used, the expansion coefficients $a(E)$, $b_n(E)$, and $c_{E'}(E)$ must be evaluated. For simplicity of analysis we shall adopt the following approximations: First, it will be assumed that the states $\{\phi_n\}$ are uniformly spaced with energy separation ϵ between consecutive states. It is then convenient to use an energy scale defining the energies of the states $\{\phi_n\}$ relative to that of the state ψ_a. Let the value $n=0$ be assigned to the nearest state of the set $\{\phi_n\}$ below ψ_a. Set $n<0$ for states lower than ψ_a and $n>0$ for states higher than ψ_a. Then the energy of a state ϕ_n in the set $\{\phi_m\}$ is

$$E_n=E_a-\alpha+n\epsilon,$$

$$\alpha=E_a-E_0. \tag{3}$$

As the second approximation, we assume that the matrix elements coupling ψ_a and all the $\{\phi_n\}$ are equal and independent of the energy. In symbols,

$$\langle\psi_a\,|\,\mathcal{H}\,|\,\phi_n\rangle=v_1=\text{const},\quad \text{all } n, \tag{4}$$

and

$$\langle\phi_n\,|\,\mathcal{H}\,|\,\xi\rangle=v_2=\text{const},\quad \text{all } n. \tag{5}$$

We have already stated, in constructing the model molecular-energy spectrum, that there is no direct coupling between the state ψ_a and the fragmentation continuum. This condition may be represented by the relation

$$\langle\psi_a\,|\,\mathcal{H}\,|\,\xi\rangle=0. \tag{6}$$

By standard procedures, using the matrix elements defined by Eqs. (4)–(6), the following set of equations is obtained for the coefficients in the representation of Ψ_E in terms of zero-order functions [Eq. (2)]:

$$(E_a-E)a+v_1\sum_n b_n=0, \tag{7}$$

$$(E_n-E)b_n+v_1a+v_2\int dE'c_{E'}=0, \tag{8}$$

$$(E'-E)c_{E'}+v_2\sum_n b_n=0,\qquad n=0,\pm1,\pm2,\cdots. \tag{9}$$

By combination of (7) and (9) we find

$$c_{E'}=(v_2/v_1)\mathcal{P}[(E-E_a)/(E-E')]a+Y(E)\delta(E'-E), \tag{10}$$

where the operator $\mathcal{P}$ indicates that the principle value of the quantity in brackets should be taken. The function $Y(E)$, which is determined by the boundary conditions on the wavefunction, will be specified below.

Having found $c_{E'}$, it is possible to evaluate b_n from Eq. (8). By substitution of (10) in (8) we find

$$b_n=(E-E_n)^{-1}\{[v_1+i\pi(v_2^2/v_1)(E_a-E)]a+v_2Y(E)\}, \tag{11}$$

and also

$$a=-\frac{(\pi/\epsilon)\cot(\pi\gamma)v_1v_2Y(E)}{\{(E_a-E)[1+i(\pi^2/\epsilon)v_2^2\cot(\pi\gamma)]+(\pi/\epsilon)v_1^2\cot(\pi\gamma)\}}, \tag{12}$$

where we have used

$$\sum_n[1/(E-E_n)]=(\pi/\epsilon)\cot(\pi\gamma), \tag{13}$$

with

$$\gamma(E)=(E-E_a+\alpha)/\epsilon. \tag{14}$$

To evaluate $Y(E)$ we proceed, as did Mies and Kraus,[4] to examine the asymptotic form of the continuum wavefunction. In terms of the fragment separation coordinate, X, this is

$$\xi_{E'}\sim c_{K'}\chi\sin(K'X+\eta), \tag{15}$$

where χ is the wavefunction of the major fragment, the minor fragment is regarded as a point mass, and X measures the separation of the centers of mass of the two fragments. The asymptotic form (15) is accurate enough for our purposes. Note, however, that although residual excitation of the major fragment is described, the minor fragment is not allowed any internal degrees of freedom. Presumably, a photochemical dissociation producing radical and a ground-electronic-state H atom, which is a common reaction, is described by (15). If the products are more complex, (15) must be modified in an obvious way. The asymptotic form of Ψ_E is now obtained by substitution of (10) in (2) followed by examination of the limit as $X\to\infty$. The result is

$$\lim_{X\to\infty}\Psi_E\sim c_K\chi[-\pi(E-E_a)a(v_2/v_1)\cos(KX+\eta)+Y\sin(KX+\eta)]$$
$$\sim(c_K\chi/2i)\{[Y-i\pi(E-E_a)a(v_2/v_1)]\exp(iKX+i\eta)-[Y+i\pi(E-E_a)a(v_2/v_1)]\exp(-iKX-i\eta)\}. \tag{16}$$

The function Y is now determined by requiring that there be unit incoming flux in the incident channel and only outgoing waves in the inelastic (fragmentation) channel. In formal terms, this condition requires that

$$Y(E)+i\pi(E-E_a)a(v_2/v_1)=1, \tag{17}$$

and by writing [see Eq. (12)]

$$a=-A(E)\,Y(E) \tag{18}$$

it follows that

$$Y(E)=[1+i\pi(E_a-E)(v_2/v_1)A(E)]^{-1}. \tag{19}$$

A combination of (19) with (11) and (12) leads to expressions for $a(E)$ and $b_n(E)$, namely

$$a(E)=-\frac{(\pi/\epsilon)\cot(\pi\gamma)v_1v_2}{\{(E_a-E)[1+(2\pi^2iv_2^2/\epsilon)\cot(\pi\gamma)]+(\pi v_1^2/\epsilon)\cot(\pi\gamma)\}}, \tag{20}$$

and

$$b_n(E)=\frac{v_2(E_a-E)}{((E-E_n)\{(E_a-E)[1+(2\pi^2iv_2^2/\epsilon)\cot(\pi\gamma)]+(\pi v_1^2/\epsilon)\cot(\pi\gamma)\})}. \tag{21}$$

A similar expression for $c_{E'}(E)$ may be obtained but will not be displayed here.

To obtain the probability of finding the molecule in the nonstationary state corresponding to one of the zero-order components, we need merely determine the squares of the absolute magnitudes of the corresponding expansion coefficients, e.g.,

$$a^*(E)a(E)=\frac{(\pi^2/\epsilon^2)v_1^2v_2^2\cot^2(\pi\gamma)}{[(E_a-E)^2Z_1^2+2(E_a-E)Z_2+Z_2^2]}, \tag{22}$$

$$b_n^*(E)b_n(E)=\frac{v_2^2(E_a-E)^2}{(E-E_n)^2[(E_a-E)^2Z_1^2+2(E_a-E)Z_2+Z_2^2]}, \tag{23}$$

$$Z_1^2=1+(4\pi^4/\epsilon^2)v_2^4\cot^2(\pi\gamma);\qquad Z_2=(v_1^2\pi/\epsilon)\cot(\pi\gamma).$$

III. THE INTERACTION BETWEEN AN ISOLATED MOLECULE AND THE RADIATION FIELD

In the preceding section we described the mixture of zero-order states that can be thought of as the generalized Fourier representation of a true eigenstate of a molecule in which a discrete zero-order state is coupled to a dense set of zero-order vibrational states belonging to a different electronic state, and in turn the vibrational states are coupled to a zero-order translational continuum. We did not, however, examine the effects of coupling the molecule to a radiation field. Since the photochemical process is initiated by photon absorption, and since the nature of the excitation is determined by the molecule-field interaction, a study of the time evolution of the excited molecule must include in the description the coupling between the molecule and the radiation field.

We consider, now, the time development of a molecule, with spectrum defined in Sec. II, under the influence of an electromagnetic field. In what follows we shall use the method of analysis employed by Bixon and Jortner[6] in the theory of radiationless processes, rather than more elaborate methods of Chock, Jortner, and Rice.[8]

Suppose the molecule is in the ground state at time $t=0$, at which time it is illuminated by a pulse of radiation for a time interval t_1, described by

$$\mathcal{H}_R(t)=\hat{e}\cdot\boldsymbol{\mu}\mathcal{E}(t),\qquad 0\leq t\leq t_1,$$
$$\mathcal{H}_R(t)=0,\qquad t<0,\ t>t_1, \tag{24}$$

where $\mathcal{E}(t)$ is the electric-field intensity at the molecule at time t, $\boldsymbol{\mu}$ is the transition dipole moment operator of the molecule corresponding to the frequency of the applied field, and $\hat{e}$ is the field polarization vector. Of course, because the pulse of radiation is of finite length, the field cannot be monochromatic. We shall later account for the polychromaticity of the field. Using first-order perturbation theory, the state vector at time t, $|\Psi(t)\rangle$, may be expressed in terms of the ground-state vector at time $t=0$, $|\Psi_0(0)\rangle$, as follows:

$$|\Psi(t)\rangle=-\frac{i}{\hbar}\int_0^\infty dE'\,|\Psi_{E'}\rangle\exp\left(-\frac{i}{\hbar}E't\right)$$
$$\times\int_0^{t_1}\exp\left(\frac{i}{\hbar}E't'\right)\mathcal{E}(t')\langle\Psi_{E'}|\hat{e}\cdot\boldsymbol{\mu}|\Psi_0(0)\rangle dt'. \tag{25}$$

As already mentioned in Sec. II, we now suppose that the molecular ground state is accurately described as a B–O state, and that the ground state and the B–O state ψ_a are connected by a dipole transition matrix element, but that dipole transitions between the ground state and the B–O states $\{\phi_n\}$ or ξ are forbidden (see Fig. 2). Thus the dipole matrix element $\langle\Psi_{E'}|\hat{e}\cdot\boldsymbol{\mu}|\Psi_0(0)\rangle$ is proportional to the coefficient, $a^*(E)$, of the B–O state in the state $|\Psi_{E'}\rangle$:

$$\langle\Psi_{E'}|\hat{e}\cdot\boldsymbol{\mu}|\Psi_0(0)\rangle=a^*(E')\langle\psi_a|\hat{e}\cdot\boldsymbol{\mu}|\Psi_0(0)\rangle$$
$$\equiv a^*(E')P_{a0}. \tag{26}$$

We now examine the amplitudes of the states $|\psi_a\rangle$

and $\{|\phi_n\rangle\}$ in the excited state of the system. From (25),

$$\langle\psi_a|\Psi(t)\rangle=-\frac{i}{\hbar}P_{a0}\int_0^{t_1}S(t,t')\mathcal{E}(t')dt', \quad (27)$$

where

$$S(t,t')=\int_0^\infty dE'\,|a|^2\exp\left(-\frac{i}{\hbar}E'(t-t')\right), \quad (28)$$

whilst

$$\langle\phi_n|\Psi(t)\rangle=-\frac{i}{\hbar}P_{a0}\int_0^{t_1}T_n(t,t')\mathcal{E}(t')dt', \quad (29)$$

where

$$T_n(t,t')=\int_0^\infty dE'a^*b_n\exp\left(-\frac{i}{\hbar}E'(t-t')\right). \quad (30)$$

Clearly, the probability of finding a molecule in the nonstationary state $|\psi_a\rangle$ at time t is determined by the square of the projection of $|\psi_a\rangle$ onto the exact eigenstate vector $|\Psi(t)\rangle$:

$$w_a(t,E)=|\langle\psi_a|\Psi(t)\rangle|^2$$
$$=\frac{P_{a0}^2}{\hbar}\int_0^{t_1}\int_0^{t_1}S(t,t')S(t,t'')\mathcal{E}(t')\times\mathcal{E}(t'')dt'dt''. \quad (31)$$

Similarly, the probability of finding the molecule in the nonstationary state ϕ_n at time t is

$$w_n(t,E)=|\langle\phi_n|\Psi(t)\rangle|^2$$
$$=\frac{P_{a0}^2}{\hbar^2}\int_0^{t_1}\int_0^{t_1}T_n(t,t')T_n(t,t'')\mathcal{E}(t')\times\mathcal{E}(t'')dt'dt''. \quad (32)$$

One of the interesting consequences of Eqs. (31) and (32) is the dependence of the probability of the molecule being in a given nonstationary state on the time correlations in the coupled radiation field. In most experimental studies the radiation field employed consists of a superposition of many frequencies with random phases. It is convenient to represent that form of field in terms of the correlation function

$$\Phi(t,t'')=\langle\langle\mathcal{E}(t')\mathcal{E}(t'')\rangle\rangle, \quad (33)$$

where the double brackets $\langle\langle\cdots\rangle\rangle$ indicate an average over the distribution of frequencies in the field. If the field has many harmonic components (as it must if the pulse is of finite length), then in place of (31) and (32) we introduce the average probabilities

$$\langle\langle w_a\rangle\rangle=\frac{P_{a0}^2}{\hbar^2}\int_0^{t_1}\int_0^{t_1}S(t,t')S(t,t'')\Phi(t',t'')dt'dt'' \quad (34)$$

and

$$\langle\langle w_n\rangle\rangle=\frac{P_{a0}^2}{\hbar^2}\int_0^{t_1}\int_0^{t_1}T_n(t,t')T_n(t,t'')\Phi(t',t'')dt'dt''. \quad (35)$$

Because of the necessary polychromaticity of the field, it is (34) and (35) that are related to observable quantities.

Suppose that the field correlation function has the form

$$\Phi(t',t'')=(8\pi I_0/c)\delta(t'-t'') \quad (36)$$

with c the velocity of light and I_0 defined by the spectral density

$$I(\nu)=I_0\exp\{-[(\nu-\nu_a)/\Delta\nu]^2\}, \quad (37)$$

which, for simplicity, is taken to be Gaussian about the frequency ν_a. Using (36) in (34) and (35) we find

$$\langle\langle w_a\rangle\rangle=\frac{8\pi I_0}{c}\frac{P_{a0}^2}{\hbar^2}\int_0^{t_1}[S(t,t')]^2dt', \quad (38)$$

$$\langle\langle w_n\rangle\rangle=\frac{8\pi I_0}{c}\frac{P_{a0}^2}{\hbar^2}\int_0^{t_1}[T_n(t,t')]^2dt'. \quad (39)$$

Finally, from (38) and (39) and the conservation of probability, we find for the probability of dissociation of the molecule the relation

$$P_{\text{diss}}(t)=1-\frac{8\pi I_0}{c}\frac{P_{a0}^2}{\hbar^2}\left(\int_0^{t_1}[S(t,t')]^2dt'+\sum_n\int_0^{t_1}[T_n(t,t')]^2dt'\right), \quad (40)$$

where, using Eqs. (11), (12), and (22),

$$S(t,t')=v_1^2v_2^2\int_0^\infty dE\frac{\exp[-iE(t-t')/\hbar]}{[(E_a-E)^2Z_1^2+2(E_a-E)Z_2+Z_2^2]}, \quad (41)$$

and

$$T_n(t,t')=-v_1^2v_2^2\int_0^\infty dE\frac{(E_a-E)(\pi/\epsilon)\cot(\pi\gamma)\exp[-iE(t-t')/\hbar]}{(E-E_n)[(E_a-E)^2Z_1^2+2(E_a-E)Z_2+Z_2^2]}. \quad (42)$$

In a number of cases the molecule under consideration has zero-order degenerate localized states, e.g., two carbonyl groups in a diketone. Interactions between the two chromophores will, in general, lift the zero-order degeneracy. In such a molecule there are, say, two discrete levels coupled to a dense set of vibrational

states belonging to another electronic state, the dense set of vibrational states being, in turn, coupled to the fragmentation continuum. An analysis of the probability of dissociation of a molecule with a spectrum of the type just described will be found in the Appendix.

IV. VIBRATION–TRANSLATIONAL MOTION COUPLING

It is now necessary to consider how the relative translational motion of two receding molecular fragments is related to the internal motions of the parent molecule. For, the translational motion corresponding to fragment separation is not usually along a normal coordinate of the parent molecule. In the classical mechanical theory of thermally induced unimolecular reactions, due to Slater,[10] the motion in a selected direction is represented as a superposition of projections on that direction of normal-mode motions. The molecule fragments when the amplitude of motion along the given direction exceeds a critical relative displacement. This formulation differs somewhat from the theory of Rice, Ramsperger, and Kassel,[11] in which anharmonic coupling between normal modes leads to internal energy transfer until a sufficient amount of energy is collected in one particular oscillator, whereupon the molecule dissociates. At the risk of pedanticism we wish to point out that both of the descriptions of unimolecular reactions cited suffer from the same deficiency as does the perturbation-theory B–O state description of radiationless processes.[12] That is, an excited molecule about to dissociate is really in a resonant scattering state, and not a bound state, so that a description of the molecule in terms of transitions between well-defined essentially uncoupled states (one of which is bound) cannot be completely satisfactory. Our analysis explicitly contains the coupling between the dense set of zero-order molecular vibrational states and the continuum, and the presence of a zero-order continuum component in the final wavefunction shows that the final state is indeed a resonant scattering state. Our problem is, then, to unravel from the formalism a physical picture descriptive of the state in terms of molecular motions, etc.

Perhaps the most pertinent observation to make at this point is that the process by which the molecule with energy spectrum hypothesized decays is simply a form of predissociation. There is one difference between the process we consider and the usual case of predissociation from a single zero-order molecular energy level. Because the exact resonant level is represented as a linear combination of the zero-order localized level, the dense set of vibrational levels, and the continuum, and because the zero-order B–O state which can be excited is spread over many exact resonant scattering states, absorption of a photon by the molecule leads to the population of resonant scattering states spread over a range of energy. Thus we deal with predissociation from a band of states, and not from a single state. Bearing this in mind, and recalling how the Franck–Condon factors and interaction matrix elements enter the description of radiationless processes,[6,12] we see that the selection rules applicable to predissociation reactions may also be used to describe the process considered in this paper.[13] (Note, however, that the usual discussions use perturbation theory and do not employ the concept of resonant state.[13,14] As shown by recent work on the theory of radiationless processes, the selection rules which emerge from the correct treatment are the same as those derived earlier.[6,7,8])

A complete description of the translational-motion–internal-motion coupling and its effects is, in principle, contained in Eqs. (40)–(42). Unfortunately, even for the simplified form of hypothetical molecular spectrum studied in this paper, we have been unable to perform the indicated quadratures. Even without actual calculation, our previous studies of the theory of radiationless processes suffice to define the following general properties of the photodissociative act:

(a) Because the zero-order B–O state which can be excited is spread over many of the exact scattering states, the usual light sources will coherently excite a set of scattering states. We anticipate, then, that there will be interference effects arising from the coherent excitation of a set of states.[6,7,8]

(b) The lifetime against decay into fragments will appear naturally (not as an added assumption) as a consequence of the mixing of continuum into the exact eigenstates and because of interference between coherently excited states. Judging from the results of the theory of radiationless processes, two lifetimes will appear, proportional to v_1^2 and v_2^2, and of a form similar to that derivable from Fermi's Golden Rule.

(c) Provided that $\rho_1 v_1^2$ and $\rho_2 v_2^2$ are of comparable magnitude, where $\rho_1 \equiv \rho_{\text{vib}}$ is the density of levels in the dense vibrational set and $\rho_2 \equiv \rho_{\text{cont}}$ is the density of states in the translational continuum, the rate of decay of the molecule will depend on both v_1 and v_2. A consequence of $\rho_1 v_1^2$ and $\rho_2 v_2^2$ being comparable in magnitude is that a nonstationary wave packet localized in the discrete state ψ_a will disperse into the nonstationary states $\{\phi_n\}$ about as rapidly as will a nonstationary

[10] See, for example, N. B. Slater, *Theory of Unimolecular Reactions* (Cornell University Press, Ithaca, N.Y., 1959).

[11] For a convenient review of the RRKM theory, see O. K. Rice, in *Energy Transfer in Gases, Proceedings of the XII Solvay Congress on Chemistry* (Interscience Publishers, Inc., New York, 1962), p. 17.

[12] G. W. Robinson and R. P. Frosch, J. Chem. Phys. **37**, 1962 (1962); **38**, 1187 (1963); S. H. Lin, *ibid.* **44**, 3759 (1966); W. Siebrand, *ibid.* **46**, 440 (1967).

[13] G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N.J., 1966).

[14] A very important and elegant treatment of predissociation using the concept of resonant state is found in R. A. Harris, J. Chem. Phys. **39**, 978 (1963).

wave packet localized in the states $\{\phi_n\}$ disperse into the translational continuum and ψ_a. Thus, in this case, in the language of kinetics, neither of the two intermanifold coupling steps can be thought of as rate limiting.

(d) If $\rho_1 v_1^2 \gg \rho_2 v_2^2$ the scattering state is very much like a state of a long-lived vibrationally hot molecule.

(e) If $\rho_1 v_1^2 \ll \rho_2 v_2^2$ the scattering state is very much like an excited molecular state which decomposes directly to fragments.

The remark made previously about the applicability of the selection rules for predissociation reactions now becomes clearer, since these selection rules merely describe properties of the matrix element v_2. That is, although no assumption about the decay process has been directly introduced, the lifetime against decay will take a form similar to that obtained from first-order time-dependent perturbation theory, and therefore be proportional to $\rho_2 v_2^2$.

Because we have not been able to evaluate (40) analytically (numerical evaluation is possible but less instructive), it is useful to consider some limiting approximations. First, suppose that $\rho_1 v_1^2 \gg \rho_2 v_2^2$, as in (d) above. Further, suppose that the lifetime of a nonstationary wave packet localized in the dense set of vibrational states is long enough that we may think of the state as quasistationary. Then, decomposition of the molecule may be represented approximately by use of the Rice–Rampsberger–Kassel–Marcus theory of unimolecular reactions.[11] We choose this form, rather than the Slater form, because of the importance of energy interchange between modes in our case. There is one important difference between the usual RRKM theory and the form which we need. In the usual unimolecular reaction collisional excitation is taken to result in a Boltzmann distribution of excited molecules. In our photochemical decomposition the distribution of molecules over the dense set of vibrational levels in the initial wave packet is determined by the quantity $\rho_1 v_1$. If there were no coupling to the translational continuum, and v_1 were independent of energy, photoexcitation of the molecule would lead to a Lorentzian distribution of amplitude of B–O state ψ_a in the dense set of exact vibrational states.[6,8] In our case, thermal excitation is not involved, hence no average over a Boltzmann distribution is taken, and therefore the molecular partition function, etc., should not appear in the expression for the rate constant.

Following the usual analysis[11] we write

$$k_1 = \int_{E_m}^{\infty} k_E W(E)\, dE, \tag{43}$$

where E_m is the minimum energy required for fragmentation along the reaction coordinate, $W(E)dE$ is the number of states excited in the energy range dE about E, and k_E is the specific rate of dissociation when the energy is E. For $W(E)$ we take

$$W(E) = \frac{\rho_1}{(\pi v_1 \rho_1)^2 + [n^2/(\rho_1 v_1)^2]}, \tag{44}$$

where n is defined by $E_n = E_a + n\epsilon$, $n = 0, \pm 1, \pm 2, \cdots$. Note that $\rho_1 \equiv 1/\epsilon$. The simplest representation of k_E in our approximate treatment is

$$k_E = (2\pi/\hbar)\rho_2 v_2^2, \tag{45}$$

so that (using $dE = \epsilon dn$),

$$k_1 = \int_{E_m}^{\infty} \frac{2\pi}{\hbar} \frac{\rho_2 v_2^2}{\rho_1} \frac{\rho_1 dn}{(\pi v_1 \rho_1)^2 + [n^2/(\rho_1 v_1)^2]}. \tag{46}$$

Suppose that v_1, v_2, ρ_1, and ρ_2 are independent of energy in the range of interest. Then

$$k_1 = (2\rho_2 v_2^2/\hbar)\{\tfrac{1}{2}\pi - \tan^{-1}[E_m/\pi(\rho_1 v_1)^2]\}. \tag{47}$$

Note that k_1 reproduces the intuitively desirable limiting results:

$$\lim_{E_m \to 0} k_1 = (\pi/\hbar)\rho_2 v_2^2, \tag{48a}$$

$$\lim_{\rho_1 v_1 \to 0} k_1 = 0. \tag{48b}$$

In particular, relation (48b) shows how stifling the coupling between ψ_a and the set of states $\{\phi_n\}$, thereby preventing indirect coupling of ψ_a with the translational continuum, prohibits molecular fragmentation. Thus, despite the fact that our quasistationary-state treatment implies that $\rho_1 v_1^2 \gg \rho_2 v_2^2$, the correct limit is found as $\rho_1 v_1^2 \to 0$. The limit (48b), in fact, displays an essential feature of the "flow of energy" characteristic of the energy spectrum and dissociation process considered in this paper, and also forcefully illustrates the general deductions (c), (d), and (e) listed above.

A different limiting case, in which the detailed structure of the quasibound-state nuclear motion and its coupling to the translational motion is less important, occurs when $\rho_1 v_1^2 \ll \rho_2 v_2^2$. A simple kinetic argument suggests that in this limit the molecule dissociates as rapidly as the nonstationary wave packet localized in ψ_a can disperse into the nonstationary states $\{\phi_n\}$. Thus, this case is analogous to, but not identical with, that considered by Peters[3]—direct excitation to a nonbonding state without intermediate intramolecular energy transfer.

It is important to remind the reader that (47) results from a serious approximation in which it is supposed that the wave packet representing the scattering state localized in the dense manifold is sufficiently long lived that it may be considered quasistationary [this assumption appears in the use of (45) and also (44)]. We emphasize that an exact representation is contained within Eq. (40), but further work will be necessary to reduce (40) to tractable form. Despite the use of the approximations leading to (47), previous experience with the theory of radiationless processes suggests that an exact evaluation of (40) will reproduce the principle features of (47).

V. CONCLUDING REMARKS

In this paper we have presented a first formal analysis of the primary act of molecular photodissociation for a well-defined molecular-energy spectrum. It has been shown how the absorption of a photon leads to the formation of a resonant scattering state. Explicit formulas, involving quadrature over the system energy spectrum, have been presented but not evaluated. When the resonant scattering state may be approximated in terms of a set of quasistationary bound states, an explicit relationship is obtained for the rate of dissociation in terms of the matrix elements coupling zero-order states and the corresponding densities of states. In principle this permits the use of experimental rate data to evaluate the matrix elements v_1 and v_2, if ρ_1 and ρ_2 can be estimated.

It is clear that the analysis we have presented is only the first step in developing a satisfactory theory of photochemical reactions. For example, the energy spectrum studied is not typical of all photodecomposable molecules, it is possible that direct photoexcitation of the bond that breaks is most important in some reactions, and that intramolecular energy transfer is important in others, etc. We hope our work will stimulate others to provide new data and to invent new concepts relevant to the theory of photochemical reactions.

ACKNOWLEDGMENTS

This research was supported by the Directorate of Chemical Sciences, AFOSR. We have also benefited from the use of facilities provided by ARPA for materials research at The University of Chicago.

APPENDIX

In this appendix we consider the photodissociation of a molecule which, in zero order, has a set of two degenerate discrete states. Interaction then removes the degeneracy of these two states, leading to a molecular spectrum consisting of two molecular states coupled to a dense set of vibrational states belonging to another electronic state, with the dense set of vibrational states coupled to the fragmentation continuum. We shall assume that the energy matrix has been partially prediagonalized so that the two nondegenerate states arising from the two zero-order degenerate states are uncoupled, i.e.,

$$\langle \psi_a \mid \mathcal{H} \mid \psi_d \rangle = 0. \tag{A1}$$

In place of Eq. (2), the exact eigenfunction corresponding to energy E is

$$\Psi_E = a(E)\psi_a + d(E)\psi_d + \sum_n b_n(E)\phi_n + \int dE' c_{E'}(E)\xi_{E'}, \tag{A2}$$

with ϕ_n and $\xi_{E'}$ defined as in Sec. II. Clearly, the coefficients in (A2) will differ from those derived earlier because of the extra state, ψ_d, in the spectrum of states.

As in the main text, we assume the $\{\phi_n\}$ are equally spaced and that

$$\begin{aligned} \langle \psi_a \mid \mathcal{H} \mid \phi_n \rangle &= v_a = \text{const}, \\ \langle \psi_d \mid \mathcal{H} \mid \phi_n \rangle &= v_d = \text{const}, \\ \langle \phi_n \mid \mathcal{H} \mid \xi \rangle &= v_2 = \text{const}, \\ \langle \psi_a \mid \mathcal{H} \mid \xi \rangle &= 0, \\ \langle \psi_d \mid \mathcal{H} \mid \xi \rangle &= 0. \end{aligned} \tag{A3}$$

The set of equations (7), (8), and (9) are now replaced by

$$\begin{aligned} (E_a - E)a + v_a \sum_n b_n &= 0, \\ (E_d - E)d + v_d \sum_n b_n &= 0, \\ (E_n - E)b_n + v_a a + v_d d + v_2 \int_0^\infty dE' c_{E'} &= 0, \\ (E' - E)c_{E'} + v_2 \sum_n b_n &= 0, \qquad n = 0, \pm 1, \pm 2, \cdots. \end{aligned} \tag{A4}$$

Following the procedure outlined in Sec. II, the expansion coefficients in Eq. (A2) are found to be

$$a = \frac{-v_a v_2 \mu}{(E_a - E)(1 + 2\pi i v_2^2 \mu) + v_a^2 \mu + v_d^2 [(E_a - E)/(E_d - E)]\mu}, \tag{A5}$$

$$d = -\frac{v_d v_2 \mu}{(E_d - E)(1 + 2\pi i v_2^2 \mu) + v_d^2 \mu + v_a^2 [(E_d - E)/(E_a - E)]\mu}, \tag{A6}$$

$$b_n = \frac{v_2 (E_a - E)}{(E - E_n)[(E_a - E)(1 + 2\pi i v_2^2 \mu) + v_a^2 \mu + v_d^2 [(E_a - E)/(E_d - E)]\mu]}, \tag{A7}$$

and

$$c_{E'} = \left[\frac{v_2^2 \mu}{(1 + \pi i v_2^2 \mu) + [v_a^2 \mu/(E_a - E)] + [v_d^2 \mu/(E_d - E)]} \mathcal{P}(E - E')^{-1} + \delta(E - E') \right] \times \left(\frac{1 + [v_a^2 \mu/(E_a - E)] + [v_d^2 \mu/(E_d - E)] + i\pi v_2^2 \mu}{1 + [v_a^2 \mu/(E_a - E)] + [v_d^2 \mu/(E_d - E)] + 2\pi i v_2^2 \mu} \right), \tag{A8}$$

where

$$\mu(E)=(\pi/\epsilon)\cot[\pi\gamma(E)],$$

$$\gamma(E)=(1/\epsilon)(E-E_a+\alpha). \tag{A9}$$

With the use of (A5)–(A8) it is possible to evaluate the probability of finding the molecule in one of the nonstationary states ψ_a, ψ_d, or $\{\phi_n\}$. The results are

$$|a|^2=\frac{\mu^2 v_a^2 v_2^2}{(E_a-E)(1+4\pi^2 v_2^4\mu^2)+v_a^4\mu^2+v_d^4\mu^2[(E_a-E)/(E_d-E)]^2+2v_a^2\mu(E_a-E)+2v_d^2\mu[(E_a-E)^2/(E_d-E)]} \tag{A10}$$

and a similar expression for $|d|^2$, while

$$|b_n|^2=v_2^2\Big/\left[(E-E_n)^2\left((1+4\pi^2 v_2^4\mu^2)+\frac{v_a^4\mu^2}{(E_a-E)^2}+\frac{v_d^4\mu^2}{(E_d-E)^2}+\frac{2v_a^2\mu}{(E_a-E)}+\frac{2v_d^2\mu}{(E_d-E)}\right)\right]. \tag{A11}$$

Again, as in Sec. III, we use time-dependent perturbation theory to study the time evolution of nonstationary states. Suppose that the ground state (assumed to be adequately represented as a B–O state) is connected via dipole transition matrix elements only to ψ_a and ψ_d, and not to the $\{\phi_n\}$ or ξ. In some cases transitions only to one of ψ_a or ψ_d will be dipole allowed. A simple modification of our formulas is then necessary. When both ψ_a and ψ_d may be reached via dipole transitions,

$$\langle\Psi_E|\hat{e}\cdot\boldsymbol{\mu}|\Psi_0\rangle=a^*(E)P_{a0}+d^*(E)P_{d0}. \tag{A12}$$

Thus, the analogue of (27) becomes

$$\langle\psi_a|\Psi(t)\rangle=-\frac{i}{\hbar}P_{a0}\int_0^{t_1}S_a(t,t')\mathcal{E}(t')dt'-\frac{i}{\hbar}P_{d0}\int_0^{t_1}R_a(t,t')\mathcal{E}(t')dt', \tag{A13}$$

where

$$S_a(t,t')=\int_0^\infty dE'\,|a|^2\exp\left(-\frac{i}{\hbar}E'(t-t')\right), \tag{A14}$$

$$R_a(t,t')=\int_0^\infty dE'd^*a\exp\left(-\frac{i}{\hbar}E'(t-t')\right). \tag{A15}$$

Similarly,

$$\langle\psi_d|\Psi(t)\rangle=-\frac{i}{\hbar}P_{a0}\int_0^{t_1}R_d(t,t')\mathcal{E}(t')dt'-\frac{i}{\hbar}P_{d0}\int_0^{t_1}S_d(t,t')\mathcal{E}(t')dt', \tag{A16}$$

where

$$S_d(t,t')=\int_0^\infty dE'\,|d|^2\exp\left(-\frac{i}{\hbar}E'(t-t')\right), \tag{A17}$$

$$R_d(t,t')=\int_0^\infty dE'da^*\exp\left(-\frac{i}{\hbar}E'(t-t')\right). \tag{A18}$$

Finally, the analogue of (29) is

$$\langle\phi_n|\Psi(t)\rangle=-\frac{i}{\hbar}P_{a0}\int_0^{t_1}T_{an}(t,t')dt'-\frac{i}{\hbar}P_{d0}\int_0^{t_1}T_{dn}(t,t')dt', \tag{A19}$$

where

$$T_{an}=\int_0^\infty dE'a^*b_n\exp\left(-\frac{i}{\hbar}E'(t-t')\right), \tag{A20}$$

$$T_{dn}=\int_0^\infty dE'd^*b_n\exp\left(-\frac{i}{\hbar}E'(t-t')\right). \tag{A21}$$

Use of the correlation function of the radiation field, Eq. (33) and (36), now gives the following formulas for the

average probability of finding the molecule in the nonstationary states ψ_a, ψ_d, or ϕ_n:

$$\langle\langle w_a\rangle\rangle=\frac{8\pi I_0}{c\hbar^2}\left\{P_{a0}^2\int_0^{t_1}[S_a(t,t')]^2dt'+P_{d0}^2\int_0^{t_1}[R_a(t,t')]^2dt'+2P_{a0}P_{d0}\int_0^{t_1}R_a(t,t')\,S_a(t,t')\,dt'\right\},\quad\text{(A22)}$$

$$\langle\langle w_d\rangle\rangle=\frac{8\pi I_0}{c\hbar^2}\left\{P_{a0}^2\int_0^{t_1}[R_d(t,t')]^2dt'+P_{d0}^2\int_0^{t_1}[S_d(t,t')]^2dt'+2P_{a0}P_{d0}\int_0^{t_1}R_d(t,t')\,S_d(t,t')\,dt'\right\},\quad\text{(A23)}$$

$$\langle\langle w_n\rangle\rangle=\frac{8\pi I_0}{c\hbar^2}\left\{P_{a0}^2\int_0^{t_1}[T_{an}(t,t')]^2dt'+P_{d0}^2\int_0^{t_1}[T_{dn}(t,t')]^2dt'+2P_{a0}P_{d0}\int_0^{t_1}T_{an}(t,t')\,T_{dn}(t,t')\,dt'\right\},\quad\text{(A24)}$$

Finally, the total probability of finding the molecule dissociated at time t is

$$P_{\text{diss}}(t)=1-\langle\langle w_a\rangle\rangle-\langle\langle w_d\rangle\rangle-\sum_n\langle\langle w_n\rangle\rangle.\quad\text{(A25)}$$

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 49, NUMBER 6 15 SEPTEMBER 1968

Raman Spectra of BaClF, BaBrF, and SrClF

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(Received 20 May 1968)

The frequencies and symmetries of the even-parity lattice vibrations of BaClF, BaBrF, and SrClF are determined by means of polarized Raman scattering from oriented single crystals. The polarizations and frequencies of the vibrations are interpreted in terms of symmetry coordinates.

INTRODUCTION

Single crystals of barium chlorofluoride, strontium chlorofluoride, and barium bromofluoride have been prepared recently, and these materials are under investigation as host lattices for rare-earth ions.[1,2] The study of the phonon spectra of these crystals has been undertaken both because it is of interest *per se* and because it may aid the understanding of ion behavior in such hosts. It has been shown recently[3,4] that spin–optical–phonon relaxation mechanisms can dominate conventional Orbach processes at moderate temperatures. Relaxation involving optical phonons requires gerade-symmetry optical modes at low frequencies.[3] As is discussed further in the present paper, the Raman-active phonon frequencies in BaClF, BaBrF, and SrClF are very low, all less than 300 cm^{-1}. Hence it appears that information from Raman spectra may be useful for investigations[5,6] of rare-earth-ion-relaxation mechanisms in these hosts. Such information should also facilitate analysis of the complex vibronic spectra of systems such as BaClF:Sm^{++} under study currently.[7]

The frequencies and symmetries of the even-parity phonon modes of BaClF, BaBrF, and SrClF have been determined in the present work by means of polarized Raman scattering from oriented single crystals. Normal-mode analysis is discussed qualitatively in terms of symmetry coordinates.

THEORY

On the basis of powder-diffraction data, BaClF and BaBrF are known to have tetragonal D_{4h}^7 symmetry, or $P4/nmm$, with two formula groups per primitive cell.[8] Accurate lattice parameters have been obtained[9] by x-ray diffraction experiments on single crystals. Ionic positions are shown in Fig. 1; note that Ba–Cl distances are much smaller than Ba–F distances. The barium (or strontium) and chlorine (or bromine) ion positions have C_{4v} (or 4 mm) symmetry, while that of the fluorine ions is D_{2d} (or $\bar{4}2$ m), resulting in a division of the $3N=18$ degrees of freedom into modes

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