Vibronic dephasing of anharmonic molecules. I. Theory and its application to the separability of intra- and intermolecular processes

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A quantum-mechanical theory of vibronic dephasing of impurity molecules in condensed media is presented. An expression for the dephasing time is derived that exhibits explicit dependences upon microscopic properties of both impurity and medium. The expression, which contains the temperature dependence *and* the cross section for dephasing, is used to predict qualitatively and semiquantitatively some features of vibronic spectral lines in solids. Of particular interest are systems in which the influence of intramolecular properties (of the impurity) upon dephasing is separable from that of intermolecular properties (of the medium). The distinction between vibrational and purely electronic effects on vibronic dephasing is also emphasized.

I. INTRODUCTION

In recent years, the phenomenon of molecular dephasing has come under intensive study. A general definition of the term "molecular dephasing" is the following: the process by which phase coherence of microscopic (i. e., molecular) states among the molecules of a system is lost. Hence, there are various types of dephasing (e. g., vibrational and electronic) corresponding to the different types of molecular motions. Some questions pertinent to dephasing are (1) What are the interrelationships among these different types of dephasing? (2) What are the experimental means of probing dephasing? (3) What is the relationship between characteristic (experimental) times, e. g., the dephasing time, and molecular processes? (4) What is the dependence of these characteristic times upon microscopic properties of the system, as determined by the potential-energy surface?

In this paper, we shall present a quantum-mechanical theory of vibronic (i. e., vibrational–electronic) dephasing of "optically active" impurity molecules dissolved in an inactive, condensed medium. The theory provides an expression for the (pure) dephasing time in terms of molecular properties of both the impurity and the medium, e. g., the equilibrium structure of the medium, the impurity–medium coupling strength, and the degree of anharmonicity of the intramolecular potential surface of the impurity.

The term "dephasing" is inherently vague and often appears to be used differently by different authors discussing the same experiments. Consequently, in Sec. II, we shall provide the explicit connections between optical absorption (or emission) and the dephasing time. We shall also delineate the physical processes which contribute to dephasing. In Sec. III, we shall develop the theory. The predictions will then be dis-

cussed qualitatively and semiquantitatively in Sec. IV. (In the following paper II, we shall apply the theory to the special case of anharmonic homonuclear diatomic impurities in low-temperature rare-gas matrices. We shall also compare our quantum results for the system Cl_2/Ar with the stochastic-classical-trajectory results obtained by Shugard *et al.*[1]) Finally, in Sec. V, we close with a summary and discussion of our principal conclusions.

II. DEPHASING OF IMPURITIES IN CONDENSED MEDIA

A. Physical system and basic assumptions

Let us consider a solution of "optically active" impurity (solute) molecules, i. e., molecules exhibiting electronic or infrared absorption (or emission) spectra, in an optically inactive medium (solvent). For simplicity, let the following conditions prevail:

(i) the solution is sufficiently dilute that interactions among impurity molecules are negligible;

(ii) the active mode of the impurity has only two energy levels, or equivalently, the relevant optical transition is well isolated from all others;

(iii) the modes of the medium are independent of the energy level of the active solute mode[2];

(iv) the coupling of the active impurity mode to other degrees of freedom of the system is *weak*.

Condition (iv) implies that the relevant optical transition is homogeneously broadened.[3]

B. Absorption line shape and correlation functions

The absorption line shape function may be expressed as[3]

$$I_a(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt \exp(-i\omega t) I_a(t) , \qquad \text{(II. 1)}$$

where

$$I_a(t) \equiv \langle \mu(0) \cdot \mu(t) \rangle_{eq} = \text{Tr}[\rho_{eq} \mu(0) \cdot \mu(t)] \qquad \text{(II. 2)}$$

and μ is the electric dipole-moment operator associated with the entire system. Then, under conditions (i)–(iv),

$$I_a(\omega) = \pi^{-1} |\mu_{if}|^2 \mathrm{Re}\left[\int_0^\infty dt \exp(-i\omega t) G_a(t) \right] , \qquad \text{(II. 3)}$$

where

$$G_a(t) \equiv \langle b(0)b^\dagger(t) \rangle_{eq} , \qquad \text{(II. 4)}$$

$$b \equiv |i\rangle\langle f| , \qquad \text{(II. 5)}$$

and i and f are the initial and final energy levels of the isolated impurity, respectively. The correlation function decays exponentially as

$$G_a(t) = G_a(0)\exp[i(\omega_{if} + \Delta\omega_{if})t - \Gamma_{if}t] , \qquad \text{(II. 6)}$$

where ω_{if} is the transition frequency, $\Delta\omega_{if}$ is the solvent shift, and the decay constant Γ_{if} is related to the dephasing time T_2 by

$$\Gamma_{if} = 1/(T_2)_{if} . \qquad \text{(II. 7)}$$

Now, substituting expression (II. 6) for G_a into Eq. (II. 3) and performing the integration, we obtain

$$I_a(\omega) \propto \Gamma_{if}[(\omega - \omega_{if} - \Delta\omega_{if})^2 + \Gamma_{if}^2]^{-1} , \qquad \text{(II. 8)}$$

i. e., the line shape is Lorentzian with a full width at half-maximum equal to $2\Gamma_{if}$.

C. Expression for T_2

For a two-level impurity coupled to a medium (thermal bath), we can write the complete Hamiltonian as

$$H = H^0 + V = H_I^0 + H_M^0 + V , \qquad \text{(II. 9)}$$

where H_I^0 and H_M^0 are the Hamiltonians of the isolated impurity and medium, respectively, and V is the impurity–medium interaction. For the case in which the medium is a solid, Jones and Zewail[4] have derived the following general expression for the dephasing rate[5]:

$$T_2^{-1} = T_1^{-1} + T_2'^{-1} , \qquad \text{(II. 10)}$$

where

$$T_1^{-1} = (T_{1i}^{-1} + T_{1f}^{-1})/2 \qquad \text{(II. 11)}$$

and

$$T_2'^{-1} = \pi\hbar^{-1} \sum_p W_p \sum_{p'} |\langle ip'|T|ip\rangle$$
$$- \langle fp'|T|fp\rangle|^2 \delta(E_p - E_{p'}) . \qquad \text{(II. 12)}$$

In Eqs. (II. 11) and (II. 12), i and f denote, respectively, the initial and final levels of the isolated impurity; p denotes a many-body state of the medium having energy E_p and probability of occupation W_p; T_{1i} and T_{1f} are the *population* relaxation times associated with impurity levels i and f, respectively; T is the transition operator, which satisfies Dyson's equation[6]

$$T = V + VG^0T , \qquad \text{(II. 13)}$$

where G^0 is the unperturbed resolvent (Green operator). Expression (II. 12) can be recast (see Appendix A) as

$$T_2'^{-1} = \tfrac{1}{2}\hbar^{-2} \int_{-\infty}^\infty \langle \Delta T(0)\Delta T(t)\rangle_M^0 dt , \qquad \text{(II. 14)}$$

where

$$\Delta T \equiv \langle i|T|i\rangle - \langle f|T|f\rangle \qquad \text{(II. 15)}$$

and $\langle \cdots \rangle_M^0$ signifies a canonical ensemble average over the states of the medium. Note carefully that $\langle i|T|i\rangle$ (or $\langle f|T|f\rangle$) is the expectation value of the *full* transition operator with the impurity in the intramolecular level i (or f) and hence depends upon the coordinates of the medium in general. As a consequence, ΔT is an operator depending only on medium variables.

Now, invoking the Born approximation, i. e., replacing T by V, we obtain from Eq. (II. 14)

$$T_2'^{-1} = \tfrac{1}{2}\hbar^{-2} \int_{-\infty}^\infty \langle\Delta V(0)\Delta V(t)\rangle_M^0 dt$$
$$= \pi\hbar^{-1} \sum_p W_p \sum_{p'} |\langle p|\Delta V|p'\rangle|^2 \delta(E_p - E_{p'}) . \qquad \text{(II. 16)}$$

Thus, it is apparent that $T_2'^{-1}$ is the zero-frequency component of the autocorrelation function of either ΔT in the exact expression [Eq. (II. 14)] or ΔV in the Born approximation [Eq. (II. 16)] thereto. This latter result [Eq. (II. 16)] is in agreement with that obtained previously by others.[7–9] It also agrees with the result reached by Diestler,[10] provided that the thermal average of ΔV vanishes, i. e.,

$$\langle\Delta V\rangle_M^0 = \mathrm{Tr}_M[\rho_M(0)\Delta V] = \sum_p W_p\langle p|\Delta V|p\rangle = 0 , \qquad \text{(II. 17)}$$

where $\rho_M(0)$ is the equilibrium canonical density operator characterizing the isolated medium.[11]

Using the general expression (II. 12), we may interpret dephasing physically as follows: From Eq. (II. 10), we see that the total rate (T_2^{-1}) of dephasing is a sum of two contributions: (1) T_1^{-1}, the rate of population relaxation, which results from *inelastic* transitions between impurity levels; (2) $T_2'^{-1}$, the rate of pure dephasing, which results from elastic scattering processes in which the population of impurity levels does not change. Let us consider pure dephasing in greater depth. The form of the argument of the Dirac delta function in expression (II. 12) tells us that pure dephasing results from elastic transitions between the states $|p\rangle$ and $|p'\rangle$ of the medium (which includes all d. f. to which the relevant impurity levels i and f are coupled). In the gas phase, the medium consists of the translational motions of the c. m. 's of the active molecules. Pure dephasing results from a sequence of simple elastic bimolecular collisions. At the other extreme, in solids the medium consists of lattice normal modes and pure dephasing takes place via phonon-scattering processes. Phonon scattering in solids may be viewed as the analog of bimolecular scattering in gases. In liquids, however, the picture is somewhat murkier, since the unperturbed many-body states of liquids cannot be simply described in terms of free translations (gas) or normal vibrations (solid). Nonetheless, under certain prescribed conditions,[4,11] expression (II. 12) still holds.

III. THEORY OF VIBRONIC DEPHASING

Previous theoretical treatments have focused on either pure vibrational dephasing or pure electronic dephasing. The purpose of this Section is to develop a general theory of *vibronic* dephasing, which includes as special cases pure vibrational and pure electronic dephasing. For

the sake of clarity, we shall restrict our consideration to the system consisting of a single molecular impurity isolated in a *solid* host. Again, we shall assume that all relevant vibronic transitions are homogeneously broadened.

A. Adiabatic Born–Oppenheimer states and the potential-energy surface

Under the standard adiabatic Born–Oppenheimer approximation, the vibronic wave functions of the entire system can be written as

$$\psi_i(\mathbf{r};\mathbf{R}) = \phi_i(\mathbf{r};\mathbf{R})\chi_i(\mathbf{R}) , \qquad \text{(III. 1)}$$

where ϕ_i is the Born–Oppenheimer electronic wave function and $\chi_i(\mathbf{R})$ is the corresponding vibrational (or, in general, rotational–vibrational) wave function. In Eq. (III. 1), $\mathbf{r}$ and $\mathbf{R}$, respectively, denote the sets of electronic and nuclear coordinates. The vibrational wave function satisfies the Schrödinger equation

$$[\mathbf{T}_N + \epsilon_i(\mathbf{R})]\chi_i(\mathbf{R}) = E_i\chi_i(\mathbf{R}) , \qquad \text{(III. 2)}$$

where $\mathbf{T}_N$ is the total nuclear kinetic-energy operator and $\epsilon_i(\mathbf{R})$ is the adiabatic potential-energy surface (PES) governing the nuclear motion of the entire system.

It is convenient to partition the nuclear coordinates into two sets: the intramolecular coordinates of the impurity $\{\mathbf{Q}\}$ and the "lattice" coordinates $\{\mathbf{u}\}$. Note that, in general, $\{\mathbf{u}\}$ includes the translational coordinates of both the impurity and host molecules and the internal (i. e., vibrational and rotational) coordinates of the host. Now, expanding the PES in a partial Taylor series in the lattice coordinates, we have

$$\epsilon_i(\mathbf{Q};\mathbf{u}) = \epsilon_i(\mathbf{Q};0) + \sum_\kappa \sum_\alpha \epsilon_{i;\kappa\alpha}^{(1)}(\mathbf{Q})u_{\kappa\alpha}$$
$$+ \frac{1}{2}\sum_\kappa \sum_\alpha \sum_l \sum_\beta \epsilon_{i;\kappa\alpha,l\beta}^{(2)}(\mathbf{Q})u_{\kappa\alpha}u_{l\beta} + \cdots , \qquad \text{(III. 3)}$$

where

$$\epsilon_{i;\kappa\alpha}^{(1)}(\mathbf{Q}) \equiv (\partial\epsilon_i/\partial u_{\kappa\alpha})_0$$
$$\epsilon_{i;\kappa\alpha,l\beta}^{(2)}(\mathbf{Q}) \equiv (\partial^2\epsilon_i/\partial u_{\kappa\alpha}\partial u_{l\beta})_0 , \qquad \text{(III. 4)}$$

and $u_{\kappa\alpha}$ is the αth Cartesian component of the displacement of the κth lattice atom from its equilibrium position. The partial derivatives defined by Eq. (III. 4) can be further expanded as

$$\epsilon_{i;\kappa\alpha,l\beta,\ldots}^{(n)}(\mathbf{Q}) = \epsilon_{i;\kappa\alpha,l\beta,\ldots}^{(n)}(0) + \sum_r (\partial\epsilon_{i;\kappa\alpha,l\beta,\ldots}^{(n)}/\partial Q_r)_0 Q_r$$
$$+ \frac{1}{2}\sum_r \sum_s (\partial^2\epsilon_{i;\kappa\alpha,l\beta,\ldots}^{(n)}/\partial Q_r\partial Q_s)_0 Q_r Q_s + \cdots , \qquad \text{(III. 5)}$$

where Q_r is the displacement of the rth internal coordinate from its equilibrium value. (Note that this two-step Taylor expansion is equivalent to a direct expansion in all coordinates.) Equation (III. 5) implicitly assumes that the intramolecular coordinates experience only small displacements from their equilibrium values and hence is not valid in the case of free (or nearly free) rotations.

For the purpose of calculating the zero-order vibronic

wave functions, we shall take the *unperturbed* adiabatic PES corresponding to the ith electronic state to be given by

$$\epsilon_i^0 = \epsilon_i^0(\mathbf{Q};\mathbf{u}) = \epsilon_i(\mathbf{Q};0) + \frac{1}{2}\sum_{\kappa\alpha}\sum_{l\beta}k_{\kappa\alpha;l\beta}u_{\kappa\alpha}u_{l\beta} , \qquad \text{(III. 6)}$$

where $\epsilon_i(\mathbf{Q};0)$ governs the intramolecular motion in the field of the lattice "frozen" at equilibrium and $k_{\kappa\alpha;l\beta}$ are force constants determining the normal modes of the lattice. Equation (III. 6), which is tantamount to a separation of the *intramolecular* vibrations of the impurity from the *intermolecular* vibrations of the lattice, is based on the assumption (iv) of Sec. II that the impurity–lattice coupling is weak. An alternate approach would view this separation as a second adiabatic approximation (analogous to the standard adiabatic Born–Oppenheimer approximation) in which the relatively high-frequency intramolecular motions [governed by $\epsilon_i(\mathbf{Q};0)$] adjust instantaneously in the effective potential field deriving from the relatively low-frequency lattice motions. Then the zero-order total vibrational wave function factors into a product of the intramolecular impurity wave function $\bar\chi_i^0$ and the lattice wave function ψ^0, i. e.,

$$\chi_i^0(\mathbf{R}) = \bar\chi_{i\mathbf{v}}^0(\mathbf{Q})\psi_\mathbf{n}^0(\mathbf{u}) , \qquad \text{(III. 7)}$$

where $\mathbf{v}$ and $\mathbf{n}$, respectively, denote sets of quantum numbers necessary to specify the intramolecular and lattice vibrational eigenstates. In the occupation-number representation, $\psi_\mathbf{n}^0$ may be expressed as

$$|\psi_\mathbf{n}^0\rangle = \prod_\nu |n_\nu\rangle = |\mathbf{n}\rangle , \qquad \text{(III. 8)}$$

where ν refers to the νth normal mode. Finally, the *total* zero-order vibronic wave function (III. 1) may be rewritten more explicitly as

$$\psi_i(\mathbf{r};\mathbf{R}) = \phi_i(\mathbf{r};\mathbf{R})\bar\chi_{i\mathbf{v}}^0(\mathbf{Q})\psi_\mathbf{n}^0(\mathbf{u}) . \qquad \text{(III. 9)}$$

Now the impurity–lattice coupling leading to vibronic dephasing can be seen from Eqs. (III. 3) and (III. 6) to be

$$V_i = V_i(\mathbf{Q};\mathbf{u}) = V_i^{(1)} + V_i^{(2)} , \qquad \text{(III. 10)}$$

where

$$V_i^{(1)} \equiv \sum_{\kappa\alpha}\epsilon_{i;\kappa\alpha}^{(1)}(\mathbf{Q})u_{\kappa\alpha} , \qquad \text{(III. 11a)}$$

$$V_i^{(2)} \equiv \frac{1}{2}\sum_{\kappa\alpha}\sum_{l\beta}\epsilon_{i;\kappa\alpha,l\beta}^{(2)}(\mathbf{Q})u_{\kappa\alpha}u_{l\beta} , \qquad \text{(III. 11b)}$$

and terms cubic and higher degree in the lattice coordinates have been neglected. Note that $\epsilon_{i;\kappa\alpha,l\beta}^{(2)}(\mathbf{Q})$ manifests the full vibronic [i. e., both vibrational ($\mathbf{Q}$) and electronic (i)] dependence of the impurity–lattice interaction responsible for dephasing.

B. General expression for T_2'

From the fact that only *elastic* phonon-scattering processes lead to *pure* dephasing, we deduce that only the term $V_i^{(2)}$ [see Eq. (III. 11b)], which is quadratic in the lattice displacements, contributes to T_2'. Furthermore, from Eq. (II. 16), it follows that we need the expectation value of the coupling potential $\langle V^{(2)}\rangle$ for the initial and final intramolecular levels. Now, since $\epsilon_i^{(2)}$ does not depend explicitly upon electronic coordinates, we have from Eq. (III. 11b)

$$\langle \phi_i \bar{\chi}^0_{i\mathbf{v}} | V_i^{(2)} | \phi_i \bar{\chi}^0_{i\mathbf{v}} \rangle$$

$$= \frac{1}{2} \sum_{\kappa\alpha} \sum_{l\beta} \langle \bar{\chi}^0_{i\mathbf{v}} | \epsilon^{(2)}_{i;\kappa\alpha,l\beta} | \bar{\chi}^0_{i\mathbf{v}} \rangle u_{\kappa\alpha} u_{l\beta} \ . \tag{III.12}$$

It is emphasized that the coupling between the lattice and the impurity is different for the different electronic states, as dictated by the index i on $\epsilon_i^{(2)}$. In other words, expression (III.12) manifests both electronic

(i) and vibrational (v) effects on pure dephasing. From Eq. (II.15), we therefore obtain

$$\Delta V^{(2)} = \frac{1}{2} \sum_{\kappa\alpha} \sum_{l\beta} [\langle \bar{\chi}^0_{i\mathbf{v}} | \epsilon^{(2)}_{i;\kappa\alpha,l\beta} | \bar{\chi}^0_{i\mathbf{v}} \rangle$$
$$- \langle \bar{\chi}^0_{f\mathbf{v}'} | \epsilon^{(2)}_{f;\kappa\alpha,l\beta} | \bar{\chi}^0_{f\mathbf{v}'} \rangle] u_{\kappa\alpha} u_{l\beta} \ . \tag{III.13}$$

Finally, employing the expansion (III.5), we can rewrite Eq. (III.13) as

$$\Delta V^{(2)} = \frac{1}{2} \sum_{\kappa\alpha} \sum_{l\beta} \{ [\epsilon^{(2)}_{i;\kappa\alpha,l\beta}(0) - \epsilon^{(2)}_{f;\kappa\alpha,l\beta}(0)] + \sum_r [(\partial\epsilon^{(2)}_{i;\kappa\alpha,l\beta}/\partial Q_r)_0 \langle \bar{\chi}^0_{i\mathbf{v}} | Q_r | \bar{\chi}^0_{i\mathbf{v}} \rangle - (\partial\epsilon^{(2)}_{f;\kappa\alpha,l\beta}/\partial Q_r)_0 \langle \bar{\chi}^0_{f\mathbf{v}'} | Q_r | \bar{\chi}^0_{f\mathbf{v}'} \rangle]$$

$$+ \frac{1}{2} \sum_r \sum_s [(\partial^2\epsilon^{(2)}_{i;\kappa\alpha,l\beta}/\partial Q_r \partial Q_s)_0 \langle \bar{\chi}^0_{i\mathbf{v}} | Q_r Q_s | \bar{\chi}^0_{i\mathbf{v}} \rangle - (\partial^2\epsilon^{(2)}_{f;\kappa\alpha,l\beta}/\partial Q_r \partial Q_s)_0 \langle \bar{\chi}^0_{f\mathbf{v}'} | Q_r Q_s | \bar{\chi}^0_{f\mathbf{v}'} \rangle] \} u_{\kappa\alpha} u_{l\beta} \ . \tag{III.14}$$

Some insights into the mechanisms of pure dephasing can be had at this point by examining in detail expression (III.14), which tells us essentially that vibronic dephasing is due to a disparity between the phonon-scattering "cross sections" of the initial and final vibronic levels. For example, the term

$$[\epsilon^{(2)}_{i;\kappa\alpha,l\beta}(0) - \epsilon^{(2)}_{f;\kappa\alpha,l\beta}(0)] \tag{III.15}$$

depends only on the electronic distribution (through index i or f) and not explicitly on the vibrational (i. e., nuclear) motion of the impurity. Thus, it represents a purely electronic contribution to the cross section and would be present even if the impurity were monatomic. On the other hand, the terms

$$\sum_r [(\partial\epsilon^{(2)}_{i;\kappa\alpha,l\beta}/\partial Q_r)_0 \langle \bar{\chi}^0_{i\mathbf{v}} | Q_r | \bar{\chi}^0_{i\mathbf{v}} \rangle$$
$$- (\partial\epsilon^{(2)}_{f;\kappa\alpha,l\beta}/\partial Q_r)_0 \langle \bar{\chi}^0_{f\mathbf{v}'} | Q_r | \bar{\chi}^0_{f\mathbf{v}'} \rangle] \tag{III.16}$$

and

$$\frac{1}{2} \sum_r \sum_s [(\partial^2\epsilon^{(2)}_{i;\kappa\alpha,l\beta}/\partial Q_r \partial Q_s)_0 \langle \bar{\chi}^0_{i\mathbf{v}} | Q_r Q_s | \bar{\chi}^0_{i\mathbf{v}} \rangle$$
$$- (\partial^2\epsilon^{(2)}_{f;\kappa\alpha,l\beta}/\partial Q_r \partial Q_s)_0 \langle \bar{\chi}^0_{f\mathbf{v}'} | Q_r Q_s | \bar{\chi}^0_{f\mathbf{v}'} \rangle] \tag{III.17}$$

represent *vibronic* contributions to the cross section. To clarify this, let us consider, for example, the term

$$(\partial^2\epsilon^{(2)}_{i;\kappa\alpha,l\beta}/\partial Q_r \partial Q_s)_0 \langle \bar{\chi}^0_{i\mathbf{v}} | Q_r Q_s | \bar{\chi}^0_{i\mathbf{v}} \rangle u_{\kappa\alpha} u_{l\beta} \ , \tag{III.18}$$

which can be rewritten as

$$(\partial^4\epsilon_i(\mathbf{Q};\mathbf{u})/\partial Q_r \partial Q_s \partial u_{\kappa\alpha} \partial u_{l\beta})_0 \langle \bar{\chi}^0_{i\mathbf{v}} | Q_r Q_s | \bar{\chi}^0_{i\mathbf{v}} \rangle u_{\kappa\alpha} u_{l\beta} \ . \tag{III.19}$$

Expression (III.19) represents a *quartic* anharmonic coupling between the intramolecular and lattice modes. An explicit dependence [in the corresponding term of the cross section, i. e., expression (III.17)] on the electronic state is carried by the index i on the anharmonic coupling constant [i. e., $(\partial^4\epsilon_i/\partial Q_r \partial Q_s \partial u_{\kappa\alpha} \partial u_{l\beta})_0$]. The influence of "pure" vibration is exerted through the expectation value $\langle \bar{\chi}^0_{i\mathbf{v}} | Q_r Q_s | \bar{\chi}^0_{i\mathbf{v}} \rangle$, which itself depends indirectly on the electronic state, since the intramolecular component of the PES [i. e., $\epsilon_i(\mathbf{Q};0)$] determines the nature of the $\bar{\chi}^0_{i\mathbf{v}}$. We note in passing that, for systems in which the separation of the intra- and intermolecular modes is difficult (e. g., because of a resonance be-

tween the impurity and lattice modes), anharmonic terms of the type (III.19) are reminiscent of those (e. g., $u_{\kappa\alpha} u_{l\beta} u_{m\gamma} u_{n\delta}$) giving rise to complicated many-body phonon-scattering processes in pure anharmonic crystals.[6]

According to Eq. (II.16), T_2' involves matrix elements of ΔV between many-body states of the medium, which in the present instance is the host crystal lattice. Hence, from Eq. (III.12), it follows that we must evaluate matrix elements of the type $\langle n | u_{\kappa\alpha} u_{l\beta} | n' \rangle$ with $| n \rangle$ defined by Eq. (III.8). This can be conveniently accomplished by expressing the lattice–atom displacements as

$$u_{\kappa\alpha} = \sum_\nu (C_{\kappa\alpha;\nu} b_\nu + C^*_{\kappa\alpha;\nu} b_\nu^\dagger) \ , \tag{III.20}$$

where b_ν and $b_\nu^\dagger$ are, respectively, the destruction and creation operators associated with the νth normal mode and $C_{\kappa\alpha;\nu}$ is a complex (i. e., nonreal) constant depending on the structure of the host lattice. Then,

$$u_{\kappa\alpha} u_{l\beta} = \sum_\mu \sum_\nu (C_{\kappa\alpha;\mu} C_{l\beta;\nu} b_\mu b_\nu + C_{\kappa\alpha;\mu} C^*_{l\beta;\nu} b_\mu b_\nu^\dagger$$
$$+ C^*_{\kappa\alpha;\mu} C_{l\beta;\nu} b_\mu^\dagger b_\nu + C^*_{\kappa\alpha;\mu} C^*_{l\beta;\nu} b_\mu^\dagger b_\nu^\dagger) \ . \tag{III.21}$$

Now, in order for the phonon scattering to be elastic, i. e., energy conserving, one phonon must be destroyed while another of the same energy is created. Therefore, the "direct" terms of Eq. (III.21), i. e., $b_\mu b_\nu$ and $b_\mu^\dagger b_\nu^\dagger$, cannot contribute to elastic scattering, as they either create or destroy *two* phonons. Moreover, the diagonal terms of the form $b_\mu^\dagger b_\nu$, where $\mu = \nu$, can be ignored.[11] Hence, we have, for the relevant contribution to $T_2'^{-1}$,

$$u_{\kappa\alpha} u_{l\beta} = \sum_\mu \sum_{\nu\neq\mu} (C_{\kappa\alpha;\mu} C^*_{l\beta;\nu} b_\mu b_\nu^\dagger + C^*_{\kappa\alpha;\mu} C_{l\beta;\nu} b_\mu^\dagger b_\nu) \ . \tag{III.22}$$

Finally, noting that $\Delta V^{(2)}$ is summed over all $\kappa\alpha$, $l\beta$, μ, and ν, we can rewrite Eq. (III.22) as

$$u_{\kappa\alpha} u_{l\beta} = 2 \sum_\mu \sum_{\nu\neq\mu} C^*_{\kappa\alpha;\mu} C_{l\beta;\nu} b_\mu^\dagger b_\nu \ . \tag{III.23}$$

From Eqs. (III.13) and (III.23), it follows that

$$\langle n | \Delta V^{(2)} | n' \rangle = \sum_\mu \sum_{\nu\neq\mu} D_{\mu\nu} \langle n | b_\mu^\dagger b_\nu | n' \rangle \ , \tag{III.24}$$

where

$$D_{\mu\nu} \equiv \sum_{\kappa\alpha} \sum_{IB} (\langle \overline{\chi}^0_{i\mathbf{v}} | \epsilon^{(2)}_{i;\kappa\alpha,IB} | \overline{\chi}^0_{i\mathbf{v}} \rangle - \langle \overline{\chi}^0_{f\mathbf{v}'} | \epsilon^{(2)}_{f;\kappa\alpha,IB} | \overline{\chi}^0_{f\mathbf{v}'} \rangle) C^*_{\kappa\alpha;\mu} C_{IB;\nu}$$

$$= \sum_{\kappa\alpha} \sum_{IB} \Big\{ [\epsilon^{(2)}_{i;\kappa\alpha,IB}(0) - \epsilon^{(2)}_{f;\kappa\alpha,IB}(0)] + \sum_r [(\partial\epsilon^{(2)}_{i;\kappa\alpha,IB}/\partial Q_r)_0 \langle \overline{\chi}^0_{i\mathbf{v}} | Q_r | \overline{\chi}^0_{i\mathbf{v}} \rangle - (\partial\epsilon^{(2)}_{f;\kappa\alpha,IB}/\partial Q_r)_0 \langle \overline{\chi}^0_{f\mathbf{v}'} | Q_r | \overline{\chi}^0_{f\mathbf{v}'} \rangle]$$

$$+ \frac{1}{2} \sum_r \sum_s [(\partial^2\epsilon^{(2)}_{i;\kappa\alpha,IB}/\partial Q_r \partial Q_s)_0 \langle \overline{\chi}^0_{i\mathbf{v}} | Q_r Q_s | \overline{\chi}^0_{i\mathbf{v}} \rangle - (\partial^2\epsilon^{(2)}_{f;\kappa\alpha,IB}/\partial Q_r \partial Q_s)_0 \langle \overline{\chi}^0_{f\mathbf{v}'} | Q_r Q_s | \overline{\chi}^0_{f\mathbf{v}'} \rangle] \Big\} C^*_{\kappa\alpha;\mu} C_{IB;\nu} , \qquad \text{(III. 25)}$$

the second line of Eq. (III. 25) following from Eq. (III. 5). Invoking the standard relation

$$\langle n | b^\dagger_\mu b_\nu | n' \rangle$$

$$= (n'_\mu + 1)^{1/2} (n'_\nu)^{1/2} \delta_{n_1 n'_1} \cdots \delta_{n_\mu n'_\mu + 1} \cdots \delta_{n_\nu, n'_\nu - 1} \cdots , \qquad \text{(III. 26)}$$

we have from Eq. (III. 24)

$$|\langle n | \Delta V^{(2)} | n' \rangle|^2 = \sum_\mu \sum_{\nu \neq \mu} |D_{\mu\nu}|^2 (n'_\mu + 1) n'_\nu$$

$$\times \delta_{n_1 n'_1} \cdots \delta_{n_\mu, n'_\mu + 1} \cdots \delta_{n_\nu, n'_\nu - 1} \cdots , \qquad \text{(III. 27)}$$

where the cross terms have been exluded since they vanish upon summing on n', as required in the evaluation of T'^{-1}_2. Now, recasting Eq. (II. 16) in the present notation as

$$T'^{-1}_2 = \pi\hbar^{-1} \sum_n W_n \sum_{n'} \Big[\sum_\mu \sum_{\nu \neq \mu} |D_{\mu\nu}|^2 (n'_\mu + 1) n'_\nu$$

$$\times \delta_{n_1 n'_1} \cdots \delta_{n_\mu, n'_\mu + 1} \cdots \delta_{n_\nu, n'_\nu - 1} \cdots \Big]$$

$$\times \delta \Big(\sum_{\mu'} \hbar\omega_{\mu'} n_{\mu'} - \sum_{\nu'} \hbar\omega_{\nu'} n'_{\nu'} \Big) \qquad \text{(III. 28)}$$

and carrying out the sums on n' and n, we obtain

$$T'^{-1}_2 = \pi\hbar^{-2} \sum_\mu \sum_{\nu \neq \mu} |D_{\mu\nu}|^2 \overline{n}_\mu (\overline{n}_\nu + 1) \delta(\omega_\mu - \omega_\nu) , \qquad \text{(III. 29)}$$

where the thermally averaged occupation number of the μth lattice mode is given explicitly by

$$\overline{n}_\mu = [\exp(\hbar\omega_\mu/k_B T) - 1]^{-1} \qquad \text{(III. 30)}$$

and k_B is Boltzmann's constant.

C. Separation of intra- and intermolecular effects on T'_2: illustrative special cases

As it stands, expression (III. 29) is quite general and the effects of both impurity and lattice upon T'_2 are interwoven in a complicated fashion in $D_{\mu\nu}$ [see Eq. (III. 25)]. It is instructive to examine some simple special cases in which the influence of the impurity is separable from that of the lattice. Here we shall concentrate on intramolecular effects, leaving the lattice in a simple harmonic potential field. Recently, Bellows and Prasad[12] have considered the effects of *lattice* anharmonicities on dephasing.

For simplicity, we shall express the impurity–lattice interaction V in terms of the strain tensor[13] and defer a treatment based on explicit consideration of $D_{\mu\nu}$ to Section IV and Paper II. Then, V can be written as

$$V = V_0 + V_1 \epsilon + V_2 \epsilon^2 + \cdots , \qquad \text{(III. 31)}$$

where, following Ref. 13, we approximate the strain by

$$\epsilon = i \sum_\mu (\hbar q^2_\mu / 2N m_s \omega_\mu)^{1/2} (b_\mu - b^\dagger_\mu) . \qquad \text{(III. 32)}$$

In Eq. (III. 32), q_μ is the wave vector associated with the μth lattice mode and m_s and N are, respectively, the mass and total number of lattice atoms. The coefficients V_i in expansion (III. 31) depend only upon the intramolecular variables (both electronic and vibrational coordinates) of the impurity and ϵ describes the coupling of the lattice to the *excited* impurity through phonon absorption and emission. Herein lies the motivation for the approach employing strain, i.e., it leads directly to a clean separation of lattice and impurity variables to all orders in ϵ.

Again, since only elastic phonon scattering gives rise to pure dephasing, the relevant interaction term is $V_2 \epsilon^2$ and hence

$$\Delta V^{(2)} = \langle \phi_f \overline{\chi}^0_{f\mathbf{v}'} | V_2 | \phi_f \overline{\chi}^0_{f\mathbf{v}'} \rangle \epsilon^2 = \mathcal{U}^{(2)}_{ff} \epsilon^2 . \qquad \text{(III. 33)}$$

By a treatment which precisely parallels that leading from Eq. (III. 20) to (III. 29), we obtain

$$T'^{-1}_2 = \pi/(N^2 m^2_s) | \mathcal{U}^{(2)}_{ff} |^2$$

$$\times \sum_\mu \sum_{\nu \neq \mu} q^2_\mu q^2_\nu / (\omega_\mu \omega_\nu) \overline{n}_\mu (\overline{n}_\nu + 1) \delta(\omega_\mu - \omega_\nu) . \qquad \text{(III. 34)}$$

Taking the lattice to be a continuum, we can replace the sums in Eq. (III. 34) by integrals according to

$$\sum_\mu \rightarrow \int_0^{\omega_{max}} \rho(\omega_\mu) d\omega_\mu , \qquad \text{(III. 35)}$$

where $\rho(\omega)$ is the frequency distribution of the lattice modes. Note that the validity of Eq. (III. 35) rests upon the fact that the summand (integrand) in Eq. (III. 34) depends only upon the magnitude of the wave vector. Now employing relation (III. 35) in Eq. (III. 34) and carrying out the integration over ω_ν, we obtain

$$T'^{-1}_2 = \pi/(N^2 m^2_s) | \mathcal{U}^{(2)}_{ff} |^2 \int_0^{\omega_{max}} d\omega \, \rho^2(\omega)$$

$$\times [q(\omega)]^4 \omega^{-2} \overline{n}(\omega) [\overline{n}(\omega) + 1] . \qquad \text{(III. 36)}$$

Hence, we see that T'^{-1}_2 is expressible as a product of an intramolecular factor $|\mathcal{U}^{(2)}_{ff}|^2$ and a lattice factor. Two cases will now be considered.

1. Debye solid

In this case,

$$\rho(\omega) = \begin{cases} 9N\omega^2/\omega^3_D , & 0 \leq \omega \leq \omega_D \\ 0 , & \omega > \omega_D , \end{cases} \qquad \text{(III. 37)}$$

and

$$q = \omega/v_s , \qquad \text{(III. 38)}$$

where v_s is the speed of sound and the cutoff frequency ω_D is given in terms of the number density (ρ_n) by

$$\omega_D = (6\pi^2\rho_n)^{1/3}v_s . \qquad \text{(III. 39)}$$

Substituting expressions (III. 30) and (III. 37)–(III. 39) into Eq. (III. 36) and simplifying, we obtain

$$T_2'^{-1} = \frac{9(k_BT/\hbar)^7}{4m_s^2\pi^3\rho_n^2 v_s^{10}} \left| \mathcal{U}_{ff}^{(2)} \right|^2 \int_0^{x_D} x^6 e^x/(e^x - 1)^2 dx , \qquad \text{(III. 40)}$$

where

$$x \equiv \hbar\omega/k_BT . \qquad \text{(III. 41)}$$

Now, for temperatures much less than the Debye temperature

$$T_D \equiv \hbar\omega_D/k_B , \qquad \text{(III. 42)}$$

expression (III. 40) can be approximated by

$$T_2'^{-1} = \frac{9 \times 6! \, \zeta(6)(k_B/\hbar)^7}{4\pi^3 \rho_m^2 v_s^{10}} \left| \mathcal{U}_{ff}^{(2)} \right|^2 T^7 , \qquad \text{(III. 43)}$$

where $\rho_m (= m_s\rho_n)$ is the mass density of the host lattice. Expression (III. 43) for $T_2'^{-1}$ has been reached previously in related contexts[4,10]; the T^7 dependence is a result of the Debye approximation. [13]

2. Quasilocal modes

Now let us suppose that the impurity is coupled to a quasilocal mode having a density of states ρ peaked sharply about ω_0. Then, in the neighborhood of this maximum in ρ, the temperature-dependent factor $\bar{n}(\omega)[\bar{n}(\omega) + 1]$ of the integrand in Eq. (III. 36) varies slowly and may be assumed constant (for a detailed treatment, see Appendix B). Hence,

$$T_2'^{-1} \propto \exp(\hbar\omega_0/k_BT)/[\exp(\hbar\omega_0/k_BT) - 1]^2 , \qquad \text{(III. 44)}$$

which may be approximated by

$$T_2'^{-1} \propto \exp(-\hbar\omega_0/k_BT) \qquad \text{(III. 45)}$$

at temperatures T such that

$$\hbar\omega_0 \gg k_BT . \qquad \text{(III. 46)}$$

This result agrees with previous calculations. [4]

Now that we have discussed how intra- and intermolecular effects on T_2' can be separated, we shall focus our attention in the remainder of this paper upon the influence of intramolecular properties on dephasing.

IV. PREDICTIONS OF INTRAMOLECULAR EFFECTS: SPECIAL CASES

Let us now restrict our attention to the case of a diatomic impurity for the sake of simplicity. Figure 1 depicts the intramolecular component $U_I^{(i)}$ [$= \epsilon_i(Q;0)$] of the PES corresponding to two different electronic states. We shall focus separately on pure electronic and vibrational dephasing by considering two extreme cases here and by presenting a numerical calculation of T_2' for a model in II. First, let us assume that the impurity–lattice coupling for the two vibronic levels is identical. Then, from Eq. (III. 25), we have
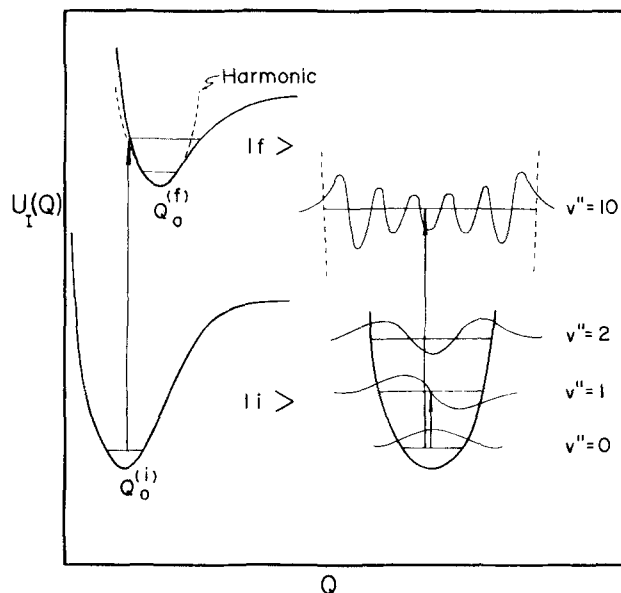

FIG. 1. Schematic representation of adiabatic intramolecular potential-energy curves corresponding to vibronic states i and f of a diatomic molecule. Q is the internuclear separation and Q_0 denotes the equilibrium separation. The schematic on the right depicts the transition $v'' = 0 \longrightarrow v'' = 10$ (not dipole allowed) for a *harmonic* curve.

$$D_{\mu\nu} = (\langle \bar{\chi}_{iv}^0 | Q | \bar{\chi}_{iv}^0 \rangle - \langle \bar{\chi}_{fv'}^0 | Q | \bar{\chi}_{fv'}^0 \rangle)D_{\mu\nu}^{(1)}$$
$$+ (\langle \bar{\chi}_{iv}^0 | Q^2 | \bar{\chi}_{iv}^0 \rangle - \langle \bar{\chi}_{fv'}^0 | Q^2 | \bar{\chi}_{fv'}^0 \rangle)D_{\mu\nu}^{(2)} , \qquad \text{(IV. 1)}$$

through terms quadratic in the intramolecular coordinate Q of the impurity, where

$$D_{\mu\nu}^{(1)} \equiv \sum_{\kappa\alpha} \sum_{l\beta} [\partial\epsilon_{\kappa\alpha, l\beta}^{(2)}(Q)/\partial Q]_0 C_{\kappa\alpha;\mu}^* C_{l\beta;\nu} ,$$

$$D_{\mu\nu}^{(2)} \equiv \frac{1}{2} \sum_{\kappa\alpha} \sum_{l\beta} [\partial^2\epsilon_{\kappa\alpha, l\beta}^{(2)}(Q)/\partial Q^2]_0 C_{\kappa\alpha;\mu}^* C_{l\beta;\nu} . \qquad \text{(IV. 2)}$$

If the deviations of Q from its equilibrium value $Q_0^{(i)}$ are small, then expression (IV. 1) is a good approximation to $D_{\mu\nu}$. Note that, in general, the linear and quadratic terms in Eq. (IV. 1) interfere with one another in determining $D_{\mu\nu}$. Let us consider the following special cases.

A. Harmonic intramolecular potential curves

In this case, the contribution of the linear term vanishes on account of the selection rule $\Delta v = \pm 1$ on Q for the harmonic oscillator. Only the quadratic term contributes to $D_{\mu\nu}$ and

$$D_{\mu\nu} = (\hbar/\mu)[(v_i + \tfrac{1}{2})/\omega_i - (v_f + \tfrac{1}{2})/\omega_f]D_{\mu\nu}^{(2)} , \qquad \text{(IV. 3)}$$

where we have invoked the relation $\langle v | Q^2 | v \rangle = \hbar(v + \tfrac{1}{2})/\mu\omega$, μ is the reduced mass of the diatomic impurity, and ω_i and ω_f are the fundamental frequencies associated with the initial and final manifolds, respectively, as determined by $\epsilon_i(Q;0)$ [see Eq. (III. 6)]. If $\omega_i = \omega_f = \omega$, then expression (IV. 3) simplifies to

$$D_{\mu\nu} = (\hbar/\mu\omega)(v_i - v_f)D_{\mu\nu}^{(2)} , \qquad \text{(IV. 4)}$$

which applies to pure vibrational dephasing within a single manifold or to dephasing of vibronic transitions

between manifolds having the *same* fundamental frequency.

1. Vibrational overtones

Although the transitions $(0, v'')$ within the same harmonic manifold are optically (dipole) forbidden, if such states v could be populated by other means, then pure vibrational dephasing could be observed and would display an interesting dependence on v''. For the overtones $(0, v'')$,

$$D_{\mu\nu} = -[\hbar D^{(2)}_{\mu\nu}/(\mu\omega)] \cdot v'' . \tag{IV. 5}$$

Substituting this expression for $D_{\mu\nu}$ into Eq. (III. 29) for $T_2'^{-1}$, we see that, at a fixed temperature, *the pure dephasing rate increases* quadratically with v''. This is an interesting result in that it means that the width of homogeneously broadened overtones associated with harmonic manifolds should increase as v''^2, if energy relaxation (T_1^{-1}) is negligible compared to pure dephasing $(T_2'^{-1})$.[14] Moreover, Eq. (IV. 5) indicates that, as the fundamental frequency associated with the oscillator increases, the pure dephasing rate decreases. It is interesting to compare this conclusion with the classical prediction. From a classical–mechanical viewpoint, one might expect that, as the frequency of the oscillator increases, it becomes less sensitive to its local environment and hence dephases more slowly. Similarly, if the oscillator becomes "heavier," i. e., μ increases, then according to Eq. (IV. 5) the dephasing rate decreases. Again, this makes sense from a classical perspective. For a fixed frequency, increasing μ decreases the classical turning point (i. e., vibrational amplitude) of the oscillator. Hence, it probes (or "feels") the local environment to a lesser extent and consequently dephases more slowly.

2. Vibronic transitions

Under the adiabatic Born–Oppenheimer and Franck–Condon approximations, the intensity of the electric–dipole transition between vibronic levels i and f is proportional to the Franck–Condon factor $|\langle \bar{\chi}^0_{iv}|\bar{\chi}^0_{fv'}\rangle|^2$. Hence, under the condition that the harmonic potential curves $U^{(i)}_I$ and $U^{(f)}_I$ have identical frequencies $(\omega_i = \omega_f = \omega)$ and minima $(Q^{(i)}_0 = Q^{(f)}_0)$, all intensity is in the $(0, 0)$ line. Moreover, from Eq. (IV. 4), it follows that the contribution of pure dephasing $(T_2'^{-1})$ to the homogeneous width vanishes. Hence, under these conditions, only energy-relaxation processes contribute to the $(0, 0)$ width. In Sec. IV C below, we shall show that, in general, T_2' does not vanish, on account of the purely electronic contribution to dephasing.

Now, if the harmonic potentials are simply displaced from one another, i. e., $Q^{(i)}_0 \neq Q^{(f)}_0$, the frequencies being held equal, then all of the various vibronic lines $(0, v')$ share intensity, with the maximum at the "vertical" transition. However, the situation with respect to dephasing remains unaltered. The contribution of $T_2'^{-1}$ to the $(0, 0)$ linewidth remains zero while that to the $(0, v')$ widths increases as v'^2. (It is emphasized that this result holds only under the approximation that the anharmonic coupling constants are independent of the electronic state.)

B. Anharmonic intramolecular potential curves

In this case, both the linear and quadratic terms contribute in general to $D_{\mu\nu}$ [see Eq. (IV. 1)]. It is interesting to note, however, that if the *shapes* of the potential curves for the two electronic manifolds are very similar, then $T_2'^{-1}$ for the $(0, 0)$ transition, and more generally for (v'', v') transitions with $v'' = v'$(i. e., pure electronic transitions), is very small, since the difference factors multiplying $D^{(1)}_{\mu\nu}$ and $D^{(2)}_{\mu\nu}$ [see Eq. (IV. 1)] nearly vanish. The physical rationale for this is that the impurity experiences the same effective force from "collisions" with the neighboring host molecules in the upper level as in the lower level. Thus, the fluctuating "level shifts" arising from phonon scattering are the same in the upper lower levels and effectively cancel out in the difference factor.

C. Pure electronic vs pure vibrational dephasing

In Secs. IV A and IV B, we have dwelt upon the extreme case in which the intramolecular vibrational effects on dephasing are more prominent than purely electronic effects. This is so because we have assumed that the impurity–lattice coupling does not depend on the electronic state of the impurity. Hence, the elastic phonon-scattering cross section depends directly on the difference in expectation values of powers of Q, e. g.,

$$\langle \bar{\chi}^0_{iv}|Q^2|\bar{\chi}^0_{iv}\rangle - \langle \bar{\chi}^0_{fv'}|Q^2|\bar{\chi}^0_{fv'}\rangle \tag{IV. 6}$$

and only indirectly on the electronic distribution, which affects the intramolecular $\bar{\chi}^0_{iv}$ through $\epsilon_i(Q;0)$. Now, from Eq. (III. 25) we see that, if the impurity–lattice coupling is assumed to depend upon the electronic state, an important additional term, namely,

$$D^{(0)}_{\mu\nu} \equiv \sum_{\kappa\alpha}\sum_{l\beta}[\epsilon^{(2)}_{i;\kappa\alpha,l\beta}(0) - \epsilon^{(2)}_{f;\kappa\alpha,l\beta}(0)]C^*_{\kappa\alpha;\mu}C_{l\beta;\nu} , \tag{IV. 7}$$

contributes to vibronic dephasing. It is clear that $D^{(0)}_{\mu\nu}$ depends only upon the difference between the electronic distributions in the initial and final vibronic levels and hence represents a purely electronic contribution to dephasing, as discussed previously in connection with Eq. (III. 14).

This point will be amplified in II where we consider a model in which the impurity–lattice couplings in the ground (i) and excited (f) levels satisfy the inequality

$$|\langle \bar{\chi}^0_{iv}|\epsilon^{(2)}_{i;\kappa\alpha,l\beta}|\bar{\chi}^0_{iv}\rangle| \ll |\langle \bar{\chi}^0_{fv'}|\epsilon^{(2)}_{f;\kappa\alpha,l\beta}|\bar{\chi}^0_{fv'}\rangle| , \tag{IV. 8}$$

i. e., the ground-state impurity–lattice coupling is much smaller than the excited-state coupling caused by the so-called electron–phonon interaction characteristic of molecular solids.[15] Clearly, under the condition (IV. 8), the $(0, 0)$ transition can be considerably broadened by purely electronic dephasing. This result is in sharp contrast to the conclusions of Secs. IV A and IV B, which were reached under the rather restrictive assumption of identical impurity–lattice couplings for the two electronic states. Note, however, that for large v, the v dependence of T_2' is essentially the same as in the previous cases.

D. Quasilocal modes and exchange effects

The dephasing of the impurity molecule by quasilocal modes proceeds by a different mechanism than dephasing by Debye modes. We note the following interesting results from Appendix B: First, at sufficiently low temperatures, the two levels i and f can interact with a distribution $\rho_L(\omega)$ of quasilocal modes (having a width $2\gamma_L$) to produce a temperature dependence in $T_2'^{-1}$ which resembles that of an activated rate process having an activation energy $\hbar\omega_0$—the peak energy of the distribution. The cross section for such a process is not, however, the pre-exponential frequency factor characteristic of an activated rate process. Rather, it is directly given by the matrix element $\mho^{(2)}$, which describes the disparity in phonon scattering between the intramolecular levels $i\mho$ and $f\mho'$. Second, the results indicate that there is no need of additional levels (beyond $i\mho$ and $f\mho'$) in order to obtain Orbach-type dephasing processes [i. e., a T dependence of $\exp(-\hbar\omega_0/k_BT)$]. Recently, it was proposed[16] that a four-level system is required to explain the T dependence of T_2' for the system pentacene in paraterphenyl. Our two-level theory predicts such a T dependence and also allows for the presence (or absence) of such dependence for impurity molecules in different host lattices. This point was discussed first in Ref. 4, which formally treats the effect of exchange (among the four levels) on dephasing. The application of this formal treatment[4] to the system pentacene in paraterphenyl can be found in Ref. 17. For this system, $\hbar\omega_0 \sim 20$ cm^{-1} and $\gamma_L \sim 1$ cm^{-1}. Using these parameters in Eq. (B7), we arrive at the following estimates for T_2': for $k_BT = 1$ cm^{-1}, $T_2' \simeq 3$ sec; for $k_BT = 10$ cm^{-1}, $T_2' \simeq 50$ nsec.

V. SUMMARY AND CONCLUSIONS

We have developed a quantum-mechanical theory of vibronic dephasing of impurity molecules in a solid host, deriving an explicit expression [Eq. (III.29)] for the pure dephasing rate $(T_2'^{-1})$ which manifests dependences upon molecular properties. We showed how intra- and intermolecular effects on dephasing can in certain instances be separated, in particular how the influence of temperature, which arises solely from the lattice, can be isolated in a single factor in the expression for $T_2'^{-1}$ for the case of a Debye solid or a solid in which a narrow quasilocal mode couples to the impurity. We also explored the dependences of $T_2'^{-1}$ upon intramolecular properties for two extreme cases in which either vibrational or electronic influences predominate. On the one hand, if the impurity–lattice coupling does not differ between the initial and final electronic states, then vibrational effects are emphasized, especially for high v' states. In the instance in which the initial and final intramolecular potential curves $[\epsilon_i(Q;0)]$ are nearly the same, the $(0, 0)$ line is negligibly broadened by pure dephasing (T_2'). On the other hand, if the coupling changes significantly in going between the initial and final electronic states, the $(0, 0)$ line may be considerably broadened. This latter broadening is due to purely electronic effects.

Within the context of harmonic approximation for the intramolecular potential curves, we have derived the explicit dependence of $T_2'^{-1}$ upon v, μ, and ω. The pre-

dictions are also in agreement with our expectations from a classical–mechanical viewpoint.

Finally, it was shown that the simple theory for two levels interacting with a medium provides reasonable cross sections for pure dephasing and also predicts the observed temperature dependence (for example, Orbach-type) *without* invoking population flow (sometimes called "exchange") among more than two levels.

In closing, we note that, in the qualitative applications of the theory presented here, only zero-phonon lines have been considered. However, the theory developed in Sec. III implicitly includes non-zero-phonon lines. This can be seen as follows: Such isolated "discrete" non-zero-phonon lines are presumably due to transitions between joint levels involving impurity and phonon modes, e. g., a local mode. The local mode could be libration of the impurity or a localized vibration arising from the impurity coupling to the neighboring lattice atoms. In the second case, we can lump the original impurity together with the nearest neighbors to form a "pseudomolecule," or complex, which functions in the theory as a "renormalized" impurity. Now transitions between the intramolecular levels of the entire complex give rise to both zero- and non-zero-phonon lines. In this renormalized picture, the coupling of the complex to the lattice would depend much less sensitively on the electronic state of the impurity, if the electronic excitations were sufficiently localized on the impurity. Strong shifts in the impurity *near-neighbor* coupling between initial and final electronic states could be handled by diagonalizing the adiabatic *intramolecular* PES of the complex. Through this diagonalization, anharmonic couplings between the modes of the original impurity and the pseudolocal modes of the complex, which are responsible for dephasing, would be taken properly into account. More on this idea will be published later.

APPENDIX A

Employing the standard relation

$$2\pi\delta(k) = \int_{-\infty}^{\infty} dx \exp(\pm ikx) , \qquad \text{(A1)}$$

we can rewrite Eq. (II. 12) as

$$T_2'^{-1} = \tfrac{1}{2}\hbar^{-2} \sum_p W_p \sum_{p'} \langle p|\Delta\mathbf{T}|p'\rangle \langle p'|\Delta\mathbf{T}|p\rangle$$
$$\times \int_{-\infty}^{\infty} dt \exp(iE_{p'}t/\hbar) \exp(-iE_p t/\hbar) , \qquad \text{(A2)}$$

where we have invoked the following property of the Dirac delta function:

$$\delta(ak) = |a|^{-1} \delta(k) . \qquad \text{(A3)}$$

We can recast Eq. (A2) as

$$T_2'^{-1} = \tfrac{1}{2}\hbar^{-2} \sum_p W_p \sum_{p'} \int_{-\infty}^{\infty} dt \langle p | \Delta T | p' \rangle$$

$$\times \langle p' | \exp(iH_M^0 t/\hbar) \Delta T \exp(-iH_M^0 t/\hbar) | p \rangle , \qquad (A4)$$

which follows from the fact that $|p\rangle$ and $|p'\rangle$ are eigenstates of H_M^0. Now, by the completeness relation

$$\sum_{p'} |p'\rangle\langle p'| = 1 , \qquad (A5)$$

Eq. (A4) simplifies to

$$T_2'^{-1} = \tfrac{1}{2}\hbar^{-2} \int_{-\infty}^{\infty} dt \sum_p W_p \langle p | \Delta T \Delta T(t) | p \rangle , \qquad (A6)$$

where

$$\Delta T(t) = \exp(iH_M^0 t/\hbar) \Delta T \exp(-iH_M^0 t/\hbar) \qquad (A7)$$

is the operator in the Heisenberg picture. Finally, since $\rho_M(0)$ is diagonal with elements W_p, we have from Eq. (A6)

$$T_2'^{-1} = \tfrac{1}{2}\hbar^{-2} \int_{-\infty}^{\infty} dt\, \mathrm{Tr}_M[\rho_M(0)\Delta T \Delta T(t)]$$

$$= \tfrac{1}{2}\hbar^{-2} \int_{-\infty}^{\infty} dt\, \langle \Delta T \Delta T(t) \rangle_M^0 . \qquad (A8)$$

Note that if we rewrite Eq. (A4) as

$$T_2'^{-1} = \tfrac{1}{2}\hbar^{-2} \sum_p W_p \sum_{p'} \int_{-\infty}^{\infty} dt$$

$$\times \langle p | \exp(-iH_M^0 t/\hbar) \Delta T \exp(iH_M^0 t/\hbar) | p' \rangle \langle p' | \Delta T | p \rangle , \qquad (A9)$$

then we get

$$T_2'^{-1} = \tfrac{1}{2}\hbar^{-2} \int_{-\infty}^{\infty} dt\, \langle \Delta T(-t) \Delta T \rangle_M^0 , \qquad (A10)$$

instead of expression (A8). Of course, Eq. (A10) also follows directly from Eq. (A8) by the general property of time-correlation functions that

$$\langle AB(t) \rangle = \langle A(-t)B \rangle . \qquad (A11)$$

Note that Eq. (A11) requires $\rho_M(0)$ to commute with H_M^0. Alternatively, either by rewriting Eq. (A4) as

$$T_2'^{-1} = \tfrac{1}{2}\hbar^{-2} \sum_p W_p \sum_{p'} \int_{-\infty}^{\infty} dt \langle p | \Delta T | p' \rangle$$

$$\times \langle p' | \exp(-iH_M^0 t/\hbar) \Delta T \exp(iH_M^0 t/\hbar | p \rangle \qquad (A12)$$

and then invoking relation (A11) or by directly casting $T_2'^{-1}$ as

$$T_2'^{-1} = \tfrac{1}{2}\hbar^{-2} \sum_p W_p \sum_{p'} \int_{-\infty}^{\infty} dt$$

$$\times \langle p | \exp(iH_M^0 t/\hbar) \Delta T \exp(-iH_M^0 t/\hbar) | p' \rangle \langle p' | \Delta T | p \rangle , \qquad (A13)$$

we arrive finally at

$$T_2'^{-1} = \tfrac{1}{2}\hbar^{-2} \int_{-\infty}^{\infty} dt\, \langle \Delta T(t) \Delta T \rangle_M^0 . \qquad (A14)$$

APPENDIX B

Here we derive explicit expressions for $T_2'^{-1}$ for the case in which the impurity is coupled to a quasilocal mode. Now, since we assume that the density $\rho(\omega)$ of

local modes is sharply peaked about ω_0, we can approximate Eq. (III. 36) by

$$T_2'^{-1} = (\pi/N^2 m_s^2)|v_{ff}^{(2)}|^2 q^4(\omega_0)\omega_0^{-2}\bar{n}(\omega_0)$$

$$\times [\bar{n}(\omega_0)+1] \int_0^{\omega_{\max}} d\omega[\rho(\omega)]^2 , \qquad (B1)$$

where we have removed from under the integral sign the slowly varying (as a function of ω) factors evaluated at the peak of the distribution. Since $\rho(\omega)$ falls off rapidly as $|\omega - \omega_0|$ increases, we can extend the limits of integration to $\pm\infty$. Hence, we need to evaluate the integral

$$I \equiv \int_{-\infty}^{\infty} d\omega[\rho(\omega)]^2 , \qquad (B2)$$

where $\rho(\omega)$ must be normalized according to

$$\int_{-\infty}^{\infty} \rho(\omega)\, d\omega = N_Q , \qquad (B3)$$

N_Q being the total number of quasilocal modes. Let us now consider two special cases:

(i) $\rho(\omega)$ is Lorentzian: In this case, the distribution is given by

$$\rho_L(\omega) = \pi^{-1} N_Q^L \gamma_L / [(\omega - \omega_0)^2 + \gamma_L^2] , \qquad (B4)$$

where γ_L is equal to one half the full width at half-maximum (FWHH), i.e.,

$$(\mathrm{FWHH})_L = 2\gamma_L . \qquad (B5)$$

Substituting Eq. (B4) into (B2) and evaluating the integral by elementary techniques, we get

$$I_L = (N_Q^L)^2/(2\pi\gamma_L) , \qquad (B6)$$

and from Eq. (B1) we have

$$(T_2'^{-1})_L = (1/2\gamma_L)(N_Q^L/N)^2 m_s^{-2} |v_{ff}^{(2)}|^2 q^4(\omega_0)\omega_0^{-2}$$

$$\times \bar{n}(\omega_0)[\bar{n}(\omega_0)+1] . \qquad (B7)$$

(ii) $\rho(\omega)$ is Gaussian: In this case, we express the distribution as

$$\rho_G(\omega) = N_Q^G (2\pi\gamma_G^2)^{-1/2} \exp[-(\omega - \omega_0)^2/2\gamma_G^2] , \qquad (B8)$$

where γ_G is now related to the FWHH by

$$(\mathrm{FWHH})_G = 2(2\ln 2)^{1/2}\gamma_G . \qquad (B9)$$

Substituting expression (B8) into Eq. (B2) and doing the integral as before gives

$$I_G = (N_Q^G)^2/(2\pi^{1/2}\gamma_G) \qquad (B10)$$

and from Eq. (B1) we obtain finally

$$(T_2'^{-1})_G = (\pi^{1/2}/2\gamma_G)(N_Q^G/N)^2 m_s^{-2}|v_{ff}^{(2)}|^2 q^4(\omega_0)\omega_0^{-2}$$

$$\times \bar{n}(\omega_0)[\bar{n}(\omega_0)+1] . \qquad (B11)$$

We note that, in both special cases (i) and (ii), the expression for the dephasing rate has the form given by Eq. (III. 44). Hence, in the limit of low temperature, both Eqs. (B7) and (B11) assume the form of Eq. (III. 45). Moreover, comparing Eqs. (B7) and (B11), we see that both $(T_2'^{-1})_L$ and $(T_2'^{-1})_G$ depend inversely on the width (proportional to γ) of the distribution. If $N_Q^G = N_Q^L$ and $\gamma_G = \gamma_L$, then the dephasing rates corresponding to the two distributions differ only by the constant factor of $\pi^{1/2}$. Note that in the limit $\gamma \to 0$, $T_2' \to 0$, reflect-

ing the fact that the medium is no longer a continuum in this limit. However, this is in contradiction of one of the the basic assumptions made at the outset of our treatment, namely, that the correlation time of the medium is very short. Hence, within the context of the present theory a nonzero width of the local mode distribution is required.

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[5]We note that the system of optically active two-level molecules is analogous to a system of spin-1/2 nuclei; T_1 corresponds to the longitudinal relaxation time and T_2 to the transverse relaxation time. The characteristic spin–relaxation times are related by Eq. (II.10). See, for example, C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963).

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[11]From Eq. (II.14) or (II.16), it would appear that, in general, both the diagonal (i.e., $b_\mu^\dagger b_\mu$) and nondiagonal (i.e., $b_\mu^\dagger b_\nu$, $\mu \neq \nu$) terms contribute to T_2^{-1}. We note that, in the case of a dense medium (e.g., solid), T is actually the *connected* many-body transition operator. However, expression (II.14) for T_2^{-1} retains its validity if the coupling is weak or the phonon density is low. Now the diagonal elements of ΔV are contained in the thermal average $\langle V \rangle_M^0$. Since $\langle V \rangle_M^0$ is usually grouped with the zero-order Hamiltonian [see, for example, R. J. Abbott and D. W. Oxtoby, J. Chem. Phys. **70**, 4703 (1979)], the dephasing rate (T_2^{-1}) is determined by the off-diagonal elements of ΔV. This is also the apparent basis for the common statement in the solid-state literature that only off-diagonal terms in the impurity–lattice coupling are responsible for the widths of spectral lines.

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