A Uniform Theory of Preparation, Dissociation, and Product Formation in the Decay of Overlapping Resonances

Moshe Shapiro

Department of Chemical Physics, The Weizmann Institute of Science, Rehovot, 76100 Israel

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We present a uniform treatment of (the weak field) preparation and evolution of a superposition of overlapping resonances. We show that the manner of (the optical) preparation has profound effect on the observed decay dynamics when resonances overlap. Depending on the preparation pulse width, we find that the time evolution of the population and the fluorescence are different and that, contrary to common wisdom, fluorescence *is not* proportional to the autocorrelation ("survival") function. Moreover, we find that the interference between decaying overlapping resonances gives rise to transient surges in the total bound-state population. We also derive an analytic expression for the evolution of the various products states from inception to assumption of their long-time limits. We find that initially the formation of the products is dominated by off-resonance processes in which products appear and disappear instantaneously with the pulse. Only after the pulse vanishes does the build up of the product populations take place over time scales related to spectral features. This average buildup is shown to be modulated by bursts due to interference between resonances.

1. Introduction

It is customary to view dissociation and ionization as irreversible processes. However, in quantum mechanics, the irreversibility of the decay of a state is a function of the "flatness" of the continuum to which it is coupled. If the continuum is "flat" (i.e., the relevant cross section varies only little over energy scales comparable with the energetic width of the decaying state), the decay of an isolated resonance is guaranteed to be a monotonically decreasing function of time.[1−5] The same holds true for photodissociation (or photoionization) where the decay is induced by an oscillating electromagnetic field. Even if the field is strong, the decay is monotonic as long as the continuum is slowly varying.[6,7] In contrast, if the continuum is structured,[8−10] recurrences occur and the process is not entirely unidirectional.

An interesting question arises: can interferences between many decaying states, each coupled to a "flat" continuum, hence representing an irreversible decay, cause decay reversals? In other words, can an isolated molecule recombine spontaneously following its dissociation? A related question is whether under such circumstances decay (or reversal) occurs continuously or in bursts, as in classical mechanics.[11]

In this paper we endeavor to answer these questions by looking at a generic model of a superposition of overlapping resonances evolving in time. We examine the high-resolution spectrum, the time-dependent fluorescence to the ground state, and the overall population. Among other things, we find that the assumed proportionality between the fluorescence and the system autocorrelation function (the "survival") does not hold under normal (noninstantaneous) pulse preparation conditions. Moreover, we find that that the overall population decay is accompanied by bursts of population buildup in which reverse flux flows from the continuum to the bound manifold.

This paper is organized as follows: In section 2 we write down general expressions for the population, survival, and fluorescence of a superposition state prepared by a pulsed laser excitation. In section 3 we generalize the treatment to the case of the superposition of overlapping resonances. In section 4 we discuss the evolution of the product space. In section 5 we present computations exemplifying the formulation of sections 2−4 in which we examine the dependence of the various observables on the pulse

2. Population, Survival, and Fluorescence of a Decaying Superposition State

Assume that we create at time $t = t_0$ a superposition state,

$$|\Psi(t_0)\rangle = \sum_s a_{s,g}(t_0)|\phi_s\rangle \exp(-iE_s t_0/\hbar) \qquad (1)$$

where $|\Psi(t)\rangle$ is the system wave function at time t and $|\phi_s\rangle$, $s = 1, ..., N$ are a set of electronically excited bound states. In eq 1 $a_{s,g}(t)$ are the preparation coefficients of the superposition state from some precursor state $|\phi_g\rangle$ belonging to the ground electronic state. We consider preparation by an optical pulse, and if the pulse electric field, denoted as $\epsilon(t)$, is weak enough, we can use first-order perturbation theory to obtain that[12]

$$a_{s,g}(t) = (i/\hbar)\langle\phi_s|\mu|\phi_g\rangle\epsilon(\omega_{s,g},t) \qquad (2)$$

where μ is the transition-dipole operator, $\omega_{s,g} \equiv (E_s - E_g)/\hbar$ and

$$\epsilon(\omega,t) \equiv \int_{-\infty}^{t} \mathrm{d}t'\, \epsilon(t') \exp(i\omega t') \qquad (3)$$

is the finite-time Fourier transform of the pulse electric field amplitude. Due to this form and as shown elsewhere[12,13] the early time behavior $a_{s,g}(t)$ is dominated by *off-resonance* $\omega_{s,g}$ frequencies that are well outside the $\bar{\epsilon}(\omega)$ ($\equiv \lim_{t\to\infty} \epsilon(\omega,t)$) frequency profile of the pulse.

The overall population in the excited bound manifold at any subsequent time t is given as the sum over the probabilities to observe the system in each of the $|\phi_s\rangle$ states

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$$P(t) = \sum_s |\langle \phi_s | \Psi(t) \rangle|^2 \tag{4}$$

We note that $P(t)$ is an *incoherent* sum of terms (though each term may be the square of a *coherent* sum of amplitudes).

The "survival", or the system autocorrelation function, is given as

$$S(t_0,t) \equiv |\langle \Psi(t_0) | \Psi(t) \rangle|^2 = |\sum_s a_{s,g}(t_0) \exp(iE_s t_0/\hbar) \langle \phi_s | \Psi(t) \rangle|^2 \tag{5}$$

It contains the square of a coherent sum and is in general not equal to the population in the excited state manifold.

The fluorescence to the ground state is written as,

$$F_g(t) = A|\sum_s \langle \phi_g | \mu | \phi_s \rangle \langle \phi_s | \Psi(t) \rangle|^2 = A|\langle \phi_g | \mu | \Psi(t) \rangle|^2 \tag{6}$$

where A is a proportionality constant depending on the emitted frequency and $|\phi_g\rangle$ is the ground state the system emits to.

Before proceeding further we note that the usual assumption that the fluorescence is proportional to the survival,[14] holds true only when we assume excitation with an $\epsilon_0 \delta(t)$ (i.e., instantaneous) pulse. Under theses circumstances, we have from eqs 2 and 3 that

$$a_{s,g}(0) = (i/\hbar) \langle \phi_s | \mu | \phi_g \rangle \epsilon_0 \tag{7}$$

and (using eq 5) the survival is given as

$$S(0,t) = (\epsilon_0/\hbar) \sum_s \langle \phi_g | \mu | \phi_s \rangle \langle \phi_s | \Psi(t) \rangle|^2 = (\epsilon_0/\hbar)^2 |\langle \phi_g | \mu | \Psi(t) \rangle|^2 \tag{8}$$

Comparison of eqs 6 and 8 shows that for instantaneous ($\delta(t)$) pulses the survival is indeed proportional to the fluorescence. However, a pulse can be considered "instantaneous" only when its bandwidth encompasses the whole absorption spectrum.[12] In most situations this is not the case and we have from eq 3 that if t_0 occurs after the pulse

$$a_{s,g}(t_0) = (2\pi i/\hbar) \langle \phi_s | \mu | \phi_g \rangle \bar{\epsilon}(\omega_{s,g}) \tag{9}$$

where $\bar{\epsilon}(\omega)$ is the laser frequency profile

$$\bar{\epsilon}(\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}t\, \epsilon(t) \exp(i\omega t) \tag{10}$$

Under these circumstances, it follows from eq 5 that

$$S(t_0,t) = (2\pi/\hbar) \sum_s \bar{\epsilon}(\omega_{s,g}) \exp(iE_s t_0/\hbar) \langle \phi_g | \mu | \phi_s \rangle \langle \phi_s | \Psi(t) \rangle|^2 \tag{11}$$

and the survival is *not* proportional to the fluorescence.

3. Decay of a Superposition of Overlapping Resonances

The formulas developed in the previous section apply to the case where $|\phi_s\rangle$ are the eigenstates of the radiation free Hamiltonian. If each $|\phi_s\rangle$ state is coupled to a (dissociative) continuum, it ceases to be an eigenstate and becomes a *resonance*, i.e., a set of scattering eigenstates $|E,n^-\rangle$ of different energies E and fragment quantum numbers n, peaked about some energy value. The *incoming* $|E,n^-\rangle$ states, rather than the more conventional $|E,n^+\rangle$ states, are used,[2,15,16] because (as also shown in section 4) each $|E,n^-\rangle$ state correlates in the far *future* to a *single* asymptotic state.

Contrary to the previous section, the photon-absorption step now prepares a continuous superposition of $|E,n^-\rangle$ states, each acquiring an $\exp(-iEt/\hbar)$ phase factor as time progresses. It is still assumed that the $|E,n^-\rangle$ state is part of the electronically excited manifolds, hence

$$\langle \phi_g | E,n^- \rangle = 0 \tag{12}$$

The electronically excited state wave packet being created by the process of photon absorption is therefore given as

$$|\Psi(t)\rangle = \sum_n \int \mathrm{d}E |E,n^-\rangle a_{E,n}(t) \exp(-iEt/\hbar) \tag{13}$$

where $a_{E,n}(t)$ are continuum preparation coefficients, given in analogy to eq 3 as

$$a_{E,n}(t) = (i/\hbar) \langle E,n^- | \mu | \phi_g \rangle \epsilon(\omega_{E,g},t) \tag{14}$$

where $\omega_{E,g} \equiv (E - E_g)/\hbar$. Assuming that only the space spanned by the $|\phi_s\rangle$ states is optically coupled to $|\phi_g\rangle$ (i.e., the $|\phi_s\rangle$ states act as "doorway" states), we can write $\langle E,n^- | \mu | \phi_g \rangle$ as

$$\langle E,n^- | \mu | \phi_g \rangle = \sum_{s'} \langle E,n^- | \phi_{s'} \rangle \langle \phi_{s'} | \mu | \phi_g \rangle \tag{15}$$

and using eqs 13−15, we can write the amplitudes to observe a $|\phi_s\rangle$ states at time t as

$$\langle \phi_s | \Psi(t) \rangle = (i/\hbar) \sum_{s'} \langle \phi_{s'} | \mu | \phi_g \rangle \int_{-\infty}^{t} \mathrm{d}t'\, \epsilon(t') \exp(-iE_g t'/\hbar)$$

$$\sum_n \int \mathrm{d}E \exp[-iE(t - t')/\hbar] \langle \phi_s | E,n^- \rangle \langle E,n^- | \phi_{s'} \rangle \tag{16}$$

For noninteracting (though still overlapping) resonances we can parametrize the $\langle \phi_s | E,n^- \rangle$ overlap integrals as[2]

$$\langle \phi_s | E,n^- \rangle = \frac{V(s|E,n)}{E - E_s - \Delta_s(E) - i\Gamma_s(E)/2} \tag{17}$$

where $V(s|E,n\rangle$ denotes the Hamiltonian matrix element between the zero-order $|\phi_s\rangle$ state and some zero-order continuum states $|E,n;0\rangle$. The other quantities in eq 17 are defined in terms of $V(s|E,n)$ as

$$\Gamma_s(E) \equiv \sum_n 2\pi |V(s|E,n)|^2 \tag{19}$$

$$\Delta_s(E) \equiv \mathrm{P}_v \sum_n \int \mathrm{d}E' \frac{|V(s|E',n)|^2}{E - E'} \tag{20}$$

with P_v denoting a Cauchy principal value integral. It is possible to adopt the parametrization of eq 17 even when the ϕ_s resonances do interact. In that case the form of eq 17 arises from the diagonalization of the $\langle \phi_s | (E - H)^{-1} | \phi_{s'} \rangle$ sub-matrix.[2,3] It follows from eqs 13 and 17 that,

$$\langle \phi_s | \Psi(t) \rangle = (i/\hbar) \sum_{s'} \langle \phi_{s'} | \mu | \phi_g \rangle \int_{-\infty}^{t} \mathrm{d}t'\, \epsilon(t') \exp(-iE_g t'/\hbar)$$

$$\sum_n \int \mathrm{d}E \{V(s|E,n) V(E,n|s') \exp[-iE(t - t')/\hbar]\} / \{[E - E_s - \Delta_s(E) - i\Gamma_s(E)/2] \times [E - E_{s'} - \Delta_{s'}(E) + i\Gamma_{s'}(E)/2]\} \tag{21}$$

The above expression has two poles, one [at $E = E_s + \Delta_s(E) + i\Gamma_s(E)/2$] residing in the upper half of the complex E plane, and the other [at $E = E_{s'} + \Delta_{s'}(E) - i\Gamma_{s'}(E)/2$] residing in the lower-half of the complex E plane. The inclusion of the preparation step guarantees that in our formulation $t-t'$ is always positive,[17] and hence the $\exp[-iE(t-t')/\hbar]$ factor is zero on a sufficiently large semicircle in the lower half of the complex E plane. Hence, we can supplement the real-axis integration path by a semicircle in the lower half-plane and obtain from the residuum theorem that

$$\langle\phi_s|\Psi(t)\rangle = -2\pi i\sum_{s'}\frac{i}{\hbar}\langle\phi_{s'}|\mu|\phi_g\rangle\epsilon(\mathrm{w}_{s',g},t) \exp(-i\mathsf{E}_{s'}t/\hbar)\sum_n\frac{V(s|\mathsf{E}_{s'},n)V(\mathsf{E}_{s'},n|s')}{\mathsf{E}_{s'} - E_s - \Delta_s(\mathsf{E}_{s'}) - i\Gamma_s(\mathsf{E}_{s'})/2} \quad (22)$$

where

$$\mathsf{E}_{s'} = E_{s'} + \Delta_{s'}(\mathsf{E}_{s'}) - i\Gamma_{s'}(\mathsf{E}_{s'})/2 \quad (23)$$

and $\epsilon(\mathrm{w}_{s',g},t)$ is the finite time Fourier transform of the pulse, calculated at the complex frequency $\mathrm{w}_{s',g}$, given as

$$\mathrm{w}_{s',g} \equiv [\mathsf{E}_{s'} - E_g]/\hbar = [E_{s'} + \Delta_{s'} - E_g - i\Gamma_{s'}/2]/\hbar = \omega'_{s',g} - i\Gamma\omega'_{s',g}/2\hbar \quad (24)$$

with $\omega'_{s',g} = \omega_{s',g} + \Delta_{s'}/\hbar$.

Equation 23 is solved by restricting $V(s|\mathsf{E},n)$ to be a real function, satisfying

$$V(s|\mathsf{E},n) = V(s|R_e\mathsf{E},n) \quad (25)$$

Using eq 20, we can write

$$\Delta_s(\mathsf{E}_s) = \sum_n\int \mathrm{d}E'\,\frac{|V(s|E',n)|^2}{\mathsf{E}_s - E'} = \sum_n\int \mathrm{d}E'\,\frac{|V(s|E',n)|^2[(R_e\mathsf{E}_s - E') - i\,I_m\mathsf{E}_s]}{(R_e\mathsf{E}_s - E')^2 + (I_m\mathsf{E}_s)^2} \quad (26)$$

hence from eq 23

$$R_e\mathsf{E}_s = E_s + \sum_n\int \mathrm{d}E'\frac{|V(s|E',n)|^2(R_e\mathsf{E}_s - E')}{(R_e\mathsf{E}_s - E')^2 + (I_m\mathsf{E}_s)^2} \quad (27)$$

and

$$I_m\mathsf{E}_s = -I_m\mathsf{E}_s\sum_n\int \mathrm{d}E'\,\frac{|V(s|E',n)|^2}{(R_e\mathsf{E}_s - E')^2 + (I_m\mathsf{E}_s)^2} + \sum_n 2\pi|V(s|R_e\mathsf{E}_s,n)|^2 \quad (28)$$

It follows from eq 28 that $I_m\mathsf{E}_s$ is a solution of the implicit equation

$$I_m\mathsf{E}_s = \frac{\sum_n 2\pi|V(s|R_e\mathsf{E}_s,n)|^2}{1 + \sum_n\int \mathrm{d}E'|V(s|E',n)|^2/[(R_e\mathsf{E}_s - E')^2 + (I_m\mathsf{E}_s)^2]} \quad (29)$$

This equation can be solved iteratively by starting with a zero guess in which of

$$\mathsf{E}_s^{(0)} = E_s + \Delta_s(E_s) + i\Gamma_s(E_s + \Delta_s(E_s)) \quad (30)$$

Once a solution of eq 29 for $I_m\mathsf{E}_s$ is obtained, we calculate $R_e\mathsf{E}_s$ by solving eq 27, again in an iterative fashion, starting this time with $E_s + \Delta_s(E_s) + i\,I_m\mathsf{E}_s$ as the zero guess for E_s. Once a solution for $R_e\mathsf{E}_s$ is obtained, it is substituted in eq 29 and the process is repeated until convergence. Having obtained E_s by the above iterative procedure, we make the identification

$$\Delta_s(\mathsf{E}_s) \equiv R_e\mathsf{E}_s - E_s, \quad \text{and } \Gamma_s(\mathsf{E}_s) \equiv I_m\mathsf{E}_s \quad (31)$$

and proceed with the evaluation of $\langle\phi_s|\Psi(t)\rangle$ according to eq 22.

If we assume a Gaussian pulse of the form

$$\epsilon(t) = \frac{\epsilon_a}{2\pi^{1/2}\alpha}\exp\left[-\left(\frac{t}{2\alpha}\right)^2 - i\omega_a t\right] \quad (32)$$

we can express $\epsilon(\omega_{s',g},t)$ analytically[12,13] as

$$\epsilon(\mathrm{w}_{s',g},t) = (\epsilon_a/2)\exp[-\alpha^2(\omega'_{s',g} - \omega_a)^2 + i\alpha^2(\omega'_{s',g} - \omega_a)\Gamma_{s'}] \{1 + \mathrm{sgn}(t')(1 - \exp[\beta^2(E,t)]W[\mathrm{sgn}(t')\beta(E,t)])\} \quad (33)$$

where $\omega'_{s',g}$ is defined in eq 24, $t' \equiv t - \alpha^2\Gamma_{s'}$, $\mathrm{sgn}(t') = 1$ for $t' \geq 0$, $\mathrm{sgn}(t') = -1$ for $t' < 0$. $W[z]$ is the complex error function[18] whose argument is given in terms of

$$\beta(E,t) = \alpha(\mathrm{w}_{s',g} - \omega_a) + it/(2\alpha) \quad (34)$$

We see from eqs 4 and 22 that the total population in the bound ($|\phi_s\rangle$) manifold is given as an incoherent sum of terms, each being the square of a *coherent* sum of amplitudes. Although each amplitude of eq 22 decays due to the presence of the imaginary part of $\mathsf{E}_{s'}$ (i.e., $\Gamma_{s'}/2$), the coherent sum over these amplitudes may in principle bring about constructive interferences, representing a momentary *surge* in the population. Each surge in the total population in the bound manifold must be interpreted as a manifestation of a transient recombination process. It remains to be seen under what conditions such recombinations can actually be observed.

4. Evolution of the Products' Space

In this section we complete the derivation by examining the time dependence of the products of the decay (dissociation) process. We first study excitation with a continuous wave (CW) source. In this case the observables of interest have to do with the long time outcome of the decay process. This limit is usually expressed in terms of the (frequency resolved) *partial* cross sections $\sigma(E,n)$, which are the (steady state) rates of populating products in various final channels n divided by the incoming (photon) flux. Also of interest is the total photodissociation cross section $\sigma(E)$, given as

$$\sigma(E) = \sum_n\sigma(E,n) \quad (35)$$

For excitation with weak fields the partial photodissociation cross sections are given as[12]

$$\sigma(E,n) = \frac{4\pi^2\omega_{E,g}}{c}|\langle\phi_g|\mu|E,n^-\rangle|^2 \tag{36}$$

Assuming, as in the above, that only the manifold spanned by the ϕ_s states is coupled optically to the ground state ϕ_g, we can write eq 36 as

$$\sigma(E,n) = \frac{4\pi^2\omega_{E,g}}{c}|\sum_s\langle\phi_g|\mu|\phi_s\rangle\langle\phi_s|E,n^-\rangle|^2$$

$$= \frac{4\pi^2\omega_{E,g}}{c}|\sum_s\frac{\langle\phi_g|\mu|\phi_s\rangle V(s|E,n)}{E - E_s - \Delta_s(E) - i\Gamma_s(E)/2}|^2 \tag{37}$$

In the pulsed case we can no longer define a cross section. In this case, two types of observables are of interest: (1) the evolution of the populations of the various products states and (2) the ultimate fate of the products channels in the long time limit. We now examine the probability to populate the various product states in the long time limit. In that limit, the detection process invariably involves the breakup of $|\Psi(t)\rangle$ to its energy components. This is the case for example when the kinetic energy of the outgoing fragments is monitored. In that case, all coherences between the different energy eigenstates $|E,n^-\rangle$ which make up the excited state wave packet $|\Psi(t)\rangle$ of eq 13 are lost. What we observe in the pulsed case are weighted averages over individual energy-dependent rates. Such weighted averages, denoted as R_n, are proportional to

$$R_n \propto \int \mathrm{d}E\, |\bar{\epsilon}(\omega_{E,g})\langle\phi_g|\mu|E,n^-\rangle|^2 = \int \mathrm{d}E\, \bar{\epsilon}^2(\omega_{E,g})\left|\sum_s\frac{\langle\phi_g|\mu|\phi_s\rangle V(s|E,n)}{E - E_s - \Delta_s(E) - i\Gamma_s(E)/2}\right|^2 \tag{38}$$

When detection is performed over a finite range of nonasymptotic times, no energy resolution can be imposed on the evolving wave packet and coherence between its different energy components is not lost. In principle, we can detect the time evolution of a given product state $|E,m;0\rangle$ given as $|\langle E,m;0|\Psi(t)\rangle|^2$. Because the $|E,m;0\rangle$ states are not the eigenstates of the full Hamiltonian, the computation of $|\langle E,m;0|\Psi(t)\rangle|^2$ at finite times does not entail energy resolution, and the coherence between different energy components of $|\Psi(t)\rangle$ is not lost. We obtain, using eq 16, that

$$\langle E',m;0|\Psi(t)\rangle = (i/\hbar)\sum_{s'}\langle\phi_{s'}|\mu|\phi_g\rangle \int_{-\infty}^{t} \mathrm{d}t'\, \epsilon(t') \exp(-iE_g t'/\hbar) \sum_n \int \mathrm{d}E \exp[-iE(t-t')/\hbar]\langle E',m;0|E,n^-\rangle\langle E,n^-|\phi_{s'}\rangle \tag{39}$$

Defining the (P) projection operator on the space spanned by the $|E,n;0\rangle$ states as

$$\mathrm{P} = \sum_s \int \mathrm{d}E\, |\, E,n;0\rangle\langle E,n;0| \tag{40}$$

and the (Q) projection operator on the space spanned by the $|\phi_s\rangle$ states as

$$\mathrm{Q} = \sum_s|\phi_s\rangle\langle\phi_s| \tag{41}$$

we can apply the general relation[2] between the components of $|E,n^-\rangle$

$$\mathrm{P}|E,n^-\rangle = |E,n;0\rangle + [E - i\epsilon - \mathrm{P}H\mathrm{P}]^{-1}\mathrm{P}H\mathrm{Q}|E,n^-\rangle \tag{42}$$

to obtain that

$$\langle E',m;0|E,n^-\rangle = \delta(E-E')\delta_{n,m} + \sum_s(E - i\epsilon - E')^{-1}V(E',m|s)\langle\phi_s|E,n^-\rangle \tag{43}$$

Substitution in eq 39 yields

$$\langle E',m;0|\Psi(t)\rangle = \frac{i}{\hbar}\sum_{s'}\langle\phi_{s'}|\mu|\phi_g\rangle\Bigg\{\epsilon(\omega_{E',g},t)\exp[-iE't/\hbar]\langle E',m^-|\phi_{s'}\rangle + \sum_{s,n}\int_{-\infty}^{t}\mathrm{d}t'\,\epsilon(t')\exp(-iE_g t'/\hbar)\int \mathrm{d}E\, \frac{\exp[-iE(t-t')/\hbar]V(E',m|s)\langle\phi_s|E,n^-\rangle\langle E,n^-|\phi_{s'}\rangle}{E - i\epsilon - E'}\Bigg\} \tag{44}$$

Using eq 17 we can write eq 44 as

$$\langle E'm;0|\Psi(t)\rangle = \frac{i}{\hbar}\sum_{s'}\langle\phi_{s'}|\mu|\phi_g\rangle\Bigg\{\epsilon(\omega_{E',g},t)\exp[-iE't/\hbar]\frac{V(s'|E',m)}{E' - E_{s'}} + \sum_{s,n}\int_{-\infty}^{t}\mathrm{d}t'\,\epsilon(t')\exp(-iE_g t'/\hbar)\int \mathrm{d}E\, \frac{\exp[-iE(t-t')/\hbar]V(E',m|s)V(s|E,n)V(E,n|s')}{[E - i\epsilon - E'][E - E_s^*][E - E_{s'}]}\Bigg\} \tag{45}$$

This expression has three poles, two (at $E = E' + i\epsilon$ and $E = E_s^*$) residing on the upper half of the complex E-plane, and one (at $E = E_{s'}$) residing on the lower half of the complex E-plane. As in the above, $t - t'$ is always positive and we can supplement the real energy integration with a large semicircle in the lower half of the complex E-plane where $\exp[-iE(t-t')] = 0$ and obtain from the residuum theorem that

$$\exp[iE't/\hbar]\langle E',m;0|\Psi(t)\rangle = \frac{i}{\hbar}\sum_{s'}\langle\phi_{'}|\mu|\phi_g\rangle\Bigg\{\epsilon(\omega_{E',g},t)\frac{V(s'|E',m)}{E' - E_{s'}} - 2\pi i\sum_{s,n}\epsilon(\mathrm{w}_{s',g},t)\frac{\exp[-i\mathrm{w}_{s',E'},t]V(E',m|s)V(s|E_{s'},n)V(E_{s'},n|s')}{[E_{s'} - E'][E_{s'} - E_s^*]}\Bigg\} \tag{46}$$

where $\mathrm{w}_{s',E'} = [E_{s'} + \Delta_{s'} - E' - i\Gamma_{s'}/2]/\hbar$.

The second term of eq 46 decays as $t \rightarrow \infty$ due to the $\Gamma_{s'}/2\hbar$ imaginary parts of the $\mathrm{w}_{s'E'}$ frequencies. Hence the first term in eq 46 yields the long time limit of $\exp[iE't/\hbar[\langle E',m;0|\Psi(t)\rangle$

$$\lim_{t\to\infty}\exp[iE't/\hbar]\langle E',m;0|\Psi(t)\rangle = \frac{2\pi i}{\hbar}\sum_{s'}\langle\phi_{s'}|\mu|\phi_g\rangle\bar{\epsilon}(\omega_{E',g})\frac{V(s'|E,m)}{E' - E_{s'}} = \frac{2\pi i}{\hbar}\langle E',m^-|\mu|\phi_g\rangle\bar{\epsilon}(\omega_{E',g}) \tag{47}$$

The simplicity of eq 47, which leads directly to the cross-section expressions of eqs 36 and 37, is the reason we use the *incoming* states $|E,n^-\rangle$ in photodissociation problems.[2,15,16]

At nonasymptotic times, the second term in eq 46 does not vanish. The probability to observe a final state $|E,m;0\rangle$, given as

$$P_{E',m}(t) = |\langle E',m;0|\Psi(t)\rangle|^2 \tag{48}$$

is therefore influenced by the (constructive or destructive) interference between the first (DC) term and the second oscillatory term of eq 46.

In the pulsed case we might be interested in the energy summed branching ratios. If many resonances contribute to the process the ratio between the partial cross sections, $\sigma(E,n)$ is a result of a complicated interference because the dependence on n, embodied in the $V(s|E,n)$ terms of eq 37, is entangled in the summation over s. However, if one resonance dominates the dissociation process it follows from eq 38 that the branching ratio $R_n/R_{n'}$ is given as

$$R_n/R_{n'} = \frac{\int \mathrm{d}E\bar{\epsilon}^2(\omega_{E,g})|V(s|E,n)|^2/|E - E_s - \Delta_s(E) - i\Gamma_s(E)/2|^2}{\int \mathrm{d}E\bar{\epsilon}^2(\omega_{E,g})|V(s|E,n')|^2/|E - E_s - \Delta_s(E) - i\Gamma_s(E)/2|^2} \tag{49}$$

If $|V(s|E,n')|^2$ varies much more slowly with energy than the laser power spectrum $\bar{\epsilon}^2(\omega_{E,g})$ (this is the "slowly varying continuum approximation"[6,7,19] which is often realized), we have that,

$$R_n/R_{n'} = |V(s|\bar{E},n)|^2/|V(s|\bar{E},n')|^2 \tag{50}$$

where $\bar{E}$ is some mean energy. We see that in this case the dependence of the branching ratio on the pulse shape has completely disappeared!

If many resonances contribute to the process, we can no longer factor out the power spectrum from the expression for the branching ratios. It is clear, however, that even in this case the branching ratios to the various dissociation channels are independent of the phase of the electric field which make up the pulse[6,20,21] This result holds true even in the strong field regime, provided that the optical excitation (in the present case, that of the superposition of the overlapping resonances) involves no more than *one* common "precursor" state,[6] (e.g., $|\phi_g\rangle$ in the present case).

5. Computational Examples

In this section we illustrate the outcome of our formulation in the case, depicted in Figure 1, of a Morse potential crossed by the repulsive part of another Morse potential. The two curves are coupled by constant coupling term of 100 cm^{-1} in magnitude, which is roughly the coupling between the B state and Y state in IBr.[10,22] The reduced mass of the system is chosen as 23 amu, the ground state fundamental frequency as 200 cm^{-1}, and the excited state fundamental frequency as 15 cm^{-1}. Because curve-crossing situations allow for a wide variation in the resulting $V(s|E,n)$ matrix elements[22] and the $E_s + \Delta_s$ energy spacings,[22] the model hopefully addresses many of the generic features[1,5,23-25] of decaying molecular systems.

Having calculated E_s and $V(s|E,n)$ resulting from the model of Figure 1, and Δ_s and Γ_s according to eqs 18−20, we obtain $\langle\phi_s|\Psi(t)\rangle$ from eq 22). $P(t)$, the population in the bound manifold, is obtained from eq 4, and $F_g(t)$, the fluorescence to the ground state (or other states), − from eq 6. The cross section, $\sigma(E,n)$, is obtained from eq 37 and the evolution of the product population $P_{E',m}(t)$ from eqs 47 and 48.

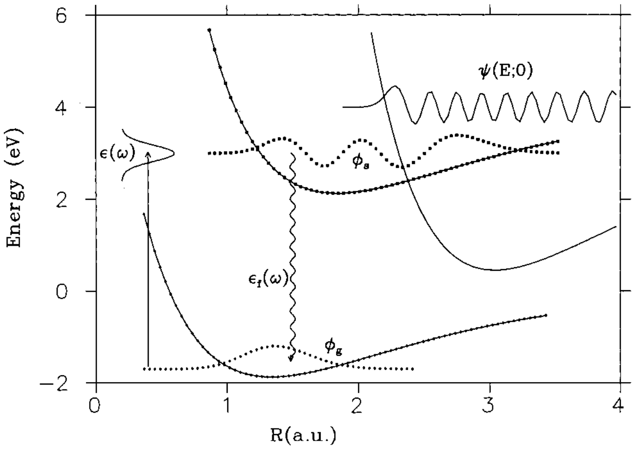

Figure 1. A schematic illustration of the excitation and decay of a superposition state. A system initially in state ϕ_g is excited by pulse with an $\epsilon(\omega)$ profile, to a bound manifold, spanned by the ϕ_s states, coupled to a continuum manifold, spanned by the $\Psi(E,n;0)$ states. While evolving, the system may fluoresce back to the ground states, emitting bursts of photons characterized by profiles such as $\epsilon_f(\omega)$.

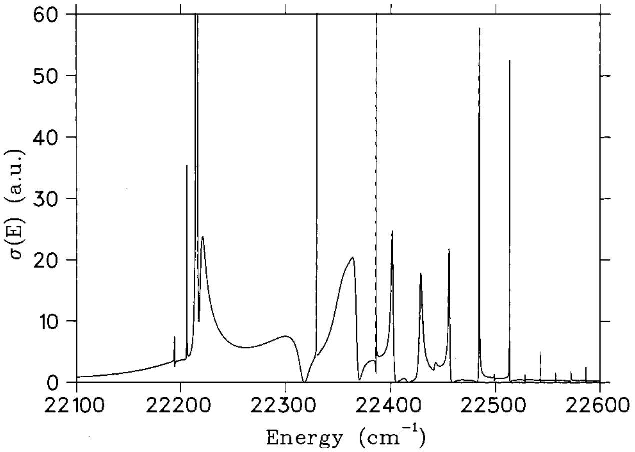

Figure 2. Total photodissociation cross section resulting from the model depicted in Figure 1.

We first display (in Figure 2) the total cross section $\sigma(E)$. It is composed of a series of interfering resonances of varying widths. The essence of this interference is not that resonances interact via some nondiagonal bound-continuum matrix elements of the Q$(E - H)^{-1}$Q submatrix, but that $\sigma(E,n)$ is given as the square of a coherent sum. As mentioned above, even in the case where resonances do interact via some off-diagonal matrix elements, it is always possible (by diagonalizing the Q$(E - H)^{-1}$Q matrix) to recast the formulas for the cross section (and other quantities such as $P(t)$ and $F_g(t)$) as resulting from a sum of noninteracting terms.

In contrast to $\sigma(E,n)$, the temporal behavior of the system is very much a function of the laser pulse phase and shape. In Figure 3a,b we look at the time evolution under excitation with a relatively "narrow" pulse (frequency fwhm of 50 cm^{-1}, corresponding to temporal fwhm of ∼600 fs), centered at 22 500 cm^{-1}. As can be seen in the cross-section plot of Figure 2, at that central frequency and bandwidth only two resonances are being excited. Indeed, as shown in Figure 3a, the total population displays an almost monotonic decay, modulated by a simple beat term. This modulation is more pronounced in

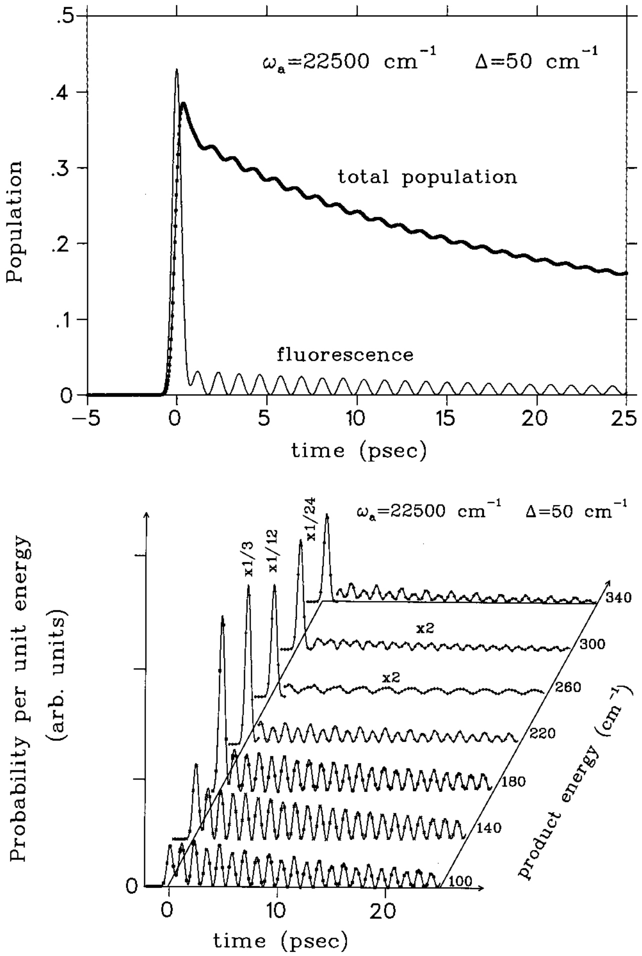

Figure 3. (a, top) Total population in the bound manifold and the fluorescence to the ground vibrational state as a function of time for excitation by a pulse whose central frequency is 22 500 cm^{-1} and bandwidth of 50. (b, bottom) Evolution of seven of the product states for the case studied in part a.

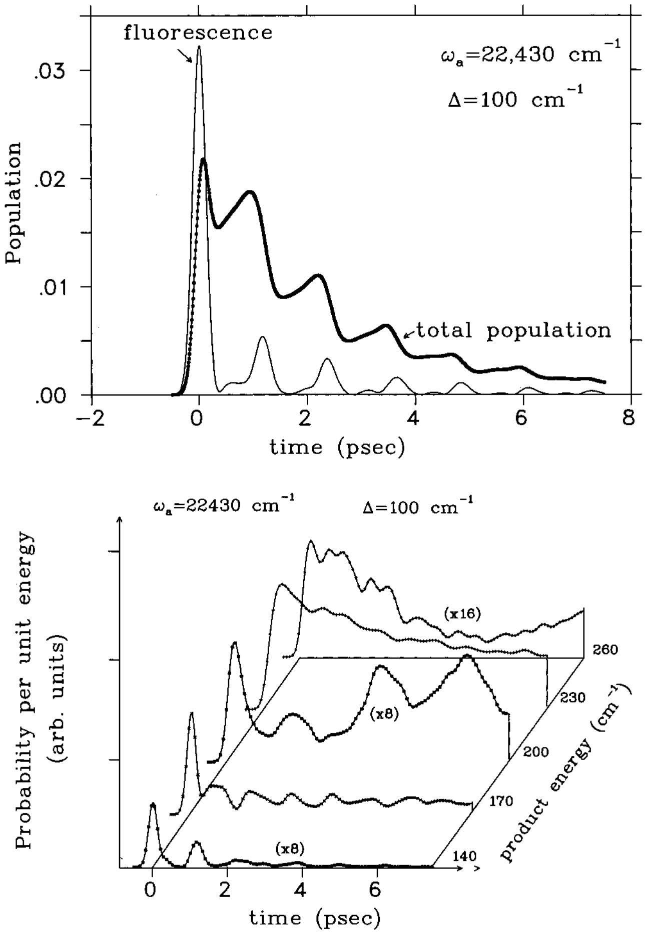

Figure 4. (a, top) Same as in Figure 3a for excitation with a pulse centered at 22 430 and bandwidth of 100. (b, bottom) Same as in Figure 3b for the pulse parameters of part a.

the fluorescence signal: After the fast, off-resonance dominated initial rise and fall, the fluorescence signal undergoes a series of recurrences at the same beat frequency which modulates the total bound-state population.

The temporal evolution of the product state distribution is shown in Figure 3b. The most surprising aspect of that figure is that at early times the product populations mirror the pulse evolution: the product states appear and disappear with the rise and fall of the pulse in a manner analogous to the behavior of the bound state populations. Contrary to classical mechanics, and all theories that do not include the process of preparation,[5,26,27] we see that there is no delay between the onset of the pulse and the first appearance of flux in the products space. This behavior is, as in the fluorescence signal, due to the contributions of off-resonance levels. Only after the first 600 fs, when the pulse is essentially over, does an on-resonance decay develop as evidenced by the emergence of a beat pattern which converges to the asymptotic values dictated by the first (DC) term of eq 46. In a sense, because the asymptotic values are known all along, one can treat the final outcome as "predestined": According to eq 46, all time evolution is viewed as arising from the interference of the known final outcome with decaying terms.

The decay dynamics becomes even richer when we excite at 22 430 cm^{-1} where, as shown in Figure 2, a larger number of resonances overlap. By increasing the bandwidth to 100, as in Figure 4a,b, or to 1000, as in Figure 5a,b, we allow more and more resonances to contribute to the process. Indeed we find the "backward bursts" of the population decay to become more and more pronounced. This can best be seen by comparing Figure 4a to Figure 5a and both figures to the mild oscillations of Figure 3a.

Although backward bursts have not yet been observed, a steplike behavior in the decay pattern has been recorded in NaI by Zewail et al.[8] who monitored the *appearance* of the Na product. In that study, the steplike behavior was attributed to bursts occurring while a localized superposition state passes through the ionic−covalent crossing region. No decay was thought to occur when the wave packet is outside these regions. The present work shows that such bursts are much more ubiquitous in that they occur in the absence of localization, can actually give rise to backward flows, and are simply due to interferences between individually decaying terms.

A comparison of the population to the fluorescence ($F_g(t)$ of eq 6), is given in Figure 4a and 5a. The two quantities are seen to exhibit a different behavior. In particular, the periodicity of the backward bursts in the population does not coincide with the recurrences in the fluorescence signal. The two quantities are different because the fluorescence signal is obtained as the square of a double ("coherent") sum of terms (over s and s', see eqs 6 and 22, whereas the population is a result of an "incoherent" sum (eq 4), of squares, each being a single sum over s' (eq 22).

The fluorescence signal recurs whenever the superposition state returns to a region of favorable Franck−Condon overlaps

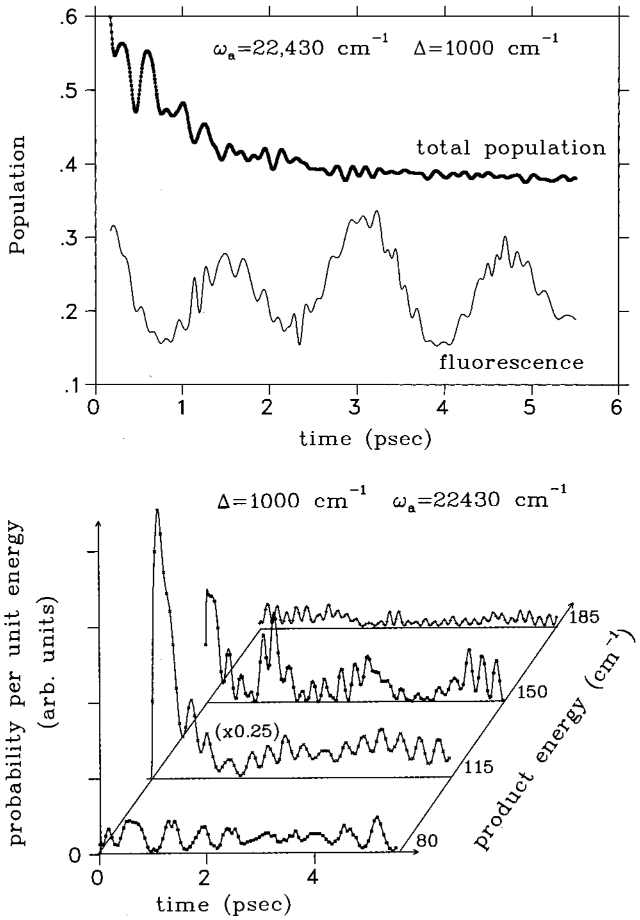

Figure 5. (a, top)) Same as in Figure 3a for excitation with a pulse centered at 22 430 and bandwidth of 1000. **(**b, bottom) Same as in Figure 3b for the pulse parameters of part a.

with one or more ground state wave functions at roughly the classical frequency. At the shortest pulsed excitation considered here (bandwidth of 1000, i.e., fwhm pulse duration of ∼30 fs), displayed in Figure 5, both the population and the fluorescence develop a secondary oscillatory structure due to the interference between energetically remote resonances.

6. Conclusions

In this paper, we have developed a uniform theory for the preparation and decay of a system of overlapping resonances. We have shown that in fact the very notion that one “prepares” resonance states, which then decay, is a misguided one. The fact that one does not prepare a resonance state whenever the pulse bandwidth is narrower than the spectral feature associated with a given resonance was realized in the past.[12] Here we show that this notion is wrong even if the pulse bandwidth is energetically much broader than the resonance feature, i.e., even in the ultrashort pulse limit. We have demonstrated that flux in the product space appears *instantaneously* with the onset of the pulse. The products space gets populated and depopulated with the pulse due to off-resonance effects which at intial times completely dominate the decay process. Only after the pulse is over do we see the decay of the population of the bound space and the buildup of the product space populations governed by time constants which are related to the resonance spectral features. Even at such late times the evolution of the bound state and product space populations is far from being intuitive. In particular, we have demonstrated the existence of bursts of flux reversals in which the system periodically partially recombines while undergoing a dissociative decay process.

An additional finding of this paper is that the assumption that fluorescence measures the system autocorrelation function is simply not true for overlapping resonances: the fluorescence, autocorrelation and the total bound state population behave differently.

The computations presented here may necessitate a reexamination of the interpretation of past experiments where the dissociative decay and radiationless transitions in large (and small) molecules have been probed.

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(17) In contrast, conventional resonance theories which do not include the preparation stage and simply assign the resonance a complex (Siegert) eigenvalue E_s, give rise to the $\exp(-\Gamma_s t/2\hbar)$ term which grows exponentially for $t < 0$. This problem cannot be solved by simply deciding that the state only exists from $t = 0$ onwards, because of the inherent discontinuity in such an assumption. Moreover, much of the interesting physics derived here via the proper inclusion of the preparation process is then lost.

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