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Coherence effects between intramolecular vibrational relaxation and dissociation in triatomic van der Waals systems

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Time-independent [Halberstadt and co-workers, *J. Chem. Phys.* **96**, 2404 (1992); **97**, 341 (1992)] and time-dependent quantum mechanical calculations that describe the intramolecular vibrational relaxation (IVR) of $\text{Ar}\cdots\text{Cl}_2$ are used to develop analytical models for this process. It is shown that time-resolved experiments should reveal an oscillatory dissociation rate. It is found that the oscillations will be different for different rotational levels, and may tend to wash out if insufficient state selection is achieved in the initial excitation step. This may explain why no such oscillations were observed for $\text{Ar}\cdots\text{I}_2$. It is also predicted that the observed product state rotational distribution will change with the initially excited rotational state.

I. INTRODUCTION

Intramolecular vibrational relaxation (IVR) is a fundamental radiationless process in the photophysics of isolated polyatomic molecules.^{1,2} It takes place when a zero-order "bright" state (responsible for the photon absorption) is coupled to a quasidegenerate manifold of zero-order "dark" states in the same electronic state.^{3,4} This mixing produces complicated absorption spectra and anomalous radiative lifetimes. Jortner and co-workers^{3,4} have defined regimes of IVR as resonant, intermediate and statistical, depending on whether a single, several or many dark states couple with the bright state. They also note that coupling is largest when the difference between the bright and dark state quantum numbers is smallest.

Usually, IVR is observed by studying the fluorescence of polyatomic molecules. One technique for studying IVR is the "chemical timing" technique⁵ in which only "prompt" fluorescence is observed due to fast collisional quenching. Such results were interpreted using the formalism of Freed and Nizan.^{6,7} The fluorescence intensity is proportional to the population of the zero-order bright state.⁶ When several eigenstates of the system are coherently excited, IVR in the intermediate and resonant cases produces an oscillatory behavior of the fluorescence as a function of time (quantum beats).^{3,4,6-11} From the analysis of those quantum beats it is then possible to determine energies and couplings of the zero-order states that are involved. Quantum beats in large molecule fluorescence were first observed by Zewail and co-workers¹² for anthracene and *t*-stilbene. They were able to observe the different regimes of IVR by varying the excitation energy. Similarly, Nathanson and McClelland used fluorescence depolarization to study the role of molecular rotation in IVR.¹³

Van der Waals molecules provide particularly clear model systems for studying intramolecular relaxation because of the natural separation between the "fast" intramolecular modes and the "slow" intermolecular degrees of

freedom. Beswick and Jortner¹⁴ and Ewing¹⁵ provided the theoretical framework for interpreting vibrational predissociation data. In particular, the energy gap law,¹⁴ and the momentum gap law¹⁵ have become common tools for the analysis of the dissociation rate in terms of molecular properties. These laws apply to examples for which the initially excited quasibound state couples directly to the dissociative continuum, and exponential decay of the excited state is observed. For van der Waals molecules in which the initially excited level relaxes via a sequential mechanism, IVR can lead to nonexponential relaxation of the excited level. Heppener *et al.*¹⁶ first observed such a sequential decay in real time in their study of the $\text{Ar}\cdots\text{C}_2\text{N}_4\text{H}_2$ molecule.

Van der Waals complexes formed by a diatomic molecule *BC* and a rare gas atom are particularly interesting for studying IVR because of their simplicity for both theoreticians and experimentalists. When the van der Waals interaction is larger than the spacing between two vibrational levels of *BC*, IVR may compete with the direct coupling of the initial level to the dissociative continuum. For instance, for $\text{He}\cdots\text{I}_2$, the dissociation rate changes smoothly with *v*, the I_2 stretching quantum number, in the $\Delta v = -2$ regime.¹⁷⁻¹⁹ This implies a direct coupling of the quasibound state to the dissociative continuum. In contrast, the more strongly bound $\text{Ne}\cdots\text{I}_2$ molecule shows an erratic dependence of the resonance widths as a function of *v*, for $v = 28-34$, due to the interaction of two "zero-order" quasibound levels.²⁰ $\text{Ar}\cdots\text{I}_2$ dissociates via a sequential $\Delta v = -3$ mechanism. This has been studied in time independent experiments by Levy and co-workers,²¹ and in time-dependent experiments by Zewail and co-workers.²² Gray²³ performed time-dependent quantum mechanical calculations for this problem. Although nonexponential dissociation would be predicted on the basis of Gray's calculation, the experiment showed an exponential decay rate.

It has been shown that the dissociation of $\text{Ar}\cdots\text{Cl}_2$

involves IVR in the sparse limit when it is excited to the $v=10$ and 11 vibrational levels of the B electronic state.¹ Highly structured product state distributions, that were different for each initially excited Cl_2 stretching level,²⁴ initially provided evidence for such a process. Reference 1 provides a time-independent quantum mechanical description of the states and couplings which determine the dynamics. $\Delta v = -2$ dissociation of $\text{Ar} \cdots \text{Cl}_2$ is particularly well suited for studying IVR because the intermediate resonance is well defined. In this paper we provide a time-dependent analysis of the $\text{Ar}-\text{Cl}_2$ result. In particular, we explore the implications of IVR for possible time-dependent experiments, and we examine the role of rotation in the dissociation dynamics.

First, we examine the $\text{Ar} \cdots \text{Cl}_2$ dynamics in two dimensions, where the complex is restricted to a T-shaped angular configuration. Time-independent and time-dependent quantum calculations are performed in this reduced dimensional space to test the applicability of simple analytical models (similar to those commonly used to explain IVR^{3,4,6-11}) based on two zero-order bound states coupled to a continuum. Coherent excitation of the resulting eigenstates leads to oscillations in the dissociation rate analogous to quantum beats in fluorescence. Second, the model is extended to three dimensions, and the role of rotational motion of the complex is explored. It is found that rotational excitation about the intermolecular axis has a pronounced effect on the product state distributions. However, the oscillatory behavior of the dissociation rate will persist if sufficient selection of the initial states is attained. The IVR models developed in this study should prove to be useful in discussing more complicated examples such as $\text{Ar} \cdots \text{I}_2$.

The organization of the paper is as follows. In Sec. II the theory for the “exact” numerical calculations is outlined. In Sec. III the application of analytical IVR models to van der Waals molecules is discussed. In Sec. IV we present two-dimensional time-dependent and time-independent numerical results for the dissociation of the $\text{Ar} \cdots \text{Cl}_2$ complex frozen to its angular equilibrium geometry and three-dimensional time-independent numerical results. The comparison with the analytical models is discussed in detail. Section V is devoted to conclusions.

II. THEORY

A. Time-independent approach

The formalism used in these calculations has already been presented elsewhere.²⁵ It is reviewed here in order to facilitate the comparison with the time-dependent calculations. In the framework of the first order perturbation theory for electric dipole transitions, the cross section for excitation of a system from an initial bound state Ψ_i , with energy E_i , to a final continuum state, Ψ_{fE} , with the fragments in a particular state denoted by f , is given by

$$\sigma_{f \leftarrow i}(E) = \frac{4\pi^2(E - E_i)}{\hbar c} |\langle \Psi_{fE} | \mathcal{M} \cdot \mathbf{e} | \Psi_i \rangle|^2 \quad (1)$$

with $E = E_i + \hbar\omega$,

where $\mathbf{e}$ is the polarization vector and $\hbar\omega$ the energy of the incident photon, and $\mathcal{M}$ is the transition dipole moment of the molecular system for the electronic transition being considered. Ψ_i is the nuclear wave function in the ground electronic state X of the complex, while Ψ_{fE} is the continuum wave function in the excited electronic state, and the usual Born–Oppenheimer separation is assumed.

For triatomic systems of the type $X \cdots BC$, Ψ_i and Ψ_{fE} are eigenfunctions of nuclear Hamiltonians of the form

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + \frac{l^2}{2mR^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{j^2}{2\mu r^2} + V^\epsilon(r, R, \theta), \quad (2)$$

where $\mathbf{R}$ is the vector which joins X and the center of mass of BC , r is the BC interatomic distance, and θ is the angle between $\mathbf{R}$ and $\mathbf{r}$. In Eq. (2) l and j are the angular momentum operators associated with $\mathbf{R}$ and $\mathbf{r}$, respectively. The total angular momentum is $\mathbf{J} = \mathbf{l} + \mathbf{j}$. $m = m_X m_{BC} / (m_X + m_{BC})$ and $\mu = m_B m_C / (m_B + m_C)$ are the reduced masses of the total system and of the diatomic fragment BC , respectively. Finally, V^ϵ is the interaction potential in a given electronic state, ϵ .

In the asymptotic region ($R \rightarrow \infty$) where the intermolecular interaction has vanished, the diatomic fragments are described by the product $\chi_v^\epsilon(r) \Theta_{j\Omega}^{JM}(\hat{r}, \hat{R})$. χ_v^ϵ are “free” vibrational wave functions of BC ,

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + V_{BC}^\epsilon(r) - E_v \right\} \chi_v^\epsilon(r) = 0 \quad (3)$$

and $\Theta_{j\Omega}^{JM}$ are rotational functions in the body-fixed frame with the z axis attached to $\mathbf{R}$,²⁶

$$\Theta_{j\Omega}^{JM}(\hat{r}, \hat{R}) = \left[\frac{2J+1}{4\pi} \right]^{1/2} D_{M\Omega}^{J*}(\phi_R, \theta_R, 0) Y_{j\Omega}(\theta, \phi) \quad (4)$$

M and Ω are the projections of the total angular momentum $\mathbf{J}$ on the z axis of the space-fixed and body-fixed frames, respectively. $\hat{r} \equiv (\phi, \theta)$ are the polar angles specifying the direction of $\mathbf{r}$ with respect to the triatomic body-fixed frame, while $\hat{R} \equiv (\phi_R, \theta_R)$ are the polar angles of $\mathbf{R}$ in the space-fixed frame. $D_{M\Omega}^{J*}$ and $Y_{j\Omega}$ are the usual Wigner and spherical harmonics rotational functions.²⁷

The initial wave function Ψ_i is expanded as^{1,25}

$$\Psi_i(\mathbf{r}, \mathbf{R}) = \sum_v \sum_{j\Omega} \sum_n a_{vj\Omega n}^i \varphi_n(R) \chi_v^\epsilon(r) \Theta_{j\Omega}^{JM}(\hat{r}, \hat{R}), \quad (5)$$

where $\varphi_n(R)$ is an adapted basis set to describe the R coordinate. Introducing Eq. (5) in the corresponding Schrödinger equation and diagonalizing the resulting Hamiltonian matrix gives the eigenvalues E_i and the coefficients $a_{vj\Omega n}^i$.

The dissociative wave functions $|\Psi_{fE}\rangle$, $f \equiv (\epsilon JM \Omega v j)$, are also expanded as^{1,25}

$$\Psi_{fE}(\mathbf{r}, \mathbf{R}; E) = \sum_{v' j' \Omega'} \varphi_{v' j' \Omega'}^f(R; E) \chi_{v'}^\epsilon(r) \Theta_{j' \Omega'}^{JM}(\hat{r}, \hat{R}), \quad (6)$$

where the coefficients $\varphi_{v' j' \Omega'}^f$ are solutions of the system of second order coupled differential equations

$$\left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dR^2} + B_v j(j+1) - E \right\} \varphi_{vj\Omega}^{JMv\Omega}(R;E) \\ = - \sum_{v'j'\Omega'} \left\{ V_{vj\Omega, v'j'\Omega'}^\epsilon(R) \right. \\ \left. + \frac{\delta_{jj'}\delta_{vv'}}{2mR^2} \langle \Theta_{j\Omega}^{JM} | I^2 | \Theta_{j'\Omega'}^{JM} \rangle \right\} \varphi_{v'j'\Omega'}^{JMv\Omega}(R;E) \quad (7)$$

with the usual boundary conditions

$$\Psi_{fE}(\mathbf{r}, \mathbf{R}) \propto 0, \quad R \rightarrow 0$$

$$\Psi_{fE}(\mathbf{r}, \mathbf{R}) \propto \frac{e^{ik_{vj}R}}{\sqrt{k_{vj}}} \chi_v^\epsilon(r) \Theta_{j\Omega}^{JM}(\hat{r}, \hat{R}) - \sum_{v'j'\Omega'} S_{vj\Omega, v'j'\Omega'}^*(E) \\ \times \frac{e^{-ik_{v'j'}R}}{\sqrt{k_{v'j'}}} \chi_{v'}^\epsilon(r) \Theta_{j'\Omega'}^{JM}(\hat{r}, \hat{R}). \quad (8)$$

In Eq. (7), the following notations were introduced:

$$B_v = \left\langle \chi_v^\epsilon \left| \frac{\hbar^2}{2\mu r^2} \right| \chi_v^\epsilon \right\rangle, \\ V_{vj\Omega, v'j'\Omega'}^\epsilon(R) = \delta_{\Omega\Omega'} \langle \chi_v^\epsilon \Theta_{j\Omega}^{JM} | V^\epsilon(r, R, \theta) | \Theta_{j'\Omega'}^{JM} \chi_{v'}^\epsilon \rangle, \\ \langle \Theta_{j\Omega}^{JM} | I^2 | \Theta_{j'\Omega'}^{JM} \rangle = \delta_{jj'} \delta_{\Omega\Omega'} [J(J+1) + j(j+1) - 2\Omega^2] \\ - \delta_{jj'} \delta_{\Omega\Omega' \pm 1} [J(J+1) - \Omega'(\Omega' \pm 1)]^{1/2} \\ \times [j(j+1) - \Omega'(\Omega' \pm 1)]^{1/2}, \quad (9)$$

$$k_{vj} = \sqrt{2m[E - E_v - B_v j(j+1)]/\hbar}.$$

The transition operator is expressed as

$$\mathcal{M} \cdot \mathbf{e} = \sum_{pt} (-1)^p (\mathbf{e})_{-p} D_{pt}^{1*}(\phi_R, \theta_R, 0) (\mathcal{M})_t(r, R, \theta, \phi), \quad (10)$$

where $(\mathbf{e})_p$ and $(\mathcal{M})_t$ are spherical components of $\mathbf{e}$ and $\mathcal{M}$ referred to the space-fixed and body-fixed frames, respectively.

Finally, the total cross section for photodissociation is given by

$$\sigma_i(E) = \sum_f \sigma_{f-i}(E), \quad (11)$$

from which the final state distribution of the fragments can be calculated as

$$P_f(E) = \sigma_{f-i}(E)/\sigma_i(E). \quad (12)$$

B. Time-dependent approach

In a time dependent approach, the total cross section is given by²⁸

$$\sigma_i(E) \\ = \frac{2\pi(E - E_i)}{\hbar^2 c} \int_{-\infty}^{\infty} dt e^{iEt/\hbar} \langle \Psi(\mathbf{r}, \mathbf{R}; t=0) | \Psi(\mathbf{r}, \mathbf{R}; t) \rangle, \quad (13)$$

where

$$|\Psi(\mathbf{r}, \mathbf{R}; t=0)\rangle = \mathcal{M} \cdot \mathbf{e} |\Psi_i(\mathbf{r}, \mathbf{R})\rangle, \quad (14) \\ |\Psi(\mathbf{r}, \mathbf{R}; t)\rangle = e^{-iHt/\hbar} |\Psi(\mathbf{r}, \mathbf{R}; t=0)\rangle.$$

H is the nuclear Hamiltonian corresponding to the excited electronic state.

The wave packet $|\Psi(t)\rangle$ is expanded in the basis set defined in Eqs. (3) and (4)

$$|\Psi(\mathbf{r}, \mathbf{R}; t)\rangle = \sum_{vj\Omega} \varphi_{vj\Omega}^J(R; t) |\chi_v^\epsilon(r)\rangle |\Theta_{j\Omega}^{JM}(\hat{r}, \hat{R})\rangle \quad (15)$$

and the coefficients $\varphi_{vj\Omega}^J(R; t)$ are solution of the system of first order differential equations

$$i\hbar \frac{\partial \varphi_{vj\Omega}^J(R; t)}{\partial t} = \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + B_v j(j+1) \right\} \varphi_{vj\Omega}^J(R; t) \\ + \sum_{v'j'\Omega'} \left\{ \delta_{\Omega\Omega'} V_{vj\Omega, v'j'\Omega'}^\epsilon(R) \right. \\ \left. + \frac{\delta_{jj'}\delta_{vv'}}{2mR^2} \langle \Theta_{j\Omega}^{JM} | I^2 | \Theta_{j'\Omega'}^{JM} \rangle \right\} \varphi_{v'j'\Omega'}^J(R; t). \quad (16)$$

The population of the different (v, j, Ω) channels as a function of time can then be expressed as

$$P_{vj\Omega}^J(t) = \frac{\int_0^\infty \varphi_{vj\Omega}^{J*}(R; t) \varphi_{vj\Omega}^J(R; t) dR}{\sum_{v'j'\Omega'} \int_0^\infty \varphi_{v'j'\Omega'}^{J*}(R; t) \varphi_{v'j'\Omega'}^J(R; t) dR} \quad (17)$$

which should go to zero as t grows infinite for closed channels. The denominator in Eq. (17) is necessary because the wavepacket as defined in Eq. (14) is not normalized.

C. Application to van der Waals molecules

For van der Waals molecules the interaction potential in an electronic state denoted by ϵ can be written as

$$V^\epsilon(r, R, \theta) = V_{BC}^\epsilon(r) + W^\epsilon(r, R, \theta), \quad (18)$$

where $V_{BC}^\epsilon(r)$ is the intramolecular potential of the chromophore and $W^\epsilon(r, R, \theta)$ is the intermolecular interaction. There is a natural separation between the fast intramolecular motion (in this case, the BC vibration) and the slow intermolecular motions (van der Waals stretch and bend). Therefore, the following diabatic basis set is well adapted to these systems. The intramolecular diatomic mode is described by $\chi_v^\epsilon(r)$ given in Eq. (3). The total Hamiltonian is partitioned as $H = H_0 + V$ where

$$H_0 = \sum_v |\chi_v^\epsilon\rangle H_v^\epsilon(\hat{r}, \mathbf{R}) \langle \chi_v^\epsilon| \quad \text{with} \quad H_v^\epsilon = \langle \chi_v^\epsilon | H | \chi_v^\epsilon \rangle,$$

$$V = \sum_v \sum_{v' \neq v} |\chi_v^\epsilon\rangle V_{vv'}^\epsilon(\hat{r}, \mathbf{R}) \langle \chi_{v'}^\epsilon| \quad \text{with} \quad V_{vv'}^\epsilon = \langle \chi_v^\epsilon | H | \chi_{v'}^\epsilon \rangle. \quad (19)$$

The eigenfunctions of H_v^ϵ are taken as the basis set for the intermolecular motion. These functions are of two types: the discrete ones, Φ_{vn}^ϵ , corresponding to a given stretching-bending van der Waals state n , with energy E_{vn}^ϵ ; and the continua $\Phi_{vj\Omega E}^\epsilon$ with total energy E , corresponding to a final rotational state (j, Ω) of the BC fragment. The diabatic separation is very accurate for the initial wave function

$$\Psi_i(\mathbf{r}, \mathbf{R}) \approx \chi_{v=0}^{\epsilon=X}(r) \Phi_{v=0, n=0}^{\epsilon=X}(\hat{r}, \mathbf{R}) \quad (20)$$

because the vibrational frequency for BC is usually quite large.

The exact wave function for the final (dissociative) state [Eq. (6)] can be analyzed in terms of the diabatic basis set^{10,29,30}

$$\begin{aligned} \Psi_{fE}(\mathbf{r}, \mathbf{R}) = & \sum_{v'} \chi_{v'}^\epsilon(r) \left\{ \sum_{n'} a_{v'n'}^f(E) \Phi_{v'n'}^\epsilon(\hat{r}, \mathbf{R}) \right. \\ & \left. + \sum_{j'\Omega'} \int dE' b_{v'j'\Omega'E'}^f(E) \Phi_{v'j'\Omega'E'}^\epsilon(\hat{r}, \mathbf{R}) \right\}. \end{aligned} \quad (21)$$

An important simplification is introduced to calculate the $a_{v'n'}^f(E)$ and $b_{v'j'\Omega'E'}^f(E)$ coefficients when only the couplings corresponding to $\Delta v = \pm 1$ are included. This approach is based on the fact that experimentally the first energetically accessible v level of the final vibrational distribution of the diatomic molecule BC typically accounts for more than 95% of the total probability.²⁴ Also it has been shown¹ that when all the couplings with $|\Delta v| > 1$ are neglected, the vibrational branching ratios change by less than 2% as compared with the “exact” results.

In the case of the Cl_2 complexes with He, Ne, and Ar, the van der Waals interaction $W(r, R, \theta)$ are very similar for the ground and the B excited electronic state. The van der Waals functions in each electronic state only differ by a geometric factor introduced by the different χ_v^ϵ functions. This conclusion is based on the fact that no progressions on the van der Waals modes are observed in the spectra. Hence the potentials for the van der Waals modes have quite similar anharmonicities and equilibrium distances, and the corresponding functions in the X and B states differ very little, i.e.,

$$\langle \Phi_{vn}^\epsilon | \Phi_{v'n'}^{\epsilon'} \rangle \approx \delta_{nn'}, \quad (22)$$

$$\langle \Phi_{vn}^\epsilon | \Phi_{v'j'\Omega'E-}^{\epsilon'} \rangle \approx 0.$$

This is not always the case and very recently it has been shown that the van der Waals interaction changes dramatically for open-shell systems like $\text{Ar} \cdots \text{OH}$.^{31,32}

A second major characteristic of these systems is that the oscillator strength is mainly carried by the diatomic molecule. The components of the transition dipole in the body fixed frame [Eq. (10)] are given by²⁵

$$(\mathcal{M})_i = \sum_d D_{id}^{1*}(\phi, \theta, 0) (\mathcal{M})_d. \quad (23)$$

$(\mathcal{M})_d$ are the tensorial components of the electric dipole transition operator in the diatomic body-fixed frame. The transition operator in Eq. (10) takes the form

$$\begin{aligned} \mathcal{M} \cdot \mathbf{e} = & \sum_p \sum_i \sum_d (-1)^p (\mathbf{e})_{-p} D_{pi}^{1*}(\phi_R, \theta_R, 0) \\ & \times D_{id}^{1*}(\phi, \theta, 0) (\mathcal{M})_d(r). \end{aligned} \quad (24)$$

In Eq. (23), the transition is either parallel ($d=0$) or perpendicular ($d=\pm 1$) for the diatomic molecule. However, with respect to the total system the transition will have a mixed character given by the rotation between the diatomic and the triatomic body-fixed frames, as expressed in Eq. (23).

In what follows we shall consider several models for describing the single and multiple resonance cases. Based on the preceding considerations, simplified expressions will be obtained for the two main quantities of interest in this context, i.e., the photoabsorption cross section and the time evolution of the population of the zero order states.

D. Direct vibrational predissociation: Isolated resonance

When the van der Waals bond energy is less than the separation between two adjacent vibrational levels of the diatomic fragment, the dissociative wave function in the vicinity of a given zero order bound level $\Phi_{vn}^\epsilon \chi_v^\epsilon$ can be written as²⁹

$$\begin{aligned} \Psi_{fE}(\mathbf{r}, \mathbf{R}) \approx & a_{vn}(E; f) \Phi_{vn}^\epsilon(\hat{r}, \mathbf{R}) \chi_v^\epsilon(r) \\ & + \sum_{j'\Omega'} \int dE' b_{v-1j'\Omega'E'}^f(E) \\ & \times \Phi_{v-1j'\Omega'E'}^\epsilon(\hat{r}, \mathbf{R}) \chi_{v-1}^\epsilon(r). \end{aligned} \quad (25)$$

As expressed in Eq. (22), direct excitation of the zero-order continuum is forbidden for the Cl_2 complexes and no Beutler–Fano profiles are observed. Defining the quantities²⁹

$$\begin{aligned} \Delta(E) = & \sum_{f'} \mathcal{P} \int dE' \frac{|V_{v,n,f',E'}^\epsilon|^2}{E - E'}, \\ \Gamma(E) = & \sum_{f'} \Gamma_{f'}(E) = \sum_{f'} \pi |V_{v,n,f',E'}^\epsilon|^2, \end{aligned} \quad (26)$$

$$V_{v,n,f',E}^\epsilon = \langle \Phi_{vn}^\epsilon | V_{vv'}^\epsilon | \Phi_{v'j'\Omega'E-}^\epsilon \rangle,$$

where $V_{v,n,f',E}^\epsilon$ is considered to be constant in the vicinity of the resonance, the partial cross section [Eq. (1)] near the energy of the resonance, $E_r = E_{vn}^\epsilon + \Delta$, takes the form

$$\sigma_{f \rightarrow i}(E) \approx \frac{4\pi^2(E-E_i)}{\hbar c} \frac{\Gamma_f/\pi}{(E-E_r)^2 + \Gamma^2} \left| \sum_d \langle \chi_{v'=0}^{\epsilon'=X}(r) | (\mathcal{M})_d | \chi_v^{\epsilon}(r) \rangle \right. \\ \left. \times \sum_{pt} (-1)^p (\mathbf{e})_{-p} \langle \Phi_{v'=0, n'=0}^{\epsilon'=X}(\hat{r}, \mathbf{R}) | D_{pt}^{1*}(\hat{R}) D_{td}^{1*}(\hat{r}) | \Phi_{vn}^{\epsilon}(\hat{r}, \mathbf{R}) \rangle \right|^2. \quad (27)$$

In Eq. (27) the energy dependence is Lorentzian as given by the second term on the right-hand side (neglecting the slow linear dependence with the photon energy). This behavior has been confirmed in exact calculations, showing that the preceding approximations are generally correct. The third term on the right-hand side of Eq. (27) only depends on the vibration of the diatomic subunit and the Franck-Condon approximation usually holds. The last term gives a selection rule: since the Wigner matrices only depend on the orientation of the vectors, no excitation can be obtained in the stretching van der Waals mode because of the similarity of the van der Waals potentials in the ground and electronically excited states. Also, only one rotational quantum is transferred by photon excitation.

In this case, the time evolution of the dissociation is exponential

$$P_d(t) = 1 - e^{-2\Gamma t/\hbar}. \quad (28)$$

Each final state is populated at the same rate but with a fraction depending on its partial width

$$P_d^f(t) = 1 - \frac{\Gamma_f}{\Gamma} e^{-2\Gamma t/\hbar}. \quad (29)$$

III. MODELS FOR IVR IN VAN DER WAALS MOLECULES

When the van der Waals bond energy is greater than the separation between two vibrational levels of the diatomic subunit, the zero-order bright level, $E_{vn=0}^{\epsilon}$, may be close to one or more zero-order dark states, $E_{v'n'}^{\epsilon}$ with $v' < v$ and $n' \gg 0$. The dark states do not have oscillator strength from the ground level because of small Franck-Condon factors for the van der Waals modes. When the coupling between the different v channels is included, the bright and dark states mix and the oscillator strength is shared. This is the time-independent description of IVR. Several general formalisms have been proposed for describing IVR in different situations.^{3,4,10}

For $\text{Ar} \cdots \text{Cl}_2$, $v=10$ and 11 , IVR occurs in the sparse limit.¹ This means that the IVR is mainly due to the interaction of two zero-order discrete states, the $(v, n=0)$ bright state and one $(v-1, n' \gg n)$ dark state. The absorption spectrum exhibits two peaks in the region of the $(v, n=0)$ resonance, corresponding to the resulting diagonalized states. Their intensities are proportional to the bright character and their width to the dark character (the squared coefficient of the bright or dark zero-order state) of these quasibound eigenstates. Since the dark level corresponds to high excitation in the van der Waals modes, its nodal pattern was too complicated to be assigned to a specific bend-stretch pair of quantum numbers. The calculated final ro-

tational distributions for the two peaks were almost identical, since the dissociation dynamics are determined by the same dark character for the two eigenstates. Since a different dark state will be active for each vibrational level of Cl_2 initially excited, this explains why a different rotational distribution is observed for each initial Cl_2 level. This is in contrast to the behavior for $\text{He} \cdots \text{Cl}_2$ and $\text{Ne} \cdots \text{Cl}_2$, which dissociate by direct coupling of the initial state with the continuum and therefore show little dependence of the product state distribution on the Cl_2 stretching level.

An experimental signature of IVR, in the sparse and the intermediate regimes, is nonexponential decay of the initially excited state.^{7,10} Zewail and co-workers have measured the time evolution of dissociation for $\text{Ar} \cdots \text{I}_2$,²² for which IVR is expected to be important.²³ However, only exponential decay was observed. This is probably due to either a high density of states in the dark manifold or rotational congestion. $\text{Ar} \cdots \text{Cl}_2$ is a good candidate for observing nonexponential decay, since the density of dark states is low. One purpose of this study is to estimate the effect of rotational congestion, which should be less for $\text{Ar} \cdots \text{Cl}_2$ than for $\text{Ar} \cdots \text{I}_2$.

A. Zero-order two-state model

First, we consider the two zero-order bound states relaxing to a continuum. The bright state ($\psi_b \equiv \chi_v^{\epsilon} \Phi_{v,n=0}^{\epsilon}$) and the dark state ($\psi_d \equiv \chi_{v-1}^{\epsilon} \Phi_{v-1,n \gg 0}^{\epsilon}$) have energies E_b and E_a , respectively. The continuum family of states is represented as $\psi_E \equiv \chi_{v-2}^{\epsilon} \Phi_{v-2,E}^{\epsilon}$. It is assumed that these states are sufficient to describe the exact wave function, i.e.,

$$1 = |\psi_b\rangle\langle\psi_b| + |\psi_d\rangle\langle\psi_d| + \int dE |\psi_E\rangle\langle\psi_E|. \quad (30)$$

We consider the following coupling scheme, illustrated in Fig. 1:

FIG. 1. Zero-order model diagram.

$$\begin{aligned} V_{bd} &= \langle \psi_b | H | \psi_d \rangle, \\ V_{bE} &= \langle \psi_b | H | \psi_E \rangle = 0, \\ V_{dE} &= \langle \psi_d | H | \psi_E \rangle. \end{aligned} \quad (31)$$

V_{dE} is assumed to be constant in the vicinity of the resonance and all the other couplings are neglected.

Using the Lippmann–Schwinger equation

$$\Psi(E) = \psi_E + G^+(E) V \psi_E \quad (32)$$

with

$$\lim_{\nu \rightarrow 0^+} (E + i\nu - H) G^+(E) = 1$$

and introducing the closure relation of Eq. (30) the total wave function of the system is expressed as

$$\Psi(E) = b(E) \psi_b + d(E) \psi_d + \int dE' c_{E'}(E) \psi_{E'}. \quad (33)$$

The coefficients $b(E)$, $d(E)$, $c_{E'}(E)$ depend on the matrix elements of the resolvent operator, $G^+(E)$. They are obtained by solving the system of equations resulting from introducing the closure relationship

$$\begin{aligned} 1 &= (E - H) \left\{ |\psi_b\rangle \langle \psi_b| + |\psi_d\rangle \langle \psi_d| \right. \\ &\quad \left. + \int dE |\psi_E\rangle \langle \psi_E| \right\} G^+(E) \end{aligned} \quad (34)$$

into the expression of the overlaps between the zero-order functions.

In addition, we assume that only the bright state carries oscillator strength from the ground level [i.e., $\langle \Psi_i | \mathbf{M} \cdot \mathbf{e} | \Psi(E) \rangle \approx \langle \Psi_i | \mathbf{M} \cdot \mathbf{e} | \psi_b \rangle b(E)$], so that the absorption cross section takes the form

$$\sigma(E) \approx \frac{4\pi^2(E - E_i)}{\hbar c} |\langle \Psi_i | \mathbf{M} \cdot \mathbf{e} | \psi_b \rangle|^2 \frac{|V_{bd}|^2 \Gamma / \pi}{(E - E_b)^2 [(E - E'_d)^2 + \Gamma^2] + |V_{bd}|^4 - 2(E - E_b)(E - E'_d)|V_{bd}|^2}, \quad (35)$$

where

$$\begin{aligned} \Gamma &= \pi |V_{dE}|^2 \\ E'_d &= E_d + \mathcal{P} \int dE \frac{|V_{dE}|^2}{E_d - E} \end{aligned} \quad (36)$$

and $\mathcal{P}$ denotes the “principal part.”

We now consider the time evolution of dissociation. The initial wave packet (to within a multiplicative constant) is approximately equal to the bright state, i.e., $\Psi(t=0) = \Psi_b$ and its time evolution is given by $\Psi(t) = e^{-iHt/\hbar} \Psi_b$. The fractional population of a zero-order state ψ_α is given by the square of the matrix element of the evolution operator between ψ_b and ψ_α . For the evaluation of these matrix elements we use^{7,11,33}

$$\langle \psi_\alpha | e^{-iHt/\hbar} | \psi_b \rangle = \frac{i}{2\pi} \int_{-\infty}^{\infty} dE e^{-iEt/\hbar} \langle \psi_\alpha | G^+(E) | \psi_b \rangle \quad (37)$$

for $t \geq 0$, where α and β can be b , d or E , as needed.

After integration in the complex plane the probabilities of finding the system in a given state at time t are

$$\begin{aligned} P_b(t) &= \frac{e^{-\Gamma t/\hbar}}{4|\omega|^2} \{k_1 e^{\omega t/\hbar} + k_2 e^{-\omega t/\hbar} - k_3 \cos \omega t/\hbar \\ &\quad + k_4 \sin \omega t/\hbar\}, \\ P_d(t) &= \frac{e^{-\Gamma t/\hbar}}{|\omega|^2} |V_{bd}|^2 \{e^{\omega t/\hbar} + e^{-\omega t/\hbar} - 2 \cos \omega t/\hbar\} \end{aligned} \quad (38)$$

$$\begin{aligned} P_c(t) &= 1 - \frac{e^{-\Gamma t/\hbar}}{4|\omega|^2} \{ (k_1 + 4|V_{bd}|^2) e^{\omega t/\hbar} \\ &\quad + (k_2 + 4|V_{bd}|^2) e^{-\omega t/\hbar} - (k_3 + 8|V_{bd}|^2) \} \end{aligned}$$

$$\times \cos \omega t/\hbar + k_4 \sin \omega t/\hbar\},$$

where

$$\begin{aligned} \omega &= \omega_r + i\omega_i = \sqrt{(\delta + i\Gamma)^2 + 4|V_{bd}|^2}, \\ \delta &= E_b - E'_d, \\ k_1 &= (\delta + \omega_r)^2 + (\Gamma + \omega_i)^2, \\ k_2 &= (\delta - \omega_r)^2 + (\Gamma - \omega_i)^2, \\ k_3 &= 2(\delta^2 - \omega_r^2 + \Gamma^2 - \omega_i^2), \\ k_4 &= 4(\delta\omega_i - \Gamma\omega_r) \end{aligned} \quad (39)$$

and it is assumed that $\omega_i < \Gamma$.^{8,10}

If the coupling to the continuum is zero,^{30,34} $\Gamma = 0$ and the populations of the bound states oscillate. The oscillation frequency is $\omega_r/\hbar = |E_b - E'_d|/\hbar$. The time-dependent population of the zero-order states is given by

$$\begin{aligned} P_b(t) &= 1 - \frac{2|V_{bd}|^2}{\omega_r^2} \left(1 - \cos \frac{\omega_r t}{\hbar} \right), \\ P_d(t) &= \frac{2|V_{bd}|^2}{\omega_r^2} \left(1 - \cos \frac{\omega_r t}{\hbar} \right). \end{aligned} \quad (40)$$

Note that the populations are out of phase by π .

When coupling to the continuum is included, the zero-order populations, Eq. (38), include an exponential decay. The decay rate is that of the dark state. The dephasing

between the bound state populations is no longer π . In addition, the dissociation probability is not simply the sum of two decaying exponentials. It is modulated by oscillating terms which have a clear physical explanation. Since only the dark state is coupled to the continuum, the dissociation rate is directly related to the population of this state, and thus follows its oscillations. This is analogous to fluorescence quantum beats as described by Freed and Nitzan.⁷ While the fluorescence oscillates with the population of the zero-order state, the probability of dissociation at time t is given by the integrated probability from $t=0$ to t .

B. First-order two-state model

In the zero-order model discussed above, there is no direct coupling between the bright state and the continuum. Although such coupling is small for $\text{Ar} \cdots \text{Cl}_2$, it can play an important role in the proper description of the dynamics. In this section, we consider the effects of competition between direct dissociation and dissociation *via* IVR.

It is convenient to first diagonalize the discrete subspace as

$$\begin{aligned}\psi_1 &= \alpha \psi_b + \beta \psi_d, \\ \psi_2 &= -\beta \psi_b + \alpha \psi_d.\end{aligned}\quad (41)$$

Both ψ_1 and ψ_2 absorb and they are both coupled to the continuum, as illustrated in Fig. 2,

$$\begin{aligned}\langle \Psi_i | \mathcal{M} \cdot \mathbf{e} | \psi_1 \rangle &= \alpha \langle \Psi_i | \mathcal{M} \cdot \mathbf{e} | \psi_b \rangle, \\ V_{1E} &= \langle \psi_1 | H | \psi_E \rangle = \alpha V_{bE} + \beta V_{dE}, \\ \langle \Psi_i | \mathcal{M} \cdot \mathbf{e} | \psi_2 \rangle &= -\beta \langle \Psi_i | \mathcal{M} \cdot \mathbf{e} | \psi_b \rangle, \\ V_{2E} &= \langle \psi_2 | H | \psi_E \rangle = -\beta V_{bE} + \alpha V_{dE}.\end{aligned}\quad (42)$$

For convenience, we make the following definitions which are analogous to the ones of Eq. (36):

$$\begin{aligned}E'_1 &= E_1 + \mathcal{P} \int dE \frac{|V_{1E}|^2}{E_1 - E}, \\ E'_2 &= E_2 + \mathcal{P} \int dE \frac{|V_{2E}|^2}{E_2 - E}, \\ \mathcal{P} \int dE \frac{V_{2E} V_{1E}^*}{E' - E} &\approx 0, \\ \Gamma_1 &= \pi |V_{1E}|^2, \\ \Gamma_2 &= \pi |V_{2E}|^2, \\ \Gamma_{12} &= \sqrt{\Gamma_1 \Gamma_2}.\end{aligned}\quad (43)$$

The photoabsorption cross section is then given by

$$\begin{aligned}\sigma(E) &= \frac{4\pi^2(E-E_i)}{\hbar c} |\langle \Psi_i | \mathcal{M} \cdot \mathbf{e} | \psi_b \rangle|^2 \left[\frac{\alpha^2 \Gamma_1 / \pi \{(E-E'_2)^2 + \Gamma_2^2\} + \beta^2 \Gamma_2 / \pi \{(E-E'_1)^2 + \Gamma_1^2\}}{\{(E-E'_1)^2 + \Gamma_1^2\} \{(E-E'_2)^2 + \Gamma_2^2\} + \Gamma_{12}^4 - 2\Gamma_{12}^2 \{(E-E'_1)(E-E'_2) - \Gamma_{12}^2\}} \right] \\ &\quad - \frac{2\alpha\beta\Gamma_{12}(E-E'_1)(E-E'_2) + \Gamma_{12}^2 \{\alpha^2\Gamma_2 + \beta^2\Gamma_1\}}{\{(E-E'_1)^2 + \Gamma_1^2\} \{(E-E'_2)^2 + \Gamma_2^2\} + \Gamma_{12}^4 - 2\Gamma_{12}^2 \{(E-E'_1)(E-E'_2) - \Gamma_{12}^2\}}.\end{aligned}\quad (44)$$

This will reduce to Eq. (35) when $\Gamma_1 = \beta^2\Gamma$ and $\Gamma_2 = \alpha^2\Gamma$, i.e., when no direct coupling from the bright state to the continuum is considered. Using a procedure analogous to that of the previous section, the population of the zero-order states as a function of time are given by

$$\begin{aligned}P_b(t) &= \frac{e^{-(\Gamma_1 + \Gamma_2)t/\hbar}}{4|\omega|^2} \{k_{b1} e^{\omega t/\hbar} + k_{b2} e^{-\omega t/\hbar} \\ &\quad - k_{b3} \cos \omega t/\hbar - k_{b4} \sin \omega t/\hbar\} \\ P_d(t) &= \frac{e^{-(\Gamma_1 + \Gamma_2)t/\hbar}}{|\omega|^2} \frac{k_d}{4} \{e^{\omega t/\hbar} + e^{-\omega t/\hbar} - 2 \cos \omega t/\hbar\} \\ P_c(t) &= 1 - \frac{e^{-(\Gamma_1 + \Gamma_2)t/\hbar}}{4|\omega|^2} \{(k_{b1} + k_d) e^{\omega t/\hbar} \\ &\quad + (k_{b2} + k_d) e^{-\omega t/\hbar} - (k_{b3} + 2k_d) \cos \omega t/\hbar \\ &\quad - k_{b4} \sin \omega t/\hbar\},\end{aligned}\quad (45)$$

where

$$\begin{aligned}\omega &= \omega_r + i\omega_i = \sqrt{(\delta + i\gamma)^2 + 4\Gamma_{12}^2}, \\ \delta &= E'_1 - E'_2, \\ \gamma &= \Gamma_2 - \Gamma_1, \\ k_{b1} &= \nu^2 + |\omega|^2 + 2\omega_i\nu + 2\omega_r\mu, \\ k_{b2} &= \nu^2 + |\omega|^2 - 2\omega_i\nu - 2\omega_r\mu, \\ k_{b3} &= 2(\nu^2 + \mu^2 - |\omega|^2), \\ k_{b4} &= 4(\mu\omega_i - \nu\omega_r), \\ k_d &= (2\alpha\beta\delta)^2 + [2\Gamma_{12}(\beta^2 - \alpha^2) + 2\alpha\beta\gamma]^2, \\ \mu &= \delta(\alpha^2 - \beta^2), \\ \nu &= 4\alpha\beta\Gamma_{12} + \gamma(\alpha^2 - \beta^2),\end{aligned}\quad (46)$$

and it has been assumed that $\omega_i < \Gamma_1 + \Gamma_2$.

Again, the dissociation probability oscillates with time if the eigenstates are coherently excited. The physical interpretation of the oscillating dissociation probability is

FIG. 2. First-order model diagram.

analogous to that of the zero-order model, except that the coupling between the two eigenstates occurs indirectly via their coupling to the same continuum.

The origin of the oscillating dissociation probability is illustrated by considering the special case for which the width of each resonance is small compared to its distance from the other resonance, Γ_{12} can be assumed to be zero and the spectrum is given by the sum of two Lorentzian functions^{2,30}

$$\sigma(E) = \frac{4\pi^2(E-E_i)}{\hbar c} |\langle \Psi_i | \mathcal{M} \cdot \mathbf{e} | \psi_b \rangle|^2 \left[\frac{\alpha^2 \Gamma_1 / \pi}{(E-E_1')^2 + \Gamma_1^2} + \frac{\beta^2 \Gamma_2 / \pi}{(E-E_2')^2 + \Gamma_2^2} \right] \quad (47)$$

The populations of the two bound states again oscillate with a phase difference of π but the dissociation probability does not oscillate

$$\begin{aligned} P_b(t) &= \alpha^4 e^{-2\Gamma_1 t/\hbar} + \beta^4 e^{-2\Gamma_2 t/\hbar} \\ &\quad + 2\alpha^2 \beta^2 e^{-(\Gamma_1 + \Gamma_2)t/\hbar} \cos(E_1 - E_2)t/\hbar, \\ P_d(t) &= \alpha^2 \beta^2 \{ e^{-2\Gamma_1 t/\hbar} + e^{-2\Gamma_2 t/\hbar} \\ &\quad - 2e^{-(\Gamma_1 + \Gamma_2)t/\hbar} \cos(E_1 - E_2)t/\hbar \}, \\ P_c(t) &= 1 - \alpha^2 e^{-2\Gamma_1 t/\hbar} - \beta^2 e^{-2\Gamma_2 t/\hbar}. \end{aligned} \quad (48)$$

This is the case often applied to fluorescence quantum beats due to IVR^{6,7,22} for which the fluorescence intensity is proportional to the population of each zero-order state.⁶ The populations $P_b(t)$ and $P_d(t)$ given by Eqs. (45) and (48) are similar and either can describe the fluorescence intensity in the sparse limit. However, the probability of dissociation $P_c(t)$ is not the same for the two cases. In the sparse limit the coherence between IVR and dissociation may be important and then the first-order will give a more accurate description.

This model can easily be extended to the intermediate case, for which many dark states must be included, if it is assumed that the dark states are evenly spaced and each state has the same dissociation probability.^{3,4,6-11} As the number of dark states increases, the oscillatory behavior of

the dissociation probability is washed out. In the statistical limit, IVR becomes irreversible and $P_c(t)$ will decay exponentially as in Eq. (48).

C. Extension to three dimensions

For real molecules in three dimensions, there are many dissociative channels. Each channel corresponds to a specific final rovibrational state of the fragments. To treat this case, we consider two prediagonalized bound states, ψ_1 and ψ_2 , coupled to N families of continua, $\psi_{jE} \equiv \chi_{v-2} \Phi_{ev-2}^{jE-}$ (where j denotes the rovibrational state of the diatomic fragment). The continua are also prediagonalized, i.e.,

$$\langle \psi_{jE} | H | \psi_{j'E'} \rangle = E \delta(E - E') \delta_{jj'}. \quad (49)$$

The couplings are defined as

$$\begin{aligned} \Gamma_1 &= \pi \sum_j |\langle \psi_1 | H | \psi_{jE} \rangle|^2, \\ \Gamma_2 &= \pi \sum_j |\langle \psi_2 | H | \psi_{jE} \rangle|^2, \\ \Gamma_{12} &= \pi \sum_j \langle \psi_2 | H | \psi_{jE} \rangle^* \langle \psi_1 | H | \psi_{jE} \rangle. \end{aligned} \quad (50)$$

We have neglected the indirect couplings between the different continua via the discrete states:

$$\langle \psi_i | H | \psi_{jE} \rangle^* \langle \psi_{i'} | H | \psi_{j'E} \rangle \approx 0 \quad (51)$$

for $j \neq j'$ and $i, i' = 1, 2$. The absorption spectrum is given by Eq. (44).

If these assumptions are made, the total dissociation probability will be the same as that of the first-order model, Eq. (45). If the couplings of Eq. (51) were added to the model, this would add an additional coherence between the dissociation channels, and the dissociation into a particular state of the fragments would have a more complicated interference pattern.

IV. APPLICATION OF THE IVR MODELS TO $\text{Ar} \cdots \text{Cl}_2$

In this section we apply the IVR models developed above to the dissociation dynamics of $\text{Ar} \cdots \text{Cl}_2$ excited to $v=11$ of the Cl_2 stretch. First, we consider the two-dimensional case of a T-shaped complex dissociating to a single continuum. The two-dimensional model is useful to illustrate the fundamental aspects of IVR without the additional complications of bending motions in the complex and product rotational motion. In particular, the models show that the dissociation rate oscillates in time, in agreement with an exact time-dependent calculation. Next, the three-dimensional model is examined to determine if the oscillating dissociation rate can be observed for real molecules at a finite temperature. Also, the effect of rotational motion of the complex on the dissociation dynamics is investigated. Finally, the results of this study are applied to discuss the dissociation dynamics of $\text{Ar} \cdots \text{I}_2$.

A. IVR in two dimensions: Zero-order model

In order to apply the two-dimensional models to $\text{Ar} \cdots \text{Cl}_2(v=11)$, it is necessary to determine the appro-

FIG. 3. $\text{Ar}\cdots\text{Cl}_2$ absorption spectrum in the region of the transition to $\text{Ar}\cdots\text{Cl}_2(B, v=11)$. The origin corresponds to the $\text{Ar}+\text{Cl}_2(B, v=11) \leftarrow \text{Ar}\cdots\text{Cl}_2(X, v=0, n=0)$ transition. The continuous lines correspond to the numerical calculations while dotted lines correspond to the analytical zero-order model results using the parameters given in the text.

appropriate parameters. This was done by performing a time-independent spectrum calculation using the potential of Ref. 1, but fixing the angle between the van der Waals bond and the Cl_2 axis to $\pi/2$. The basis set for the calculation contains three Cl_2 stretching levels, $v=9, 10$, and 11 . Equation (7) was integrated between 2.5 and 15.0 Å using the Fox–Godwin–Numerov propagator with a grid of 1000 points. The results of this calculation are shown as the solid line in Fig. 3. Two resonances are observed, a sharp, intense one at -188.9 cm^{-1} , and a broad, weak one at -190.9 cm^{-1} . These correspond to the IVR eigenstates, and have mainly bright (-188.9 cm^{-1}) and dark (-190.9 cm^{-1}) character.

Next, exact time-dependent calculations for this potential were performed. At $t=0$, the wave function is taken to be the bright state obtained by coherent excitation of the two eigenstates observed in Fig. 3. Equation (16) was integrated between 2 and 180 Å using the split operator method³⁵ with a radial grid 2048 points. The results are shown as a solid line in Fig. 4. The wave packet is observed to oscillate between the bright and the dark states, and the dissociation products are produced at a rate proportional to the dark state probability.

The parameters of the zero-order model are then fitted to reproduce the numerical results shown in Fig. 3. The values obtained are $E_b = -189.19\text{ cm}^{-1}$, $E_d = -190.64\text{ cm}^{-1}$, $\Gamma = 0.2\text{ cm}^{-1}$, and $|V_{bd}|^2 = 0.5\text{ cm}^{-1}$. The model accurately reproduces the spectrum of Fig. 3. The interpretation of the time-independent IVR model has been given in detail previously.¹ In brief, the intensity from the bright state is shared by the dark state, and the width of the dark state is shared by the bright state.

As shown in Fig. 4, the zero-order IVR model is also able to reproduce the time-dependent populations of the

FIG. 4. Time evolution of the population probabilities of $v=9, 10$, and 11 . Lines correspond to the numerical results while dots correspond to the results obtained with the zero-order model.

bright state, dark state, and dissociation products. After photon excitation populates the bright ($v=11$) state, it is coupled by V_{bd} to the dark state ($v=10$). In this zero-order picture, this coupling causes an oscillatory energy transfer between the Cl_2 stretching mode and the $\text{Ar}\cdots\text{Cl}_2$ van der Waals modes. Since the dark state is coupled to the continuum ($v=9$), the rate of dissociation is proportional to the dark state probability, and oscillates in time. That the dark state acts as the doorway state is clearly illustrated in Fig. 4 since the build-up of dissociation products stops whenever the dark state probability is zero. Therefore the dissociation process is best described as sequential: from the bright state, to the dark state, to the continuum.

The evolution of the product state wave packet, $|\varphi_{v=9}|^2$, is shown in Fig. 5. The oscillating dissociation rate leads to an oscillation in the wave packet along the dissociative coordinate since when the dark state probability is zero no new dissociation products are produced. In addition, there is a high frequency oscillation of the product wave packet due to the complicated nodal pattern of the dark state wave function.

B. IVR in two dimensions: First-order model

In the first-order model, the possibility of coupling between the bright state and the continuum is added. The parameters for the model were fitted to the time-independent calculations as above, and the results are shown in Figs. 6 and 7. The parameters of the fit are $E_1 = -188.9104\text{ cm}^{-1}$, $E_2 = -190.8929\text{ cm}^{-1}$, $\Gamma_1 = 0.0249\text{ cm}^{-1}$, $\Gamma_2 = 0.1814\text{ cm}^{-1}$, and $\alpha^2 = 0.83$. Although it will be shown below that the coupling between the bright state and the continuum will account for only 3% of the dissociation, the fit of the first-order model to the exact 2D calculation is much better than that of the zero-order model, because the functional form of the

FIG. 5. Norm of the dissociative component of the wave packet [i.e., $|\varphi_{0=9}(R;t)|$] for different propagation times.

model directly reproduces the two Lorentzians of the spectrum. Unfortunately, it is not possible to obtain directly the parameters for the zero-order model from those of the first-order model because of the energy shifts induced by the coupling to the continuum.

The first-order model allows us to determine the relative importance of direct vs sequential dissociation of the bright state. The widths of the zero-order states, Γ_b and Γ_d , are obtained from Γ_1 and Γ_2 by rearranging Eqs. (42) and (43) to give

$$\begin{aligned}\Gamma_b &= \alpha^2 \Gamma_1 + \beta^2 \Gamma_2 - 2\alpha\beta \sqrt{\Gamma_1 \Gamma_2} = 0.0010 \text{ cm}^{-1}, \\ \Gamma_d &= \beta^2 \Gamma_1 + \alpha^2 \Gamma_2 + 2\alpha\beta \sqrt{\Gamma_1 \Gamma_2} = 0.2053 \text{ cm}^{-1}.\end{aligned}\quad (52)$$

The rate for direct dissociation of the bright state is proportional to Γ_b . The rate Γ_s for sequential dissociation of the bright state is given the mixing between the bright and dark states times the rate of dissociation for the dark state

$$\Gamma_s = \beta^2 \Gamma_d = 0.035 \text{ cm}^{-1}. \quad (53)$$

Sequential dissociation thus accounts for 97% of the total dissociation, direct dissociation for only 3%.

In the first-order model, the two resonances are coherently excited and dissociate into the same continuum. Therefore, there is an indirect coupling between the two states via the continuum. Since the total dissociation prob-

FIG. 6. Absorption spectra obtained in the numerical calculations (lines) and in the analytical fit (dots) using the first order model.

ability is given by the square of the sum of the eigenstate dissociation probability amplitudes, the crossed term leads to an interference. The width of the excitation pulse needed to observe this phenomenon is of the order of $|E_1 - E_2| \approx 1 \text{ cm}^{-1}$.

As discussed in Sec. III B, the oscillations in the dissociation rate for this model are due to the Γ_{12} interference term. The independent Lorentzian model,⁶ Eqs. (47) and (48), which is often used to describe the oscillations of bright and dark states, is equivalent to this model with $\Gamma_{12} = 0$. The time dependence predicted by the independent Lorentzian model is shown in Fig. 8. The model accurately reproduces the oscillations of the bright and dark states,

FIG. 7. Time evolution of the population probabilities on $v=9$, 10, and 11. Lines correspond to the numerical results while dots correspond to the first order model.

FIG. 8. Same as Fig. 7 where dots correspond to the two noninteracting Lorentzian models.

but it does not reproduce the oscillations in the dissociation rate. This shows why the independent Lorentzian model can be successfully used to interpret fluorescence quantum beats, but the more complete model presented here will be necessary when dissociation products are monitored.

C. IVR in three dimensions

In going to three dimensions, the van der Waals bending mode is added to the description of the $\text{Ar}\cdots\text{Cl}_2$ complex, and Cl_2 rotation is added to the description of the dissociation product. This adds considerable complexity to the exact numerical calculations, but the appropriate IVR model described in Sec. III C is quite similar to the two-dimensional case. The exact three-dimensional calculation of the spectrum for excitation of $\text{Ar}\cdots\text{Cl}_2$ in the region of the $v=10$ bright state has been described in detail elsewhere.¹ As shown in Fig. 9(a), the bright state is found to be mixed with a single dark state that in zero order corresponds to $v=9$ of the Cl_2 stretch and the 36th even van der Waals level. It was found that the product rotational distribution was the same for excitation of either of the two resonances. This was taken to be confirmation of the fact that the bright state mainly dissociates via a sequential mechanism through the dark state.¹

When the first-order IVR model is fitted to the exact spectrum, the following parameter values are obtained: $E_1 = -177.28077 \text{ cm}^{-1}$, $E_2 = -176.6928 \text{ cm}^{-1}$, $\Gamma_1 = 0.0288 \text{ cm}^{-1}$, $\Gamma_2 = 0.0827 \text{ cm}^{-1}$, and $\alpha^2 = 0.70$. Using these parameters, the time-dependent probabilities can be calculated and they are shown in Fig. 10. The oscillations of the bright and dark state probabilities and in the dissociation rate are qualitatively similar to those of the two-dimensional model.

FIG. 9. Absorption spectra for the transition $\text{Ar}\cdots\text{Cl}_2(v=0, \epsilon=X) \xrightarrow{h\nu} \text{Ar}\cdots\text{Cl}_2^*(v=10, \epsilon=B) \xrightarrow{P} \text{Ar} + \text{Cl}_2(v=6,7,8, \epsilon=B)$ for different initial J values and $\Omega=0$. Points correspond to numerical results while lines correspond to the fit obtained using the first order model (the parameters are listed in Table I). (a) $J=0$, $\Omega=0$, (b) $J=1$, $\Omega=0$, (c) $J=2$, $\Omega=0$, (d) $J=3$, $\Omega=0$, (e) $J=4$, $\Omega=0$, and (f) $J=5$, $\Omega=0$.

D. The role of rotation of the complex

The calculations performed above were for $J=0$. Unfortunately, it is difficult to impose this constraint on experimental results. Therefore, we investigate the role of rotational excitation of the $\text{Ar}\cdots\text{Cl}_2$ molecule on the IVR dynamics. In particular, we want to estimate whether it will be possible to observe the nonexponential production of dissociation products. The spectra for several values of J and Ω were calculated using the Coriolis decoupling approximation, which has been shown to be accurate for similar molecules.³⁶ (Ω is the quantum number for the projection of $\mathbf{J}$ onto the $\text{Ar}-\text{Cl}_2$ axis.)

Figure 9 shows the spectra that are calculated for $J=0$ to 5, $\Omega=0$. As J increases from 0 to 5, the bright state energy increases faster than the dark state energy and the two resonances pass through each other at $J=3$, where the bright and dark states are evenly mixed. This is easily understood because the dark state corresponds to a high vibrational level of the van der Waals modes so that the moments of inertia for the dark state are larger than those of the bright state. Even though the degree of mixing of the zero-order states is a strong function of J , this has little

FIG. 10. Time evolution of the population probabilities on $v=8$, 9, and 10 obtained for the process $\text{Ar}\cdots\text{Cl}_2(v=0, \epsilon=X, J=0) \xrightarrow{h\nu} \text{Ar}\cdots\text{Cl}_2^*(v=10, \epsilon=B, J=0) \xrightarrow{\text{IVR}} \text{Ar}+\text{Cl}_2(v=6,7,8, \epsilon=B)$.

effect on the calculated product state distributions as shown in Fig. 11. This shows that the dissociation dynamics are controlled by the dark state, and that the dark state does not change with J for $\Omega=0$. Similar behavior was observed³⁶ for the direct dissociation of $\text{Ne}\cdots\text{Cl}_2$.

The spectra of Fig. 9 were fitted to the 3D IVR model, and the parameters are shown in Table I. These parameters were used to calculate the rate of appearance of dissociation products, and the results are shown in Fig. 12. Qualitatively, the oscillations in the rate of dissociation are independent of J for $\Omega=0$. This shows that there is little change in the dark state character with J even though the extent of mixing between the bright and dark states is a strong function of J .

Excitation of Ω has more profound effects. The first type of effect is fundamental, and is due to symmetry. Since odd Ω states are built from an odd parity basis and can only dissociate to odd values of the Cl_2 rotational quantum number, j , while even Ω states are built from an even parity basis and dissociate to even values of j , the even and odd states correspond to completely independent problems. Another effect is a kinematic constraint that requires that $j \geq \Omega$. Even within the even and odd manifolds of states, the dynamics change with Ω . This is illustrated in Figs. 13–15. Figure 13 shows the results of numerical spectrum calculations for $J=5$, $\Omega=0$ through 5. There is no obvious trend for the positions of the resonances as a function of Ω . There is a second dark state apparent in the spectra for $\Omega=3$ and 5. For $\Omega=4$, there is very little IVR mixing, and the bright state resonance is extremely narrow as expected for a direct $\Delta v=-2$ process.

The rotational distributions for excitation of the two strongest resonances for each value of J and Ω are shown in Fig. 14. Again, it is clear that different Ω states undergo quite different behavior. For $J=5$, $\Omega=0$, the two rota-

FIG. 11. Final rotational distribution of the Cl_2 fragments for different J , Ω values. Open circles correspond to E_1 , while closed circles correspond to E_2 . (a) $J=0$, $\Omega=0$, (b) $J=1$, $\Omega=0$, (c) $J=2$, $\Omega=0$, (d) $J=3$, $\Omega=0$, (e) $J=4$, $\Omega=0$, and (f) $J=5$, $\Omega=0$.

tional distributions are almost the same, indicating that the dynamics are governed by the dark state as before. For the other values of Ω , the two distributions are different in varying degrees. This is in contrast to the behavior of $\text{Ne}\cdots\text{Cl}_2$ and $\text{He}\cdots\text{Cl}_2$ which dissociate by a direct mechanism³⁶ and for which the rotational distributions were independent of both J and Ω , except for the symmetry and kinematic constraints discussed above. The dramatic variation with Ω of the product rotational distribution for dissociation of $\text{Ar}\cdots\text{Cl}_2$ indicates the varying importance of direct dissociation and contributions of a second dark state to the IVR dynamics. Also, the variation of the rotational distributions with Ω for $J=5$ is in contrast to the lack of variation with J for $\Omega=0$. This indicates that for different values of Ω the nature of the dark state is changing. As discussed above, the differences for odd versus even values of Ω are due to symmetry. However, there are also significant differences within each parity symmetry.

The dramatic effects of rotational excitation about the $\text{Ar}-\text{Cl}_2$ bond, i.e., changing Ω , are also apparent in Fig. 15, which shows the time dependence of dissociation. Both the total dissociation rate and the oscillations of the rate with time are different for each value of Ω . Clearly, if the non-exponential appearance of dissociation products is to be

TABLE I. First-order model parameters for the resonances found for $\text{Ar}\cdots\text{Cl}_2$ when it is excited to the B electronic state, $v=10$ as a function of J, Ω values. Energies (with respect to $\text{Cl}_2(B, v=10)$ asymptote) and widths are given in cm^{-1} . The energies of the transition ($E_1^B - E_{\text{ground}}^X$) are given with respect to the $\text{Cl}_2(X, v=0) \leftarrow \text{Cl}_2(B, v=10)$.

	E_{ground}^X	E_1^B	Γ_1	E_2^B	Γ_2	$E_1^B - E_{\text{ground}}^X$	$E_1^B - E_2^B$	α^2
$J=0, \Omega=0$	-179.2976	-177.2808	2.8789(-2)	-176.6928	8.2684(-2)	+2.0168	-0.588	0.70
$J=1, \Omega=0$	-179.2077	-177.1987	3.2538(-2)	-176.6235	6.5534(-2)	+2.0090	-0.5752	0.70
$J=2, \Omega=0$	-179.0280	-177.0352	3.9052(-2)	-176.4883	7.4398(-2)	+1.9928	-0.5469	0.60
$J=3, \Omega=0$	-178.7583	-176.7998	4.9753(-2)	-176.2655	6.9721(-2)	+1.9585	-0.5343	0.48
$J=4, \Omega=0$	-178.3989	-175.9584	3.5904(-2)	-176.5023	6.8837(-2)	+2.4405	-0.5439	0.60
$J=5, \Omega=0$	-177.9496	-175.5404	2.3767(-2)	-176.1698	9.2553(-2)	+2.4092	-0.6294	0.75
$J=5, \Omega=1$	-177.7477	-175.5734	5.9999(-3)	-176.0181	7.6208(-2)	+2.1743	-0.4447	0.85
$J=5, \Omega=2$	-177.1420	-175.2787	8.8159(-3)	-176.0812	1.0861(-1)	+1.8633	-0.8025	0.90
$J=5, \Omega=3$	-176.1325	-174.9795	1.1198(-2)	-174.7500	6.8503(-2)	+1.1530	-0.2295	~ 0.80
$J=5, \Omega=4$	-174.7194	-174.3643	1.1025(-3)	-173.1077	4.9836(-2)	+2.7956	-1.2566	0.98
$J=5, \Omega=5$	-172.9027	-173.5378	3.6667(-2)	-173.8722	4.6937(-2)	-0.6351	0.3344	0.58

observed in the laboratory, then one needs to limit the number of Ω values that contribute to the data. However, in order to achieve coherent excitation of the two eigenstates for each value of J and Ω , the laser bandwidth must be of the order of 1 cm^{-1} . Therefore the distribution in Ω can only be controlled by keeping the rotational temperature of the supersonic expansion as low as possible. This will also be true for high resolution experiments to observe the IVR splittings. Experiments performed to date²⁴ on $\text{Ar}\cdots\text{Cl}_2$ employed an effective rotational temperature of 1.3 K, yielding a distribution peaking at $\Omega=2$. This may be low enough to observe the oscillations in the dissociation rate. Also, it should be possible to change the experimental conditions to achieve a lower rotational temperature. Another possible technique to achieve more complete state selection to emphasize the oscillatory behavior of the dissociation rate would be to employ double resonance excitation. Although this may be difficult for $\text{Ar}\cdots\text{Cl}_2$, it may be possible for other van der Waals molecules for which

FIG. 12. Time evolution of dissociation for $J=0, 1, 2, 3, 4$, and 5 and $\Omega=0$.

infrared excitation in the ground electronic state is possible.

E. Comparison to $\text{Ar}\cdots\text{I}_2$

Gray²³ has performed three-dimensional time-dependent calculations for the vibrational predissociation of $\text{Ar}\cdots\text{I}_2$, and Zewail²² has measured the time-dependent

FIG. 13. Same as Fig. 9 but for (a) $J=5, \Omega=0$, (b) $J=5, \Omega=1$, (c) $J=5, \Omega=2$, (d) $J=5, \Omega=3$, (e) $J=5, \Omega=4$, and (f) $J=5, \Omega=5$.

FIG. 14. Same as Fig. 11 but for (a) $J=5$, $\Omega=0$, (b) $J=5$, $\Omega=1$, (c) $J=5$, $\Omega=2$, (d) $J=5$, $\Omega=3$, (e) $J=5$, $\Omega=4$, and (f) $J=5$, $\Omega=5$.

appearance of the I_2 product for this process. For the levels studied, $\text{Ar}\cdots\text{I}_2$ dissociates *via* a $\Delta v = -3$ mechanism. In the time-dependent calculation,²³ the populations of the bright state and the intermediate $\Delta v = -1$ level were found to oscillate quite similarly to the behavior of $\text{Ar}\cdots\text{Cl}_2$. The oscillations are less pronounced in the $\Delta v = -2$ population, and the period of any oscillations in the appearance of dissociation products, $\Delta v = -3$, is longer than 100 ps. This compares to a period of 50 ps for the oscillations of the bright state. In the IVR language, this illustrates that the initially excited state couples to a single dark state in the $\Delta v = -1$ manifold, which couples to a quasi-continuum in the $\Delta v = -2$ manifold before dissociation.

Even though the oscillations in the decay rate for $\text{Ar}\cdots\text{I}_2$ are less closely related to those of the initially excited level than for $\text{Ar}\cdots\text{Cl}_2$, it still appears that they should be observable. However, no oscillations were observed by Zewail *et al.* Rotational congestion will be more important for $\text{Ar}\cdots\text{I}_2$ than for $\text{Ar}\cdots\text{Cl}_2$. This could explain why no oscillations were observed in the dissociation rate. Another possible reason could be that the duration of the pump and probe pulses which overlap is of the order of 50 cm^{-1} in Zewail's experiments.²²

FIG. 15. Time evolution of dissociation for $\Omega=0, 1, 2, 3, 4$, and 5 and $J=5$.

V. SUMMARY AND CONCLUSIONS

In this paper we have described three models for IVR that can be applied to vibrational predissociation of van der Waals molecules. The ability of the models to reproduce the qualitative phenomena predicted by exact time-dependent and time-independent calculations for $\text{Ar}\cdots\text{Cl}_2$ was tested. The models accurately reproduce the spectrum and time-dependent populations for dynamics in two dimensions. The three-dimensional model was fitted to the spectrum calculation and used to predict the dissociation rate versus time. The dissociation rate was found to oscillate with time since it is proportional to the oscillating population of the dark state.

The IVR models facilitate a physical interpretation of the dynamics. Coherent excitation of the $\text{Ar}\cdots\text{Cl}_2$ complex with a laser bandwidth of the order of 1 cm^{-1} prepares the linear combination of the eigenstates corresponding to the bright state. In the zero-order model, the bright state couples to the dark state leading to oscillatory energy transfer between the Cl_2 stretching vibration and the van der Waals modes. The dark state couples to the continuum leading to vibrational predissociation. For high resolution excitation, two resonances should be observed: a narrow, intense one that has mainly bright state character; and a wider, less intense one that has mainly dark state character. Excitation of either of the two resonances leads to the same product rotational distribution because the dissociation dynamics are controlled by the dark state character of each eigenstate. The first-order model adds the possibility of direct coupling of the bright state to the continuum. For the two-dimensional case it is found that direct dissociation accounts for 3% of the total.

The qualitative behavior of the three-dimensional model was quite similar to that of the two-dimensional model. In particular, the oscillations of the rate of vibrational predissociation are not affected by the presence of

many product continuum channels. In addition, the effects of rotation of the initially excited state on the dissociation dynamics were examined. Since the bright and dark states have different moments of inertia, the degree of mixing will vary with J and Ω . In the case of $J=3$, $\Omega=0$, the mixing is complete and neither of the eigenstates is mainly a bright or dark state.

For $\Omega=0$, the different extent of mixing as a function of J between the bright and dark states has little effect on the dissociation dynamics. This shows that there is little change in the nature of the dark state with J for $\Omega=0$. In contrast, both the oscillations in the dissociation rate and the observed product state distributions are found to vary dramatically as Ω is changed for $J=5$. This can be attributed to two types of effects. First, the character of the dark state is a function of Ω for both symmetry and kinematic reasons. Second, in some cases a second dark state couples with the bright state. $J=5$, $\Omega=4$ is a particularly interesting case in that the IVR coupling is very small and the bright state mainly dissociates by a direct $\Delta v=-2$ mechanism.

Since the oscillations in the decay rate vary with Ω , rotational congestion will tend to mask these effects in experimental results. Particular care should be taken to achieve the greatest possible state selection in the laser excitation step. This could be achieved either by lowering the rotational temperature of the supersonic expansion or by double resonance excitation.

For experimental results on $\text{Ar}\cdots\text{I}_2$, no oscillations in the dissociation rate were observed²² even though such oscillations would be expected on the basis of time-dependent calculations by Gray.²³ The oscillations expected for $\text{Ar}\cdots\text{I}_2$ are less pronounced than those predicted for $\text{Ar}\cdots\text{Cl}_2$ due to the presence of a quasicontinuum in the $\Delta v=-2$ manifold of states for the $\Delta v=-3$ dissociation process. Also, rotational congestion will be even more difficult to eliminate for $\text{Ar}\cdots\text{I}_2$ than for $\text{Ar}\cdots\text{Cl}_2$.

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