Unimolecular Dissociation from a Dense Set of States

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The intramolecular dynamics in a dense set of levels at energies above the dissociation threshold are discussed. Special reference is made to the typical case where there is a high-energy barrier to dissociation so that the number of channels (=number of accessible states of the transition state) is small compared to the number of bound states to which they can couple. The bifurcation into prompt and delayed decay is discussed with special reference to computational examples. The results suggest that it is possible to access the (far fewer) promptly decaying states, which do not sample the accessible isoenergetic bound space prior to their dissociation. The role of external perturbations (e.g., due to collisions) is also discussed as a mechanism for breaking down selection rules and thereby increasing the effective density of states of the energy rich molecule.

1. Introduction

The dissociation of energy rich polyatomic molecules is being probed in both time1−4 and frequency domains.5−7 At the moment, the dynamic range available from the experiment is limited. It is therefore not yet possible to resolve the questions of deviations from RRKM8−11 behavior as discussed in a number of recent papers.12−21 Specifically, the issue is that of sampling the available phase space prior to dissociation and, in particular, if there are prompt dissociation events. If there are, then an important question22 is how to access experimentally those states that directly dissociate since this will allow selectivity in initial state selection, which is not possible for an orthoxxo RRKM molecule.8−10

An issue that is related, but which is becoming much better understood,23−27 is the variation in the rates of dissociation from different isoenergetic sharply defined initial states. It is to be expected on statistical grounds that these rates can fluctuate about the value specified by RRKM theory for states of a given energy. The simplest theoretically expected distribution of rates is unimodal (so-called, of a chi-square type23−25), and averaging over a range of states is expected to reduce the fluctuations, as is observed.28 In the language of "fluctuations", our concern in this paper is with the physical situation where the distribution of (nearly) isoenergetic rates of individual states is manifestly bimodal (or even multimodal) so that it makes sense to discuss separately the different branches of the distribution rather than to average over all states. An example of such a distribution, generated by the computations discussed below, is shown in Figure 1.

When one considers the possibility of two (or more) groups of rates, each group can be assigned its own average rate. The fast decays are "prompt" or "direct" processes, and one expects that their average rate is practically independent of the actual volume in the phase space that could be sampled, if the molecule lingered awhile. The slow or "delayed" decays correspond to

Figure 1. Bimodal distribution of the lifetimes for a single tier random model effective Hamiltonian (see section 4 for a description of the model). Plotted is the histogram of the logarithm of the lifetimes log τ (τ /ns), τ = hΓ, obtained by diagonalization of the effective Hamiltonian, H . The parameters of the model are the following: the number of bound states, N, is equal to 1000; the number of decay channels, K, is equal to 100; the total coupling strength to the channels, Tr Γ, is equal to 2.37 cm−1; the average spacing between the zeroth-order states is ⟨de⟩ = 0.0005 cm−1; the intramolecular coupling strength is ν = 0.01 cm−1. Note the clear separation of the lifetimes: the K = 100 prompt states have an average lifetime ⟨τp⟩ [eq 4.11] of 0.27 ns while the N − K delayed states have an average lifetime ⟨τd⟩ [eq 4.12] of 11.3 ns.

the traditional, Lindemann, picture of a unimolecular dissociation of an energy rich polyatomic molecule, and hence, one expects (à la RRK) that their average rate of decay decreases as 1/ρ, where ρ is the density of (quasi)bound states of the energy rich molecule at the energy of interest. The expected behavior is illustrated in Figure 2. Note that the bifurcation of the two (averaged) rates requires a certain "size" for the bound system before it happens and that it is not in conflict with the upper bound provided by transition state theory for the rate of crossing of a barrier. As one enlarges the density of states of the energy rich molecule, the prompt decay rate is essentially unaffected.

A grossly simple kinetic model that already exhibits a prompt and a delayed decay is one for intramolecular dynamics, in the oversimplified manner of RRK (see refs 29 and 30 for more refined kinetic models and ref 31 for an application of a similar model to the decay of high Rydberg states). We consider a group of energy rich states, whose number density is [n] in

[References and equations are not shown in this text.]
steady state approximation means that the two sets of states obtained from a generalization of the analytical expression obtained for the two eigenvalues of an effective Hamiltonian with \( N = 2 \) and \( K = 1 \). The bifurcation occurs for \( \rho = 1/(2v^2) \). The expression of the prompt and delayed average widths is \( \Gamma_p = \Gamma_d = v^2 \) when \( \rho < 1/(2v^2) \) and \( \Gamma_{p,d} = v^2 \pm (\sqrt{v^2 - 1} \rho)^2 \) when \( \rho > 1/(2v^2) \). They are in very good agreement with numerical results obtained from the diagonalization of random coupling effective Hamiltonians of large dimension (cf. ref 17 and Figure 6).

Figure 2. Bifurcation of the prompt and the delayed average decay widths as a function of the logarithm of the density of states, \( \log(\rho) \), for two values of the coupling strength to the decay channels, \( \nu^2 = 1 \) and \( \nu^2 = 10^{-4} \), respectively. The prompt and the delayed widths are obtained from a generalization of the analytical expression obtained for the two eigenvalues of an effective Hamiltonian with \( N = 2 \) and \( K = 1 \). The bifurcation occurs for \( \rho = 1/(2v^2) \). The expression of the prompt and delayed average widths is \( \Gamma_p = \Gamma_d = v^2 \) when \( \rho < 1/(2v^2) \) and \( \Gamma_{p,d} = v^2 \pm (\sqrt{v^2 - 1} \rho)^2 \) when \( \rho > 1/(2v^2) \). They are in very good agreement with numerical results obtained from the diagonalization of random coupling effective Hamiltonians of large dimension (cf. ref 17 and Figure 6).

Figure 3. Prompt and delayed independent decay rates for the kinetic scheme of eq 1.1, which corresponds to an energy rich molecule with two kinds of states: a group of states of number density \( n \) where the energy is spread over all the modes of the molecule so that there is not enough energy in the reaction coordinate to dissociate and a group of states of number density \( k \) with enough energy along the reaction coordinate for the dissociation to occur. The analytical expression for the prompt and the delayed decay rates is \( \lambda_{p,d} = (k_{-1} + k_1) \pm \Delta/2 \) with \( \Delta = [(k_{-1} - k_1)^2 + 4k_{-1}k_1]^{1/2} \). The decay rates \( \lambda_p \) and \( \lambda_d \) are plotted as a function of the decay rate to the products, \( k \), for values of \( k_{-1} \) and \( k_1 \) equal to 1 and 10, respectively. Also plotted is the steady state rate \( \lambda_{ss} = k_{-1} - k_1 \) (dotted line), which is almost identical to the delayed decay rate \( \lambda_d \) (full lines), while the prompt rate, \( \lambda_p \) (dashes), is approximately equal to \( (k_{-1} + k_1) \).

which the energy is spread over the molecule so there is insufficient energy in the reaction coordinate, and a group of isoenergetic states \( k \), where the required energy is localized:

\[
[n] \xrightarrow{k_{-1}} [k] \xrightarrow{k + k_{-1}} \text{products} \tag{1.1}
\]

When solved exactly, such a kinetic scheme has two decay eigenvalues: one for a prompt decay (whose magnitude is essentially \( k_{-1} + k_1 + k \)) and one for a slow decay whose magnitude is practically indistinguishable from the value \( k_{-1}k \) \( k_{-1} + k \) determined using the steady state approximation (Figure 3). The only deviation of the slow rate from the steady state value is when it is not the case that \( k_{-1} + k_{-1} + k \) \( k_{-1} + k \), which requires negligible coupling to the bound states \( n \). The steady state approximation means that the two sets of states \( k \) and \( n \) have come to a dynamic equilibrium, \( k_{-1}n = (k_{-1} + k)[k] \), so that the net rate of formation of products, which is always \( k'[k] \), has the steady state value. Note also that the RRK approximation consists of evaluating \( \langle k_{-1}/(k_1 + k) \rangle = \langle k \rangle \langle n \rangle \rangle \text{equilibrium} \) as the ratio of the respective volumes in phase space and of taking the rate constant \( k \) as a vibrational frequency.

With these identifications, the steady state rate \( \approx \text{slow eigenvalue} \) is the familiar RRK expression.

The time evolution of the densities \( n(t) \) and \( k(t) \) of the two kinds of states of the kinetic scheme of eq 1.1 for a prompt and a delayed initial state. The prompt initial state (upper panel) is taken to be selectively localized in the states with enough energy in the reaction coordinate to dissociate: \( k[0] = 1 \) and \( n[0] = 0 \). The analytical expressions for the densities as a function of time are \( n[t] = (-k_{-1}/\Delta)[\exp(-\lambda_d t) - \exp(-\lambda_p t)] \) and \( k[t] = (b \exp(-\lambda_d t) + a \exp(-\lambda_p t))/2\Delta \), with \( a = k_{-1} - k_1 - \Delta = b = k_{-1} - k_1 - \Delta \). The analytical expression for the densities \( n[t], \lambda_p, a, \delta \), and \( \Delta \) are given in the legend of Figure 3.) The decay law \( P(t) = [k][n] \) has, at shorter times, a clear prompt character. There is, however, a longer time regime of lower intensity due to the transfer of population from the \( k \) states to the \( n \) states. The delayed initial state (lower panel) is taken to be initially localized in the states that do not have enough energy along the reaction coordinate to dissociate: \( k[0] = 1 \) and \( k[0] = 0 \). The analytical expression for the densities \( n[t] = b \exp(-\lambda_d t) - a \exp(-\lambda_p t)/2\Delta \) and \( k[t] = (a - b)/\Delta[\exp(-\lambda_p t) - \exp(-\lambda_d t)] \). In this case, the decay law \( P(t) \) is clearly delayed and exhibits a single time regime. There is almost no transfer of population from the \( n \) states to the \( k \) states. The values of the rate constants used in the kinetic scheme (eq 1.1) are \( k_{-1} \approx 1, k_{-1} \approx 10, \) and \( k \approx 5 \), which leads to \( \lambda_p \approx 15.7 \) and \( \lambda_d \approx 0.32 \), respectively. The decay laws are plotted on a logarithmic time scale.

Figure 4. Time evolution of the densities \( n(t) \) and \( k(t) \) of the two kinds of states of the kinetic scheme of eq 1.1 for a prompt and a delayed initial state. The prompt initial state (upper panel) is taken to be selectively localized in the states with enough energy in the reaction coordinate to dissociate: \( k[0] = 1 \) and \( n[0] = 0 \). The analytical expressions for the densities as a function of time are \( n[t] = (-k_{-1}/\Delta)[\exp(-\lambda_d t) - \exp(-\lambda_p t)] \) and \( k[t] = (b \exp(-\lambda_d t) + a \exp(-\lambda_p t))/2\Delta \), with \( a = k_{-1} - k_1 - \Delta = b = k_{-1} - k_1 - \Delta \). The analytical expression for the densities \( n[t], \lambda_p, a, \delta \), and \( \Delta \) are given in the legend of Figure 3.) The decay law \( P(t) = [k][n] \) has, at shorter times, a clear prompt character. There is, however, a longer time regime of lower intensity due to the transfer of population from the \( k \) states to the \( n \) states. The delayed initial state (lower panel) is taken to be initially localized in the states that do not have enough energy along the reaction coordinate to dissociate: \( k[0] = 1 \) and \( k[0] = 0 \). The analytical expression for the densities \( n[t] = b \exp(-\lambda_d t) - a \exp(-\lambda_p t)/2\Delta \) and \( k[t] = (a - b)/\Delta[\exp(-\lambda_p t) - \exp(-\lambda_d t)] \). In this case, the decay law \( P(t) \) is clearly delayed and exhibits a single time regime. There is almost no transfer of population from the \( n \) states to the \( k \) states. The values of the rate constants used in the kinetic scheme (eq 1.1) are \( k_{-1} \approx 1, k_{-1} \approx 10, \) and \( k \approx 5 \), which leads to \( \lambda_p \approx 15.7 \) and \( \lambda_d \approx 0.32 \), respectively. The decay laws are plotted on a logarithmic time scale.

In this paper we consider a fully quantum mechanical description that, in its essence, leads to a time evolution with similar features. A conclusion, which will remain unchanged, is that prompt processes require that one initially accesses states of type \( k \), i.e., states with energy along the reaction coordinate. As in the simple kinetic model, we shall find it possible to center attention on two aspects. The first is the nature of the coupling to the continuum. Because dissociation occurs through a narrow bottleneck, the number \( K \) of quantum states that are directly coupled to the continuum is smaller than the number \( N \) of isoenergetic states. Indeed, in the RRK model for the counting of the number of states, \( K \ll N \) as long as the available energy is not well above the threshold for dissociation. The other point is the sampling of the bound phase space caused by the initially
accessed state not being stationary with respect to intramolecular dynamics even in the absence of dissociation. Of course, the effects of the two types of couplings are in general intertwined. We shall try, using both analytical arguments and computational examples, to examine the role of these two couplings separately. Formally, this is a paper about intramolecular dynamics in the presence of dissipation (due to dissociation), but it will also prove useful to think of it as a paper about dissipation in the presence of additional coupling.

With suitable changes, the same kinetic scheme used above can also describe the traditional Lindemann mechanism, where now the transition between the groups of states $n$ and $k$ is different since it is collision induced. We will also allow for this possibility as described below, i.e., that the number of states that can be accessed from $k$ increases because of collisions. Unlike the case of thermally induced reactions, we will discuss in particular nearly elastic collisions, which hardly change the energy of the molecule (which is typically supplied by a laser). Such long-range collisions can, however, break selection rules (conservation of “orientation” or “magnetic” quantum numbers in particular) and hence very much enlarge the range of states that can be accessed prior to dissociation. As we shall argue, some, or many, matrix elements in (2.5) may be vanishing because of selection rules. One can arrange them to be orthogonal (2.6) due to the coupling to the continuum and is isoenergetic with the zeroth-order bound state $|n\rangle$. The sum-

mation over the index $k$ in (2.3) is over the number of linearly independent isoeenergetic state of $PHP$. Physically, these are dissociative states where the intramolecular coupling is still “on”, i.e., they are what one loosely refers to as transition states. In RRK terminology these are the states with enough energy along the reaction coordinate. The range $K$ of the index $k$ is therefore the number of such states. In the notation of transition state theory, $K = N^0(E - E_0)$ where $E_0$ is the threshold energy for dissociation. For a larger molecule, most ways of partitioning the energy $E$ among the internal degrees of freedom result in insufficient energy in the reaction coordinate so that $K$ is small compared to the range $N$ of values that the index $n$ can assume.

By taking the summation in (2.3) over linearly independent contributions, one ensures, as will be shown below, that the rank of the (Hermitian) matrix $\Gamma$ is $K$. Otherwise, all that one can prove is that the rank is $\leq K$.

To demonstrate explicitly that the rank of the matrix $\Gamma$ is $K$, one writes (2.3) in a dyadic form

$$\Gamma = \sum_{k=1}^{K} v_k^i v_k^j$$

(2.4)

The $K$ vectors $v_k$ are linearly independent and are defined to have $N$ components where, if $N$ is the number of bound states,

$$v_k^i v_k^j = \sum_{n=1}^{N} \langle n|V|k\rangle \langle k|V|n\rangle$$

(2.5)

Some, or many, matrix elements in (2.5) may be vanishing because of selection rules. One can arrange them to be orthogonal

$$v_k^i v_k^j = \sum_{n=1}^{N} (v_k^i)_n (v_k^j)_n = \Gamma_k \delta_{k,l}$$

(2.6)

and can define normalized vectors $\tilde{v}_k$ such that

$$\tilde{v}_k^i \cdot \tilde{v}_l^j = \delta_{kl} \quad \text{with} \quad \tilde{v}_k = v_k / \sqrt{\Gamma_k}$$

(2.7)

so that the first $K$ vectors $\tilde{v}_k$ are eigenvectors of the $N \times N$ Hermitian matrix $\Gamma$.

$$\sum_{n=1}^{N} \Gamma_{n,n} (\tilde{v}_k^i)_{n} = \sum_{n=1}^{N} \sum_{k=1}^{K} (n')|H|k|H|n) (\tilde{v}_k^i)_{n'} = \Gamma_k (\tilde{v}_k^i)_{n'}$$

(2.8)
Note that since the matrix $\Gamma$ is positive (semi)definite, the eigenvalues $\Gamma_l$ are all nonnegative.

The other $N-K$ eigenvectors of $\Gamma$ all have zero as an eigenvalue. This follows because the nonvanishing eigenvalues of $\Gamma$ must equal those of the $K \times K$ Hermitian matrix $\Omega \equiv V\Gamma V^\dagger$. Moreover, if the vectors $\nu_l$ are linearly independent, then all the eigenvalues of $\Omega$ are finite.

The result of this section is that when there are $K$ linearly independent decay channels, the rank of the $\Gamma$ matrix is $K$. In other words, there are $K$ eigenvectors with a finite (positive) eigenvalue and $N-K$ (degenerate) eigenvectors where the corresponding eigenvalue is zero. On the other hand, the time evolution is determined by the full effective Hamiltonian $H$ and not by the rate matrix $\Gamma$ alone. One cannot therefore discuss the time evolution without reference to the matrix $H$ (cf. eq 2.2).

3. Trapping vs Dilution

In the “golden rule” approximation, the decay rates are the eigenvalues of the matrix $H$. The result that when the bound state subspace is dense $\Gamma$ is of rank smaller than the number of bound states means that, in the golden rule approximation, some of these bound states will remain bound, i.e., they are trapped states and do not decay. Of course, the “golden rule” is just the first-order approximation. But in first order it follows that states can be strictly classified as either decaying or stable states. This is as in the simple RRK picture where states have enough energy along the reaction coordinate or they do not, and only the former do dissociate.

In the simple RRK picture one implicitly assumes that there is a fast intramolecular vibrational energy redistribution (IVR). The purpose of this section is to examine explicitly the phenomena, but it is not necessary. Strict trapping is possible even when the states are not degenerate. The necessary condition is that the Hamiltonian $H$ in the bound space commutes with the matrix $\Gamma$. Here, we discussed a more general case where the two matrices commute, namely $H = H_0$, where $H_0$ is diagonal.

The general case corresponds to allowing for IVR in the effective Hamiltonian so that (3.1) is replaced by

$$H = H_0 + H_1 - i\Gamma$$

As in (3.1) we take the matrices in this equation to be defined in the basis that diagonalizes $\Gamma$ so that, in the absence of $H_1$, the effective Hamiltonian is diagonal and the dynamics manifest trapping. One final refinement that we will mention below is to add $U$ representing the coupling induced by external perturbations.

Computing the time evolution is equivalent to diagonalizing the effective Hamiltonian. One can proceed by using perturbation theory and thereby eliminate the effect of the intramolecular coupling $H_1$ in successive orders. This route is particularly useful if the perturbation $H_1$ itself has terms of different orders, as is often the case for real molecules. In this way one can also modify the sequential sampling of phase space33,40–43 with the modification that makes the separation of the levels of $H$ possible. The other route is to diagonalize exactly as is done numerically in the next section. Either way, the role of IVR is clear. It mixes the trapped and the promptly decaying states. If the mixing is so complete that one cannot uniquely correlate the eigenstates of $H$ with the eigenstates of $\Gamma$ or of $H_0$, then the distinction between trapped and promptly decaying states is lost upon diagonalization of $H$. The eigenstates cannot be said to be of one kind or the other. Since the intramolecular coupling causes a “repulsion” of the energy levels of $H$, the region of dominant coupling is when the spacings of the levels of $H$ exceed the magnitude of the eigenvalues of $\Gamma$. In the language of resonance scattering theory45,44–46 the “resonances” are far apart and the states are isolated. In such a coupling regime it is more reasonable to first diagonalize $H$ and then to regard $\Gamma$ as a perturbation. In the language we shall use below, in this range the coupling to the continuum has been effectively democratically diluted over all the states. This is the limit of a low density of states, and the merging of the two branches is clearly seen in Figure 2. Also seen therein is that the weaker the coupling to the continuum, the higher is the density of states before the bifurcation into two types of decay is evident.

For a high density of states it will typically be the case that dilution is incomplete. What this means is that when an initial state $\varphi_0(i)$ is trapped and does not decay

$$\varphi_i(t) = \exp(-iH t/\hbar)\varphi_i(0) = \sum_{l=1}^{N} c_l^* \tilde{\nu}_l(t)$$

$$= \sum_{l=1}^{K} c_l^* \exp(-i(E_l - i\Gamma_l)t/\hbar)\tilde{\nu}_l + \sum_{l=K+1}^{N} c_l^* \exp(-iE_l t/\hbar)\tilde{\nu}_l$$

(3.4)

The trapped component is the component of the initial state in the subspace of the $N-K$ trapped eigenvectors of $\Gamma$.
eigenstate $w_m$ of $H$ is expanded in the basis that diagonalizes $\Gamma$:

$$w_m = \sum_{l=1}^{K} c_l^{m} \nu_l + \sum_{l=K+1}^{N} c_l^{m} \nu_l$$  \hspace{1cm} (3.6)$$

one or the other of the two terms dominate. As an eigenstate of $H$, the state $w_m$ decays independently of all other and its rate of decay is

$$w_m \Gamma w_m = \sum_{l=1}^{K} |c_l^{m}|^2 \Gamma_l = \sum_{l=1}^{K} w_m \nu_l |^2 \Gamma_l$$  \hspace{1cm} (3.7)$$

Those eigenstates of $H$ that are made up predominately of prompt states will decay promptly and vice versa, the extent of dilution being measured by the expansion coefficients $|c_l^{m}|^2$, $l \leq K$.

The dramatic effect of the dilution of the coupling strength to the continuum caused by IVR is to endow the trapped states with a finite (but long) lifetime. Dilution also tends to extend the lifetime for the prompt decay. The overall effect of dilution is to cause a more uniform distribution of the lifetimes so that the shorter lifetimes are longer and the very long lifetimes are shorter. In other words, dilution and trapping, which are due to different terms in the effective Hamiltonian, have an essentially opposite effect.

When dilution is the dominant effect, the distribution of lifetimes is unimodal and narrower. (Increasing dilution means moving to the left in Figure 2.) When trapping dominates, the distribution of lifetimes is at least bimodal, with the long lifetimes corresponding to states that would be trapped in the absence of IVR and the short lifetimes corresponding to prompt decays. It is possible for the distribution of lifetimes to have more than two modes because IVR need not be a simple process but can manifest a sequential character. A structure in the matrix $H$ can give rise to additional bifurcations in the distribution of lifetimes.

The distinction between prompt decay and trapped states has been made here for the basis that diagonalizes the $\Gamma$ matrix. When the Hamiltonian $H$ that governs IVR in the bound space is not diagonal in that basis, the distinction between the two types of states is valid only to lowest order and the actual dynamics mixes the two types of states. It is possible to define trapped states even in the general case by diagonalizing the Hermitian operator $H - i \Gamma$, and this is equivalent to a simultaneous diagonalization of $H$ and $\Gamma$. The resulting generalized eigenvectors can be strictly classified according to whether their eigenvalue does or does not have an imaginary part, and there are $K$ of the former. However, the required transformation is not unitary, and so the generalized eigenvectors do not diagonalize functions of $H$ so that they are mixed by the time evolution (except, as in the above, to first order).

Finally, we come to external perturbations as a source of dilution. When the molecule is coupled to its environment then, strictly speaking, one should use a Hamiltonian description for the combined system. Just as we eliminated the explicit coupling to the continuum by the use of an effective Hamiltonian, one can do the same for the perturbation due to the surroundings. In the lowest order, when such perturbations are weak and essentially static, the effect is equivalent to an additional coupling mechanism, denoted as $U$ in eq 2.1. States that otherwise would be trapped can acquire a finite width when $U$ is added to eq 3.5 as an extra term in $H$. Since such a description is valid only when $U$ is a weak perturbation, one might think that the effect will be minor. The reason that this is not necessarily so is the high degeneracies that are typical of highly excited rovibrational states. This is due not only to rotational states ($M$ and $K$ degeneracies) but also to degeneracies of vibrational overtones. An example of much current interest is the coupling of the entire rotational manifold of states of a Rydberg electron by the anisotropic electrical fields due to the surrounding ions or to a combination of electrical and magnetic fields. The optical excitation of the Rydberg state typically accesses only low angular momentum states. The breaking of the spatial symmetry of the isolated atom by the external anisotropy couples in a very large number of states, many more so than are coupled when only an external electric field is applied since the latter perturbation retains the cylindrical symmetry of the problem.

4. Computational Examples

In this section, we use a random coupling model effective Hamiltonian to mimic the dynamics of a dense set of states coupled through a narrow bottleneck to a smaller number of decay channels $K, K \ll N$. For a random Hamiltonian, the spacings between the levels are drawn from Wigner Poisson distributions while the components of the wave functions are taken to have a Gaussian distribution. These Hamiltonians are particularly relevant for the unimolecular dissociation of a highly congested set of quasi bound states, where they have already been extensively used. In polyatomic molecules, vibrational spectra often exhibit a "clump" or a "nested" structure. A "clump" is an intrinsically broad feature (whose width is not due to inhomogeneous broadening), stable in a given range of energy resolution, which is resolved at the next higher level of energy resolution into a set of distinct lines. Each of these distinct spectral lines can in turn be resolved into a set of lines at the next higher energy resolution. Such structures result from the different orders of magnitude of the molecular frequencies and from the wide variation of the anharmonic couplings typical of polyatomic molecules. They have been related to a tier structure of the matrix $H$ and shown to lead to a sequential sampling of phase space. A schematic representation of a three-tier level structure is drawn in Figure 5.

In the computations presented below, we use two different schemes of intramolecular coupling that correspond to two different structures of the matrix $H$. The first one (used for the computations of Figures 6 and 7) is a single tier structure where
n to its own subset of the states of the second tier, \( n_{2b} \) is equal to the coupling strength from the first tier to the second tier, \( V_{2b} \), with an intramolecular coupling strength, \( \nu_{2b} \), where the levels cannot repel too far apart because of the presence of the neighboring states, we introduce in the model off block diagonal coupling terms between the block \((H_{ij}) \) and its next neighbors \((H_{ij})_{i+1,j} \), corresponding to the states \( i+1 \) and \( i-1 \) of the first tier, respectively. These matrix elements are also drawn from a Gaussian distribution with a coupling strength \( \nu_{2b} \). When a third tier is coupled to the second one, the block structure described in eq 4.1 is repeated a second time for each state \( j \) of the second tier; each state \( j \) of the subspace \( Q_2 \) is coupled to its own set of \( n_3 \) states, \( l \), of the third tier, \( Q_3 \), by a \( n_3 \) component Gaussian vector, \( H_{jl} \), \( l = 1, \ldots, n_3 \), of strength \( \nu_3 \). The total number of states of the third tier is \( N_3 = N_2 \times n_3 \). The elements of the \( n_2 \times n_3 \) submatrices \((H_{ij}) \) are drawn from a Gaussian distribution with an intramolecular coupling strength \( \nu_{3b} \). The coupling between adjacent groups, \((H_{ij})_{ij} \), is of strength \( \nu_{3bb} \) with Gaussian matrix elements. Note that the blocks \((H_{ij}) \) that correspond to different states \( i \) of the first tier are not coupled to one another. In all the computations reported here, \( \nu_{2b} \leq \nu_{3b} \leq \nu_{3bb} \), \( i = 2, 3 \).

The time evolution of an arbitrary initial state \( \Psi(0) \) is governed by the effective Hamiltonian \( H \). We briefly give below the expressions of the decay laws in the basis of the eigenstates \( \Psi \). The autocorrelation function \( C(t) \) is the overlap of the initial state \( \Psi(0) \) with its evolved value at time \( t \), \( \Psi(t) \):

\[
C(t) = \Psi(t)^\dagger \Psi(0) \exp(-itH/t\hbar) \Psi(0) = \sum_{m=1}^{N} a_m^2 \exp(-i\lambda_m t / \hbar) \tag{4.2}
\]

where \( \lambda_m \) is the complex eigenvalue of the effective Hamiltonian, \( \lambda_m = E_m - i\Gamma_m \), and \( a_m \) is the component of the initial state \( \Psi(0) \) on the eigenstate \( \psi_m \) of the effective Hamiltonian \( H \).

The eigenstates \( \{\psi_m\} \) of \( H \) are not orthogonal in the usual sense, and they form a biorthogonal25 basis set. The eigenvalue equation of the effective Hamiltonian \( H \) is given by

\[
H \psi_m = \lambda_m \psi_m \tag{4.3}
\]

The complex conjugate of eq 4.3 is

\[
H^* \psi_m^* = \lambda_m^* \psi_m^* \tag{4.4}
\]

and the adjoint (\( \dagger \) (adjoint) = \( ^T \) (transpose) + * (complex conjugate)) equations to (4.3) and (4.4) are

\[
\psi_m^T H^\dagger = \lambda_m^\dagger \psi_m^T \tag{4.5}
\]

\[
(H_m^\dagger \psi_m^T = \lambda_m \psi_m \dagger) \tag{4.6}
\]

respectively. Note that since the effective Hamiltonian \( H \) is a complex symmetric matrix, \( (H^T)^\dagger = H \). The orthogonality relation is obtained by subtracting eq 4.6 from eq 4.3, which leads to

\[
0 = (\lambda_m - \lambda_m^\dagger)(\psi_m^\dagger \psi_m)
\]

Therefore, with \( (\psi_n^\dagger = \psi_n \dagger) \), the orthogonality relation takes the form

\[
\psi_n \dagger \psi_m = \delta_{nm} \tag{4.7}
\]
and
\[ a_m = \Psi^T(0) \cdot w_m = w_m^T \cdot \Psi(0) \] (4.8)

The square modulus |C(t)|^2 corresponds to the survival probability of the initial state \( \Psi(0) \), that is, the probability for \( \Psi(t) \) to overlap \( \Psi(0) \) at time \( t \). On the other hand, the decay law \( P(t) \) represents the probability for the initial state to remain in the bound subspace at a given time \( t \):
\[ P(t) = \Psi^T(t) \cdot \Psi(t) = \sum_{m=1}^{N} \sum_{n=1}^{N} a_m^* a_n (w_n^T w_m) \exp(-i(\lambda_m - \lambda_n)t/\hbar) \] (4.9)

Also of interest when the bound subspace is endowed with a tier structure is the probability \( P(t) \) to be localized in a given subspace \( Q_i \) of the bound subspace \( Q, Q = \sum Q_i \). For a subspace \( Q_i \) of dimension \( N_i P(t) \) is of the form (using eq 4.8)
\[ P(t) = \Psi^T(t) Q_i \Psi(t) = \sum_{m=1}^{N_i} \sum_{n=1}^{N_i} \sum_{s=1}^{N_i} w_n^T \phi_i^T w_m a_m^* a_n \exp(-i(\lambda_m - \lambda_n)t/\hbar) \] (4.10)

with \( P(t) = \sum P_i(t) \) and \( Q_i = \sum \phi_i^* \phi_i^T \).

We first illustrate with a random coupling model the bifurcation of the lifetimes into a prompt and a delayed branch for increasing densities of states (see also the discussion related to Figure 2 in the Introduction). In order to better discriminate between the different time scales, we plot in Figure 6 the histograms of the logarithm of the lifetimes \( \log(\tau_{iN}) \), where \( \tau_i = \hbar/\Gamma_i, \) for total densities of states \( \rho = 297, 575, 2.6 \times 10^3, \) and \( 2.5 \times 10^4 \) states/cm\(^2\), respectively. The density of states, \( \rho \), is computed after the diagonalization of the real part, \( H \), of the effective Hamiltonian, \( H \) (eq 2.2):
\[ \rho = \left( \frac{1}{N-1} \sum_{i=1}^{N-1} (E_{i+1} - E_i) \right)^{-1} \]

where \( E_i \) is an eigenvalue of \( H \). The widths \( \Gamma_i \) are obtained from the diagonalization of the single tier model effective Hamiltonian discussed above. The only parameter that is varied is the number of bound states \( N (N = 10, 20, 100, 1000) \); the other parameters, that is, the average spacing of the Poisson distribution for the zeroth-order diagonal elements of the matrix \( H \), the dilution, i.e., the intramolecular coupling strength \( v \), the number of decay channels \( K \) (and, consequently, the number of \( K \) promptly decaying states), and the total coupling strength to the continua, \( \Gamma \), are kept constant \( (\langle \delta v \rangle = 0.0505 \text{ cm}^{-1}, v = 0.01 \text{ cm}^{-1}, K = 10 \), and \( \Gamma = 0.5 \text{ cm}^{-1} \)). From Figure 6, one can see that the general trends of the schematic analytical representation of Figure 2 are well recovered when an effective Hamiltonian of large dimensions is numerically diagonalized. As the density of states increases, the prompt average lifetime \( \langle \tau_p \rangle \),
\[ \langle \tau_p \rangle = \frac{K}{\sum_{s=1}^{K} \Gamma_s} \] (4.11)

remains practically constant and about 0.11 ns while the delayed averaged lifetime \( \langle \tau_d \rangle \),
\[ \langle \tau_d \rangle = \frac{1}{N-K} \sum_{s=1}^{N-K} \Gamma_s \] (4.12)

varies as 1/\( \rho \). Note that for \( N = 10, K = 10 \), the distribution of lifetimes is unimodal, since all the states of the rate matrix \( \Gamma \) have a nonzero eigenvalue and decay. The bifurcation occurs for \( N > K \).

Shown in Figure 7 are the corresponding survival probabilities \( |C(t)|^2 \) (eq 4.2) and decay laws \( P(t) \) (eq 4.9) for a “prompt” and a “delayed” initial state. We here take as the prompt initial state a state with uniform weights on the \( K \) prompt eigenstates of the rate matrix \( \Gamma \) while the delayed initial state is taken to be uniformly localized in the remaining \( N - K \) trapped eigenstates. As already evident from the histograms of Figure 6, the prompt and the delayed initial states decay in significantly different time regimes as soon as the number of bound states \( N \) is larger than \( K \). Note also that the results of the computational example are in very good agreement with the general features...
of the corresponding decay laws (plotted in Figure 4), which are the solutions of the kinetic scheme of eq 1.1.

In Figure 7, the decay laws $P(t)$ (eq 4.9) of a delayed initial state are shifted to longer lifetimes for increasing densities of states and are well described by the average lifetime $\langle \tau_d \rangle$. On the other hand, the decay of a prompt initial state is virtually not affected by the increase of the density of states ($\langle \tau_p \rangle$ remains about equal to 0.11 ns for all cases). Note that the survival probabilities $|C(t)|^2$ (eq 4.2) of the delayed initial states for the models with $N = 20$, 100, and 1000 bound states are almost identical, which results from the fact that the dilution process is kept constant in all the computations; the time scale of the first drop of $|C(t)|^2$ is governed by the intramolecular coupling strength $\nu$, $\hbar \nu = 0.53$ ns.

Another important point is that the prompt initial state decays with almost no sampling of the trapped part of the bound subspace. This can be seen from the fact that for the $N = 20$, 100, and 1000 computations, the survival probabilities $|C(t)|^2$ (eq 4.2) and the corresponding decay laws $P(t)$ (eq 4.9) of the prompt initial state are nearly identical. The only significant difference is the slower time regime of low intensity that appears in $P(t)$. This slower time regime is due to the fact that a small fraction of the prompt initial state $\Psi(0)$ is transferred to the trapped part of phase space by the dilution process.

In Figures 8–10, we use the three-tier model Hamiltonian described above (see Figure 5) to discuss the sequential character of the exploration of phase space and the role of the selectivity of the initial excitation. The coupling between the first and the second tier follows the block structure of eq 4.1. The same structure of coupling is also used between the second and the third tier. The prompt subspace $Q_1$ is of dimension $N_1 = K = 20$. Each state of the subspace $Q_2$ is coupled to its own set of $n_2$ states ($n_2 = 5$) of the subspace $Q_2$ with a coupling strength $\nu_1$ equal to 0.15 cm$^{-1}$. The dimension of the subspace $Q_2$ is $N_2 = N_1 \times n_2 = 100$. Each state of $Q_3$ is in turn coupled to a distinct subset of $n_3$ states ($n_3 = 10$) of the subspace $Q_3$ with a coupling strength $\nu_2 = 0.015$ cm$^{-1}$, the dimension of the subspace $Q_3$ being $N_3 = N_2 \times n_3 = 1000$. The total number $N$
The intramolecular coupling strength \( \tau_0 \) is equal to 1120. The intramolecular coupling strength \( \tau_0 \) to be localized in the disjoint subspaces \( Q_i \) for \( i = 1, 2, 3 \), and decay laws \( P(t) \) for the same three initial states as in Figure 9. The decay law \( P(t) \) of the initial state localized in \( Q_1 \) (upper panel) has a two time regime character. The major part of the decay takes place in the prompt time regime. However, there is a significant transfer of population to the subspaces \( Q_2 \) and \( Q_3 \), which is responsible for the longer time scale of low intensity. The decay of the \( Q_3 \) initial state occurs on the longest time regime. Note that the transfer of population to the other subspaces is smaller than for an initial state localized in \( Q_1 \). The \( Q_3 \) initial state occurs on the longest time regime. 

The histogram of the logarithm of the lifetimes, \( \log(\tau_{ns}) \), is plotted in Figure 8. It exhibits a multimodal distribution. The 20 very prompt lifetimes that correspond to the prompt eigenstates of the rate matrix \( \Gamma \) are smaller than 0.3 ns and are localized on the left side of the histogram. Their average value \( \langle \tau_{Q_1} \rangle \) is equal to 0.18 ns. Because of their large dispersion (their values range from 0.03 to 0.3 ns), they do not appear as a single peak, but they can clearly be identified by an inspection of the magnitudes of the decay widths. The interesting point is that, because of the tier structure of the bound subspace, the \( N - K \) long lifetimes that correspond to the trapped eigenstates of the rate matrix have a bimodal distribution, contrary to the model in Figure 6, which corresponds to a single tier structure. The 1000 very long lifetimes of the subspace \( Q_3 \) have an average \( \langle \tau_{Q_3} \rangle \) of 75 ns and correspond to the highest peak on the right side of the histogram. A secondary maximum due to the intermediate lifetimes of the 100 states of the \( Q_2 \) subspace appears on the left of the highest maximum. The average lifetime \( \langle \tau_Q \rangle \) is equal to 1.7 ns.

The total decay laws \( P_Q(t) \) for three different initial states, \( \Psi_i(0) \), uniformly localized in the \( Q_1 \), \( Q_2 \), and \( Q_3 \) subspaces, respectively, are plotted in Figure 9 on a logarithmic time scale. The three initial states clearly decay in different time regimes, in agreement with the three average lifetimes identified from the histogram of Figure 8. The initial state localized in \( Q_1 \) spans the prompt subspace and decays on the shortest time scale with, however, a small tail in the long time regime (see discussion below). The two other initial states, localized within the region that corresponds to the \( N - K \) trapped states of the rate matrix, decay on the two distinct longer time scales characteristic of the subspace \( Q_2 \) and \( Q_3 \), respectively.

In order to follow the sequential delocalization of the initial state in the bound subspace, we plot in the three panels of Figure 10 the survival probability \( |C(t)|^2 \) for the same three initial states as in Figure 9. The upper panel is devoted to the initial state localized in the first tier \( Q_1 \). The maxima in the probabilities \( P_1(t) \) and \( P_3(t) \) indicate a significant transfer of population from \( Q_1 \) to the trapped subspaces \( Q_2 \) and \( Q_3 \) by the dilution process. This results in a two time scale decay law, the longer time scale being of much lower intensity. Note that because of the sequential character of the exploration of phase space, \( P_2(t) \) reaches its maximum on a shorter time scale than \( P_3(t) \). The initial state localized in the \( Q_2 \) subspace (Figure 10, middle panel) decays on an intermediate time scale, with small amounts of prompt and very long time decays. On the other hand, the initial state localized in the third tier \( Q_3 \) (Figure 10, lower panel) specifically decays from the \( Q_3 \) subspace on the longest time scale, with almost no transfer to \( Q_1 \) and \( Q_2 \). Decays in specific time regimes can thus be obtained from the selective excitation of the different tiers of the bound subspace.

5. DIRECT COUPLING TO THE TRANSITION STATE?

It is a direct implication of trapping that unless IVR is very dominant it should be possible to distinguish between two types of decay: prompt and delayed. The prompt process corresponds to dissociation largely without sampling of the available phase space. The kinetic analogue has been shown in Figure 4. The analogy is also useful in that it shows that IVR can be so dominant (toward the left in Figure 3) that the prompt process is almost completely diluted. The simple RRK estimate is that prompt dissociation occurs within a vibrational period so that it may well be possible to beat IVR in this special sense. The real question is therefore “how to access directly those states which decay directly”.

While the theory gives an explicit answer, the answer is in terms of the matrix representation of the Hamiltonian. One needs to excite such initial states that are directly connected by the intramolecular coupling to the \( K \) states of the transition state, i.e., such states \( |i⟩ \) that \( \langle k |H|i⟩ \) is not zero, where \( |k⟩ \) is a dissociative state of the interacting fragments as introduced in eq 2.3. In the language of transition state theory these can be identified as the states of the transition state. The problem is that since the potential in the vicinity of the transition state is typically not known, it is not obvious how to transcribe the theoretical construction to the structural language in which intuitive chemical ideas are usually formulated.

One approach to the problem is that taken in section 4. There, a local harmonic approximation at the transition state was used to introduce a zeroth-order basis in which the anharmonicities couple states. Even in such a scheme it is not clear what
instructions are to be given to an experimentalist who wishes to access directly those states that are coupled to the transition state.

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References and Notes

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(53) In principle, the vectors \( \nu \) obtained by the sampling procedure should be orthogonal. However, this is only recovered numerically when the number of bound states, \( N \), is large enough to ensure a correct sampling. In practice, the vectors \( \nu \) are found to be orthogonal for \( N \geq 1000 \).

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