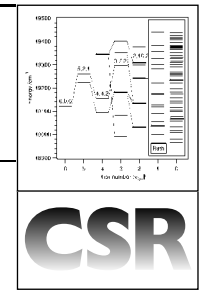
State-to-state unimolecular reaction dynamics of highly vibrationally excited molecules



A. Callegari and T. R. Rizzo

Laboratoire de chimie physique moléculaire (LCPM), École Polytechnique Fédérale de Lausanne CH-1015. Lausanne, Switzerland

Received 19th February 2001
First published as an Advance Article on the web 13th June 2001

This article presents recent work investigating the unimolecular dissociation rates of quantum state-selected molecules. Such studies provide the most stringent test for quantitative models of unimolecular reactions and their assumptions. After briefly reviewing the various experimental and theoretical techniques for state-resolved unimolecular dissociation rates, we present results obtained in our laboratory using the method of double resonance overtone photofragment spectroscopy. We focus on the unimolecular dissociation of HOCl as a textbook case in which the dissociation rate is limited by slow intramolecular vibrational energy redistribution and give a simple model to treat this particular class of systems.

1 Introduction

A unimolecular reaction is conceptually the simplest form of chemical change insofar as it involves the evolution of an isolated, energized molecule on a single potential energy surface. As such, it has served as an important meeting place for experiment and theory for several decades.[1–6] Much of the theoretical basis for calculating unimolecular reaction rates relies on statistical approaches,[2,3] such as Rice–Ramsperger–Kassel–Marcus (RRKM) Theory or the Statistical Adiabatic Channel Model (SACM).[7] In general, statistical theories treat a reactant molecule as a collection of coupled oscillators that exchange energy freely and determine the dissociation rate by considering the relative volumes of phase space available to the reactant molecule and to the molecule at the critical configuration or transition state. In a quantum mechanical formulation, the rate can be expressed as the ratio of the density of states of the reactant molecule to the number of states or 'open-channels' available to the molecule at the transition state:

$$k = \frac{N^{\ddagger}}{h\rho}$$

The key assumption of these theories is that vibrational energy in the reactant is redistributed between the internal vibrational modes in a *statistical manner on a timescale that is fast relative to that of chemical bond breaking.* While the attractiveness of such theories lies in their relative simplicity of application, their accuracy depends upon whether or not the condition of fast energy redistribution on the timescale of chemical bond breaking is fulfilled.

Early experimental measurements of unimolecular dissociation rates used thermal or chemical activation methods to

Thomas R. Rizzo was born in Queens, New York in 1956. He received in 1978 his BS in Chemistry, cum laude, from the Rensselaer Polytechnic Institute and in 1983 his PhD in Chemistry from the University of Wisconsin, working with Professor F. F. Crim. After a two year period as a research associate with Professor D. H. Levy at the James Frank Institute, University of Chicago, he joined the faculty at the University of Rochester as Assistant Professor of Chemistry. There he became Associate Professor in 1992 and Full Professor in 1993. Since 1994 he has been a Professor at the École Polytechnique Fédérale de Lausanne, Switzerland, where he is currently Head of the Chemistry Department. His research interest span the field of experimental chemical physics—particularly elementary reaction kinetics, intra- and intermolecular energy transfer, multiple-laser spectroscopy, ultrafast reaction dynamics and laser isotope separation.

Thomas R. Rizzo

Andrea Callegari was born in Montebelluna (TV), Italy in 1969. In 1993 he received his Laurea degree in Physics, cum laude, from the University of Pisa and a Diploma in Science from the Scuola Normale Superiore of Pisa. In 1998 he received his PhD in Chemistry from Princeton University, working with Professor G. Scoles and Professor K. K. Lehmann. Since then he has been a Postdoctoral Research Fellow in the Chemistry Department at the École Polytechnique Fédérale de Lausanne, Switzerland. His research interests have been focused on molecular dynamics with particular attention to the problem of regular vs. ergodic dynamics of intramolecular vibrational energy redistribtion.

Andrea Callegari

 DOI: 10.1039/a910264g

produce excited reactant molecules and, apart from special situations in which the presence of a heavy atom blocks intramolecular energy transfer,[8] the results of these experiments have largely been in good agreement with the predictions of statistical theories. Despite this generally good agreement, it has long been questioned whether the apparent success of these theories arises from the 'statistical' energy spread of the ensemble of reactant molecules rather than fast, statistical intramolecular vibrational energy redistribution (IVR) within individual molecules.

In an effort to resolve this key question, experimentalists devised a number of laser-based excitation schemes to prepare reactant molecules with a narrow energy spread. The initial approaches, reviewed by Crim in 1984,[9] included infrared multiphoton excitation, electronic excitation followed by internal conversion, overtone vibration excitation and stimulated emission pumping. The latter three techniques were able to produce considerably narrower reactant energy spreads (see Table 1 of Crim's review), and in some cases prepare a distribution of only a few rovibrational states. Even with this higher excitation selectivity, early results using these approaches were largely in agreement with the predictions of statistical theories. This led Crim to state in his review: 'Unimolecular reaction rates and product energy distributions in keeping with statistical descriptions are most common, but chemical intuition certainly suggests that preparation schemes in which the energy is not spread indiscriminately about the molecule prior to reaction are possible'. The question of the relative rates of intramolecular vibrational energy redistribution and unimolecular dissociation was still not directly addressed by these experiments.

At the same time as these efforts to prepare selectively excited molecules for unimolecular reaction studies, intense investigation into the phenomenon of IVR itself was underway in a number of research groups.[10–13] As described more fully below, IVR that occurs in the time domain shows clear spectroscopic signatures and hence can be investigated by frequency domain techniques. Using various combinations of cooling in a supersonic free-jet, high-resolution (*i.e.*, single mode) lasers, and double-resonance methods, these studies were able to completely eliminate spectral overlap and examine single eigenstates of vibrationally excited molecules.[10–12] Analysis of eigenstate-resolved spectra in a variety of molecules has revealed wide ranges of timescales for vibrational energy redistribution. In sufficiently small molecules, the timescale for IVR can be extremely long, allowing selectively excited vibrations to influence the outcome of bimolecular reactions.[14] On the other hand, certain functional groups exhibit ultrafast energy redistribution on the timescale of femtoseconds.[11, 15]

The next generation of unimolecular reaction studies employed similar laser excitation methods as these IVR studies to prepare reactant molecules in single quasi-bound eigenstates above the dissociation threshold energy.[16-27] In this case, the spectra of molecules excited to highly vibrationally excited states carry information on the initial stages of vibrational energy redistribution. Dissociation from these highly excited states was measured by the direct detection of the products as a function of time,[16–18,24,25,27]by spectroscopic probing of the disappearance of the reactant molecules,[19,20] or by the linewidths of the transitions to the quasi-bound states.[21–23,26] It is the combination of the frequency-resolved data on IVR and time-resolved data on unimolecular dissociation from the same states that enables the direct comparison of IVR and dissociation timescales. This in turn allows a critical examination of the limits of the assumptions of statistical theories of unimolecular dissociation.

The focus of this review is hence on fully eigenstate-resolved measurements of unimolecular dissociation rates. We begin by describing the framework in which one interprets eigenstate-resolved spectra to extract information on IVR. We then discuss the experimental techniques that have succeeded in achieving fully state-resolved dissociation rate measurements with a brief mention of some of the most important results obtained. We then briefly review the theoretical framework needed to go beyond traditional statistical theories and describe fully state-resolved unimolecular dissociation. Having presented this background, we go on to summarize measurements made in our laboratory on the unimolecular dissociation of HOCl as a model case in which the rate of IVR is the limiting factor in unimolecular dissociation. We compare the results with both statistical theory and the results of direct quantum mechanical calculations of dissociation rates. Finally, we show how an adapted statistical model that takes into consideration restricted IVR can be used to qualitatively interpret our results.

2 Eigenstate-resolved spectra of vibrationally excited molecules[10–13]

At sufficiently low energies of vibrational excitation, molecules behave largely like a collection of uncoupled harmonic oscillators, and this implies that the vibrational Hamiltonian will simply be a sum of harmonic terms. At higher vibrational energies, *anharmonic* terms in the potential can become significant, causing the simple harmonic picture to break down. From a perturbation theory point of view, if we consider the harmonic oscillator as the zeroth-order problem, these anharmonic terms result in a mixing between the zeroth-order states. The two factors determining the extent of mixing between any two states are the strength of their coupling to one another and their separation in energy. Hence, for significant mixing to occur, two states must be sufficiently close in energy and there must exist a term in the Hamiltonian coupling them with sufficient strength. The latter condition often implies that the coupling is mediated by a low-order anharmonic term since, generally, the strength of the coupling decreases exponentially with the order of the term responsible for it. The well-known Fermi resonance is an obvious case where the two above conditions are satisfied by the existence of two modes whose frequencies are in an approximate 2 : 1 ratio. In this case a state with two vibrational quanta in the first mode has nearly the same energy as a state with one quantum in the first mode and the two states can be coupled and mixed by a low (third) order term.

A significant role in the breakdown of the zeroth-order picture can be played by the interaction between rotations and vibrations. Coupling between vibrational levels mediated by rotations (Coriolis coupling) introduces additional terms in the Hamiltonian. Although often negligible compared to anharmonic coupling, Coriolis coupling increases rapidly with rotational excitation and can become significant in specific cases. A more subtle effect of the interaction between vibrations and rotations arises from the molecular geometry changing slightly upon excitation of vibrations. Vibrational states, then, have rotational constants similar to one another but not exactly equal and, for a given vibrational Hamiltonian, the relative energy of vibrational states—hence their mixing, as discussed above—depends on the rotational state considered.

When considering molecules excited to highly vibrationally excited levels by photon absorption, one must consider that the optically active state often corresponds to a simple vibrational motion close to one of the zeroth-order states. We call such a state the *zeroth-order bright state*, $|s\rangle$, shown schematically in Fig. 1. At sufficiently high energy where the density of states is large, there will be many other states that carry little or no oscillator strength (at least in comparison with the zeroth-order bright state), and these are called *zeroth-order dark states*, $\{|l\rangle\}$. Both types of states are eigenstates of the zeroth-order Hamiltonian that neglects anharmonic coupling terms. When the full molecular Hamiltonian that includes these coupling

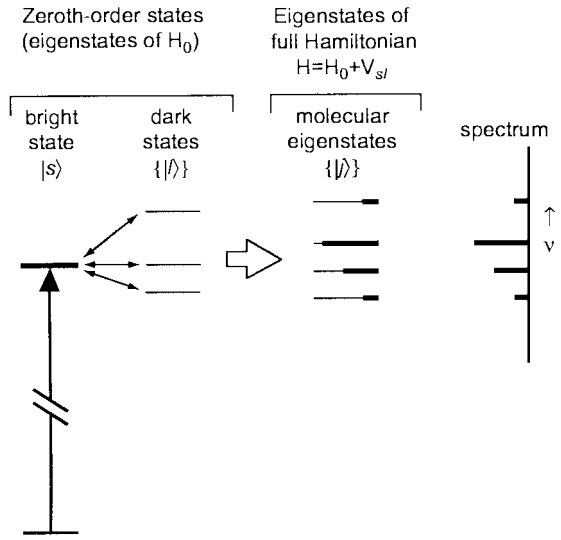


Fig. 1 Schematic representation of the optical excitation of a molecule to high-energy vibrational states below the dissociation threshold. At order zero of perturbation theory (left hand side), the molecular eigenstates are those of a conveniently simplified Hamiltonian H_0 (*e.g.* including only harmonic terms in the potential), and only one of these states is optically active ('bright'). This bright state is embedded in a bath of optically inactive 'dark' states and is coupled to them by the anharmonic terms initially neglected. Once these terms are included in the full Hamiltonian (right hand side) the resulting eigenstates are mixtures of the zeroth-order states and each one can have some bright state character, indicated by a thicker line. In the spectrum resulting from scanning the frequency of the excitation laser, each eigenstate appears with intensity proportional to its bright state character.

terms is considered, the resulting eigenstates can be expressed as linear combinations of the zeroth-order bright and dark states, and we give these states the designation, $|j\rangle$.

$$|j\rangle = c_s^j|s\rangle + \sum_l c_l^j|l\rangle$$

For example, in the case where a particular bright state is coupled to three zeroth-order dark states as illustrated in Fig. 1, we can write the corresponding four eigenstates as:

$$|1\rangle = c_s^1|s\rangle + c_{l1}^1|l_1\rangle + c_{l2}^1|l_2\rangle + c_{l3}^1|l_3\rangle$$

$$|2\rangle = c_s^2|s\rangle + c_{l1}^2|l_1\rangle + c_{l2}^2|l_2\rangle + c_{l3}^2|l_3\rangle$$

$$|3\rangle = c_s^3|s\rangle + c_{l1}^3|l_1\rangle + c_{l2}^3|l_2\rangle + c_{l3}^3|l_3\rangle$$

$$|4\rangle = c_s^4|s\rangle + c_{l1}^4|l_1\rangle + c_{l2}^4|l_2\rangle + c_{l3}^4|l_3\rangle$$

If we now consider the spectrum of molecules in the energy regime where such mixing takes place, we will see clear consequences of the coupling between zeroth-order states. In the absence of the coupling terms in the vibrational Hamiltonian, a transition to the bright state would appear as a single spectral line, because only the zeroth-order bright state, $|s\rangle$, is optically active. However, as a result of the coupling between zeroth-order states, several eigenstates $|j\rangle$ can have some component of $|s\rangle$, and each of these states will appear in the spectrum with an intensity proportional to the amount of bright state character, $|c_s^j|^2$. Thus, what would have appeared as single line in the absence of coupling may appear as a collection of two or more lines in the spectrum, as displayed schematically in Fig. 1.

There is a clear relationship between these collections or clumps of lines that are measured in the frequency domain and the rate of IVR in the time domain if all the energy were initially deposited in the bright state. To study the dynamics of the bright state, we need to express it as a linear combination of eigenstates that have bright state character, including the time-dependent part of the wave functions:

$$|s\rangle = \sum_j c_s^j|j\rangle e^{-iE_jt/\hbar}$$

or in the specific example cited previously,

$$|s\rangle = c_s^1|1\rangle e^{-iE_1t/\hbar} + c_s^2|2\rangle e^{-iE_2t/\hbar} + c_s^3|3\rangle e^{-iE_3t/\hbar} + c_s^4|4\rangle e^{-iE_4t/\hbar}$$

Because the energies of each eigenstate $|j\rangle$ are slightly different, there will be a non-trivial time evolution of the state $|s\rangle$ which leads to energy flowing from the bright state to the dark states. One can see this more clearly by looking at the survival probability of the bright state:

$$P(t) = \left|\langle s(0)|s(t)\rangle\right|^2 = \sum_j \left|c_s^j\right|^4 + 2\sum_{i\le j}\left|c_s^i\right|^2\left|c_s^j\right|^2 \cos(\omega_{ij}t)$$

$$\omega_{ij} = (E_i - E_j)/\hbar$$

If there are only two coupled states, energy will oscillate between them with a frequency related to the energy separation of the coupled states, $(E_1 - E_2)/\hbar$. In the case where more states are coupled, the rate of energy redistribution will still be related to the energy differences between the eigenstates that contain bright state character, albeit in a more complicated manner. Thus, the width over which the bright state is spread provides a measure of the timescale of energy redistribution.

To see how this is related to photoinitiated unimolecular reactions, we must consider what occurs when one excites states that are at energies above a molecule's dissociation threshold. As shown schematically in Fig. 2, in addition to the coupling

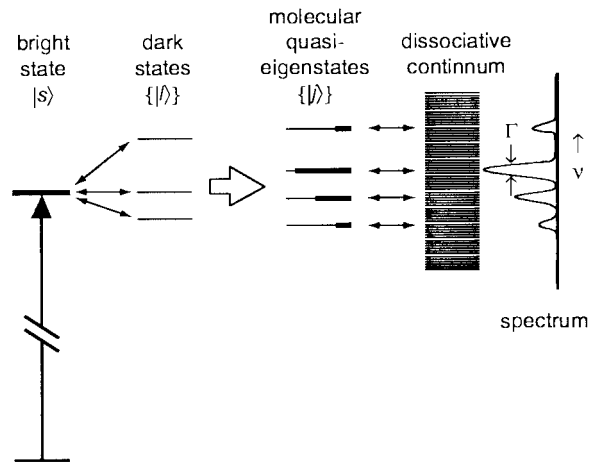


Fig. 2 Schematic representation of the optical excitation of a molecule to high-energy vibrational states above the dissociation threshold. As in the example of Fig. 1, at order zero of perturbation theory, one bright state is embedded in a bath of dark states and anharmonic coupling mixes them with one another into new states. Unlike the previous example, these are not strictly eigenstates in that they are further coupled to a dissociative continuum and, hence, have a finite decay rate. In the spectrum resulting from scanning the frequency of the excitation laser, each of these 'resonance states' appears with intensity proportional to its bright state character and a width Γ proportional to its decay rate.

between the bright and dark state, each state $|j\rangle$ is further coupled to the continuum of states corresponding to free translation of the products. In this case, the states $|j\rangle$ are no

longer strictly eigenstates but rather *resonance states*. Coupling to the continuum gives these resonance states a finite width, Γ, *which is directly related to the rate of unimolecular dissociation*.

In measuring the spectrum of highly excited molecules, there is often an ambiguity as to the source of the width of a feature measured in the spectrum. If the number of coupled states is large, a transition to a single zeroth-order state may appear as a Lorentzian profile resulting from a set of close lying dark states. In this case, the width is to be interpreted as related to the rate of IVR. However, if these states lie above the dissociation threshold, it can be difficult to distinguish such IVR broadening from the true lifetime broadening. In the examples described below, where single resonance states are prepared, this ambiguity is removed by working in sufficiently small molecules that have a low density of states.

To be precise, one should distinguish between 'eigenstates' and 'resonance states'. For the purpose of this paper, the two are used interchangeably with the understanding that we are working at energies above the dissociation threshold.

3 Eigenstate-resolved unimolecular dissociation rates

The most stringent test of statistical theories comes from experiments in which the reaction rate is measured from single, non-overlapping resonance states. To prepare such states optically, one must remove all sources of spectral overlap or inhomogeneous broadening. Over the past 25 years, the spectroscopic community has developed and employed a number of techniques for eliminating spectral congestion: cooling in a supersonic free jet expansion to reduce the number of thermally populated states; the use of high-resolution lasers or oscillators to distinguish between closely spaced spectral lines; and the use of double-resonance techniques where two resonant transitions are successively excited. In addition to the need for spectral simplification, the requirements for state-resolved unimolecular reaction studies are often more stringent than those for pure spectroscopic studies in that one must be able to access states at energies above the dissociation threshold. Direct excitation to such states is often limited by selection rules. Even when the requirements of spectral simplification and high-energy access are fulfilled, if the number of coupled states is too dense, it may be impossible to access single resonance states for unimolecular reaction studies. This can be resolved by working on sufficiently small molecules with a relatively low density of states.

A number of experiments have successfully fulfilled these requirements to perform fully state-resolved studies of unimolecular dissociation.[2,4,6,16,17,19–30] We briefly discuss a few examples below, grouping them according to the excitation scheme used.

The first experimental study of fully eigenstate-resolved unimolecular reaction rates was carried out by Moore and coworkers[21] on highly excited vibrational states of D_2CO on the ground potential energy surface. They first cooled the reactant molecules in a supersonic free-jet expansion before preparing them in single rovibrational states of the S_1 electronic state. Some of these electronically excited molecules fluoresce, while others undergo internal conversion to highly vibrationally excited states of S_0. Molecules in highly excited S_0 states can in turn tunnel through the barrier to the formation of D_2 + CO. An electric field is used to tune the relative position of S_1 and S_0 states, *via* the Stark effect, such that when the two are in close resonance, increased internal conversion, and hence unimolecular dissociation, occurs. The occurrence of these processes is monitored by a reduction in the fluorescence lifetime and quantum yield of the parent molecule. A spectrum is generated by plotting the fluorescence yield *versus* the Stark tuning voltage, and the unimolecular dissociation rates are extracted from the widths of the S_0 states. This elegant Stark-level crossing method has been used to measure the decay width of more than a thousand individual excited S_0 states, providing at the time an unparalleled opportunity to test unimolecular reaction rate theories of highly excited molecules at the most fundamental level.

Results from these experiments revealed dissociation rates of individual states in a small energy window spread over two orders of magnitude with no evident pattern, in a manner totally unaccounted for by existing theories of unimolecular reaction rates at the time. Most theories would have predicted a monotonic increase of the rate with energy, as more dissociation channels become available, and this disagreement between experimental observation and theoretical predictions was initially interpreted as a case of unimolecular reaction driven by non-statistical dynamics. However, as it soon turned out, this was to become the best-understood case of the inverse situation—a unimolecular reaction driven by statistical dynamics.[31] The extreme state-to-state rate fluctuations were shown to be a necessary consequence of the 'random' mixing among vibrational states induced by ergodic dynamics, hence a general feature of a completely statistical system. This conclusion indicated clearly the limits of treating only average properties of highly excited states dynamics.

A second approach uses stimulated-emission pumping (SEP) to access single eigenstates of highly excited molecules. In this case, one uses a two-step laser excitation scheme whereby population transfer to highly excited levels of the ground electronic state is achieved using an excited electronic state as an intermediate. The double-resonance nature of this scheme, together with cooling in a supersonic jet, has permitted the measurement of eigenstate resolved rates in HFCO,[20] CH_3O,[19] DCO[22] and HCO.[23] In the cases of HFCO and CH_3O, the dissociation rates are monitored by probing the vibrationally excited reactant molecules *via* excitation to the S_1 state with a third laser pulse and monitoring the resulting fluorescence as a function of the delay. At higher energies where the rates are faster, information on the dissociation rates comes from linewidths of the resonance states. Similar studies of HCO and DCO use the resonance linewidths to extract the dissociation rates.

The recurring theme emerging from all these studies is that unimolecular dissociation rates exhibit striking state-to-state variations and, in cases where a sufficiently wide range of energies are investigated, these variations are superimposed on a gradual increase as a function of vibrational energy. In some cases, most notably in HCO[23] and HFCO,[20] certain vibrational modes appear to preferentially enhance the dissociation rates. As will be discussed more fully below, the existence of rate fluctuations is a general characteristic of unimolecular dissociation from state selected molecules and in itself does not indicate whether vibrational energy is redistributed statistically on the timescale of unimolecular dissociation. On the contrary, the results cited above span the range from highly statistical dynamics (D_2CO, CH_3O) to somewhat mode-specific dynamics (HFCO), to extreme mode-specific dynamics (HCO).

Another approach to eigenstate resolved unimolecular dissociation studies uses a double resonance scheme in combination with direct overtone excitation.[17,18,24] A pulsed laser first excites a fundamental or low overtone of a hydrogen stretching vibration, selecting molecules in a single rotational level. A second laser pulse then further pumps the pre-excited molecules to a higher level of the same vibrational mode at an energy above the unimolecular dissociation threshold. The resulting dissociation products are then probed by laser-induced fluorescence using a third laser pulse delayed in time. Information on the IVR rates are obtained from the spectral splittings of the high vibrational overtone states and unimolecular dissociation

rates are measured either directly from the appearance time of the products or indirectly from the linewidths of the resonance states.

Accomplishing the excitation in two steps is more efficient than direct overtone excitation and results in sufficient spectral simplification that full eigenstate resolution can be achieved without supersonic cooling of the reactant molecules. This carries the added advantage that one can examine unimolecular dissociation rates of a wide range of rotational states. With respect to the previous schemes, this approach is limited to exciting quite specific initial states, in particular, those that contain most of the excitation energy in a light atom stretch mode. On the other hand, such states are easier to characterize spectroscopically.

Early implementations of this approach to HOOH(D)[18] and HONO[17] did not achieve full eigenstate resolution due to the high density of coupled states, although rate fluctuations were still observed in the latter.[17] Recent application of this approach to HOCl has permitted fully eigenstate-resolved unimolecular dissociation rate measurements,[24–27] and we present the results in Section 5 below as a textbook case for IVR limited unimolecular dissociation.

4 Theoretical treatments of eigenstate resolved rates

The value of the above-mentioned experiments lies not so much in what they reveal about the dynamics of individual molecules, but rather in their contribution to understanding the mechanisms that govern unimolecular dynamics. For this, the interplay between experiment and theory is indispensable.

Investigating unimolecular dynamics at the fully state-resolved level is no less demanding on the theoretician than on the experimentalist. Before addressing the question of intramolecular dynamics for a particular system, one needs an accurate potential energy surface. To describe the properties of individual states, the required accuracy must be comparable with the average energy level spacing. This requires computationally intensive *ab initio* calculations with large basis sets and often, small *a posteriori* adjustments (scaling) to improve the agreement with existing experimental data. Once a good potential energy surface is available, several methods can be used to study the dissociation dynamics.[2,4,32,33] While the obvious approach of time-dependent propagation of a wave-packet corresponding to the initially prepared state has the advantage of being conceptually simple, it is not necessarily computationally simple. A number of other methods have been devised that involve diagonalization of the Hamiltonian.[2-4,33] It is important to note that unlike a bound Hamiltonian, which has a discrete spectrum of eigenvalues and eigenstates with finite extension in space, an unbound Hamiltonian has a continuous spectrum and eigenstates that are not limited in space. Neither of these characteristics is particularly desirable from a computational standpoint, and clever methods have been devised to remap the problem into a finite-Hamiltonian, discrete-eigenvalue problem (absorbing potential, close-coupling, variational, complex scaling).[2,33]

Regardless of the particular implementation, these methods provide, in principle, exact results for individual states, but they are computationally intensive, and this limits their use to small molecules (3–4 atoms). However, in many cases one is not interested in the detailed properties of individual states, as much as in the ensemble properties of a number of them. In other cases, one might not have complete knowledge of the Hamiltonian and would like to know how the properties of a certain state change across the whole range of Hamiltonians that are compatible with the existing knowledge. Perhaps one simply wants to gain physical insight into a particular system without resorting to heavy numerical computation. In all these cases, it can be useful to resort to a more phenomenological approach where one starts from some previous knowledge or assumptions about the Hamiltonian and describes the system with a small number of parameters.

Often based on statistical assumptions, phenomenological models work better on larger systems, although this makes it difficult to extract the properties of an individual state. On the other hand, they work well at describing the ensemble properties of the molecular states and, being less molecule-specific than exact calculations, often give good insight on the important physical parameters that control the dynamics. The most extreme of these approaches, random matrix theory (RMT), assumes that nothing is known about the molecular Hamiltonian except that states are all strongly coupled to one another and hence completely mixed.[31] When cast into matrix form, such a Hamiltonian belongs to a special class of matrices whose elements are the most random possible, according to a given distribution. Miller and co-workers have used this approach to interpret the results of D_2CO Stark-level crossing spectroscopy discussed in the previous section.[31] With the assumption that the above-mentioned Hamiltonian suitably describes formaldehyde dynamics, they have been able to reproduce well the ensemble properties (most notably the distribution of decay rates about their average value) of hundreds of individually measured dissociation rates.

The extreme assumption of strong coupling does not always apply and, in the more general case, one is left with the task of finding the most general Hamiltonian compatible with the system under investigation and the existing knowledge about it. As we demonstrate below in the example of HOCl, the interplay between theory and experiment is extremely fruitful in guiding the process.

5 IVR limited unimolecular dissociation dynamics: the case of HOCl

5.1 Experimental approach and results

We have developed in our laboratory the technique of double resonance overtone excitation to prepare highly vibrationally molecules in selected initial states. We focus here on the applications of this approach to investigate the unimolecular dissociation dynamics of hypochlorous acid (HOCl). While a relatively simple triatomic molecule, HOCl contains most of the features that play a role in the dynamics of larger molecules; hence, it is in ideal system to study the interplay between vibrational energy redistribution and unimolecular reaction dynamics.

A typical experiment, shown schematically in Fig. 3, involves three different laser pulses of 5–8 ns duration. The first pulse promotes molecules to a specified rovibrational intermediate state, in this case a single rotational level with 2 quanta in the OH stretch [*i.e.*, the (2,0,0) level[34]]. After a delay of approximately 20 ns, the second pulse promotes only the pre-selected molecules to a higher OH stretch overtone level that has sufficient energy to dissociate the molecule into OH + Cl. Two of the three vibrational states discussed here (v_{OH} = 7 and 8) have their band origins well above the OCl bond dissociation threshold, respectively 2400 and 4800 cm^{-1}. The v_{OH} = 6 state on the other hand, has its band origin 200 cm^{-1} below the threshold and some rotational energy is also necessary for the molecule to dissociate. The molecule falls apart only as the vibrational energy leaks from the OH stretch vibration into the reaction coordinate (the OCl bond). The resulting OH fragments are detected by laser-induced fluorescence (LIF) using a third laser pulse tuned to an appropriate transition of the A–X band.

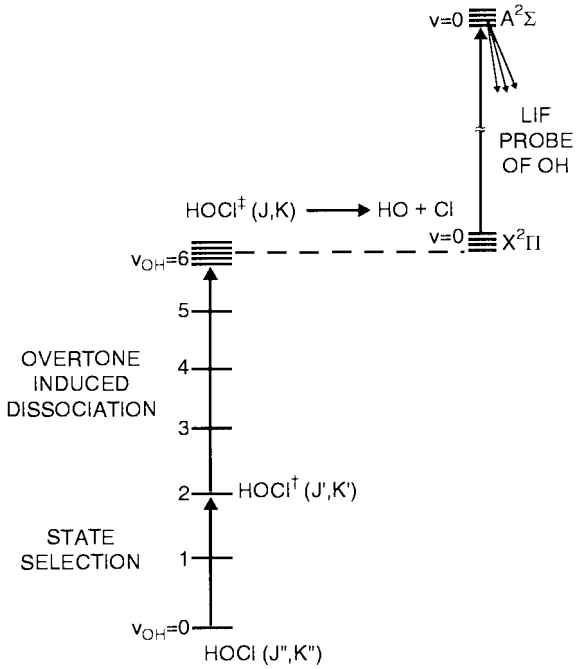


Fig. 3 Excitation scheme used in a typical double-resonance overtone photofragment spectroscopy experiment. One laser pulse excites some molecules from the ground vibrational level to a selected rotational state of an intermediate vibrational level. A second laser then excites only the selected molecules to an individual rotational–vibrational state above the dissociation threshold. A third laser probes the fragments resulting from dissociation. The particular scheme shown here is used to prepare HOCl molecules with six quanta of OH stretching, just above the dissociation threshold.

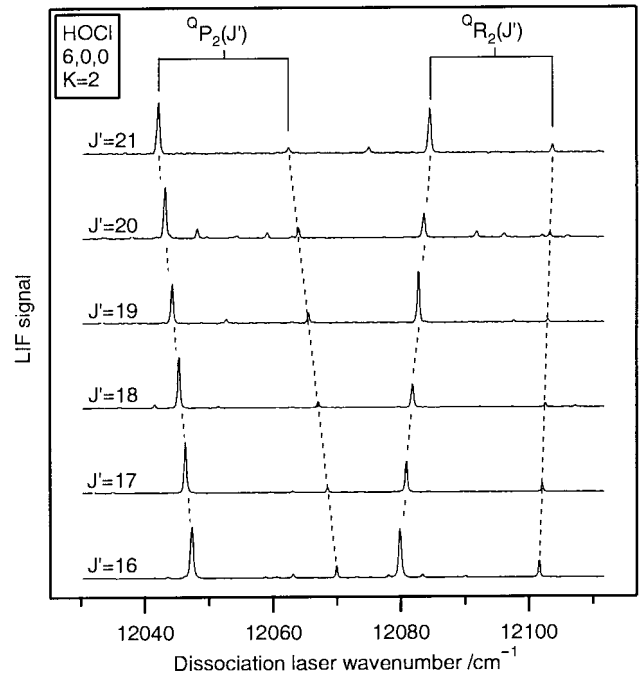


Fig. 4 Sample double-resonance spectra of the HOCl $6\nu_1 \leftarrow 2\nu_1$ band. Each spectrum in the plot originates from a selected (*J'*, *K'*) rotational state. The P and R branches, corresponding to $J - 1 \leftarrow J$ and $J + 1 \leftarrow J$ transitions respectively, are marked with dashed lines. Note the splitting into two components due to vibrational coupling of the optically active state with a perturbing 'dark' state.

Three types of information can be generated from these experiments. Scanning the frequency of the dissociation laser and collecting the total OH fluorescence, while keeping the state-selection and probe lasers fixed on specific transitions, produces a photofragment excitation spectrum of the reactant molecule in a highly-excited quasi-bound state. Analysis of the resulting spectrum allows modelling of the rotation–vibrational Hamiltonian and provides information on IVR from the initially prepared level. A second type of information comes from fixing the first two laser frequencies to prepare HOCl in a specific quasi-bound state, fixing the probe laser to detect a particular state of the OH product, and collecting the total OH fluorescence while changing the delay between the dissociation and the probe laser. The appearance time of the OH fluorescence provides a direct measure of the unimolecular dissociation rate of the parent molecule.

Finally, keeping the state-selection and dissociation laser frequencies fixed and scanning the probe laser frequency allows measuring the branching ratio of the dissociation process into the energetically available OH product channels. Since the information that we obtain with the first two types of experiments does not depend on which particular OH product state is probed, we can conveniently choose to probe states with the most favourable branching ratio.

One important parameter at our disposal is the angular momentum (*J*, *K*) of the initially prepared state. The small size of the molecule, combined with the selectivity afforded by the double-resonance approach, allows us to work in a static gas cell at low pressure instead of a molecular beam. Aside from the obvious experimental simplification, this gives us access to any rotational state with sufficient room temperature population, which for HOCl is typically $J = 0$–30, $K = 0$–5. This can be contrasted with molecular beam experiments where only $J = 0$–5, $K = 0$ would be accessible.

Fig. 4 shows typical results from the first type of experiment described above. Each spectrum in the figure is obtained by fixing the state-selection laser to prepare HOCl in a different rotational level of the (2,0,0) intermediate vibrational state and scanning the frequency of the dissociation laser in the region of the (6,0,0) level. Simple visual inspection is useful as it provides a good physical sense of the results and guides the subsequent quantitative analysis. In this particular case, it is evident that there are in each spectrum more peaks than predicted by applying the selection rules for rovibrational transitions of a near symmetric top to molecules in a single intermediate rovibrational state. Extra transitions may arise from either incomplete state-selection in the first step or from splitting of the upper levels resulting from vibrational coupling of the bright state to nearly isoenergetic dark states. It is important to distinguish between these two cases, as the latter reflects properties of the molecular Hamiltonian and hence the dynamics, while incomplete state selection is simply an experimental artifact of no consequence to the dynamics. We distinguish these possibilities by using the technique of combination differences, in which we compare spectra that access the same final state from different intermediate states. The result of this analysis indicates that each transition to a zeroth-order rovibrational level is split into two, implying significant coupling to only one other state. This indicates that the initially prepared state maintains most of its zeroth-order OH stretch character.

Quantitative analysis of the spectra using an asymmetric top Hamiltonian that includes vibrational coupling terms goes much further in characterising the observed coupled states by providing both molecular constants and coupling matrix elements. The molecular constants, together with isotope shift measurements, put strong constraints on the possible identity of the perturbing dark state. The amount of data available from the spectra of the (6,0,0) level is sufficient to unambiguously identify the main perturbing state as (4,4,2) (*i.e.*, the state containing four quanta of OH stretching, four of bending and two of OCl stretching), and to determine the magnitude of its coupling matrix element with the bright state to be 4.8 cm^{-1}. This information in turn gives an important insight on the vibrational Hamiltonian. Comparison with coupling matrix elements measured for similar, highly excited states suggest that

the measured (6,0,0) ↔ (4,4,2) coupling is too strong to arise from a direct mechanism, which would require anharmonic terms of order 8 in the potential. An indirect coupling mechanism through a nearby intermediate state is more likely. A combination of experimental observation and theoretical calculations allow us[24] to identify the resulting coupling chain to be (6,0,0) ↔ (5,2,1) ↔ (4,4,2). Coupling thus occurs through sequential steps, each mediated by a term of 4th order in the vibrational potential.

As mentioned earlier, one important parameter at our disposal is the angular momentum (*J, K*) of the initially prepared state. Because different vibrational states have slightly different rotational constants, their relative position is a function of the rotational quantum number. Moreover, the extent of mixing between vibrational states, and hence the resulting energy redistribution dynamics, depends on their relative energy. Consequently, we can use the selection of rotational state to modify slightly the vibrational Hamiltonian in such a way as to 'scan' the bright state across a number of dark background states. From this we learn, for example, that only one dark state is sufficiently coupled to the bright state to give a spectroscopically detectable effect, despite the fact that as many as 20 dark states come into resonance with the bright state over the range of *J* and *K* explored. This is a clear indication that the coupling of the bright state to the average bath state is quite weak. It is only those states that are coupled to the bright state through low order terms that appear in the spectrum with appreciable intensity. It will become apparent in Section 5.3 how much these low order couplings control the resulting dynamics and how, by unravelling them through our spectroscopic analysis we obtain direct information on the mechanism and timescale of the initial stages of vibrational energy redistribution. Comparison of these results with the direct time-resolved measurements described below allows us to determine the relative timescales of IVR and unimolecular dissociation.

Having discussed the kind of insight provided by frequency domain measurements and subsequent spectroscopic analysis, we now turn to direct time-resolved measurement of the dissociation rates. Fig. 5 shows the measured dissociation rates for several values of the rotational quantum number *J* at a given *K*, obtained by fitting the total OH product fluorescence as a function of the delay time of the probe laser (shown in the inset). Whereas the photofragment excitation spectra of Fig. 4 provides information on the flow of energy out of the initially prepared state, this second kind of measurement provides information on the flow of energy into the dissociation coordinate insofar as we detect the appearance of fragments as a function of time after reactant excitation. Perhaps the most intriguing feature of Fig. 5 is the wide state-to-state variation of the dissociation rate, with up to one order of magnitude change between states that are near in energy and have similar rotational quantum numbers. Moreover, the measured rates range between three and five orders of magnitude smaller than the 2.5×10^{11} s^{-1} average predicted by statistical theories.[35]

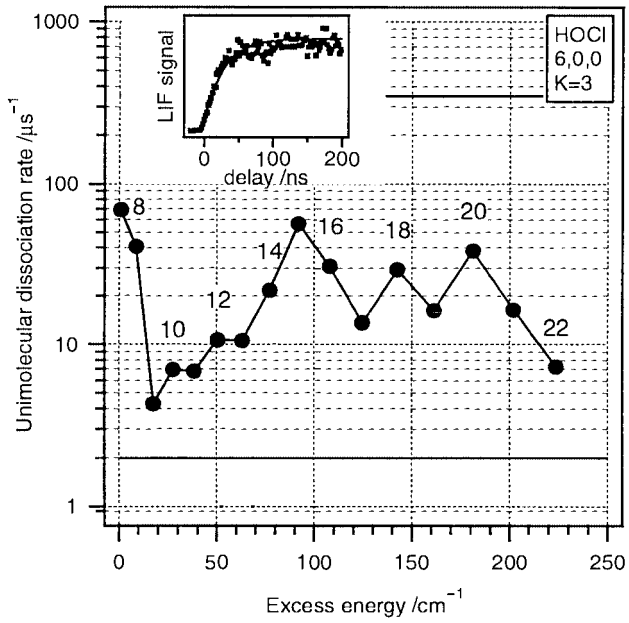


Fig. 5 Measured dissociation rates of HOCl prepared with six quanta of OH stretching *versus* their energy above the dissociation threshold. Each point corresponds to an individual rotational state (*J, K*) with J = 8–22 (indicated above the experimental points) and K = 3. The solid horizontal lines show the experimental detection limits. The inset plot shows the actual measurement of the dissociation rate of one of the states (J = 8).

It is now well accepted that large state-to-state rate fluctuations are the norm rather than the exception in state-resolved unimolecular reaction studies, the most notable example being the case of D_2CO investigated by Moore and co-workers.[21] Miller *et al.* have shown that the rate fluctuations observed in D_2CO originate from the highly mixed nature of the initially prepared states.[31] Even states that are close in energy have a completely different zeroth-order composition, and the different relative amounts of vibrations that resemble the reaction coordinate account for the difference in dissociation rates. There are important differences in the case of HOCl, however, that suggest that the same reasoning would not be appropriate. The preparation method that we use for HOCl is much more specific, since the oscillator strength is associated with the pure OH stretching overtone, which is nearly orthogonal to the reaction coordinate. Furthermore, aside from mixing with one perturbing state, there is no detectable spectroscopic evidence that the character of the initially prepared state changes between states that are 'adjacent' in rotational quantum number. From this we conclude that unlike the case of formaldehyde, the unimolecular dissociation rates we observe are determined primarily by minute changes in the eigenstate composition that are not detectable spectroscopically. Further evidence to support this conclusion comes from the slowness of the observed dissociation rates. Whereas a purely statistical model predicts that individual rates of highly mixed states should fall roughly within one order of magnitude of the RRKM average, our measured rates fall between three and five orders of magnitude below this average. This indicates that our initially prepared state is not well represented by the average highly mixed state, but rather keeps a well-defined identity throughout the whole range of rotational quantum number investigated. Taken together, these observations paint a coherent picture in which the special features of HOCl vibrational energy redistribution dynamics control the rate of unimolecular dissociation. The weakness of vibrational coupling apparent from the spectroscopic analysis implies that energy flow among vibrational modes is restricted. This, in turn, is reflected in the slowness of the dissociation rates, since the energy initially deposited in the non-dissociating OH stretching mode has to leak out to the OCl dissociation coordinate.

5.2 Results of exact calculations

The experimental and theoretical investigation of HOCl unimolecular dynamics have synergistically driven each other during the past few years, with the groups of Bowman[36,37] and of Schinke[35,38] tackling the latter with high quality *ab initio* calculations of the potential energy surface and dissociation dynamics. The complementarity of these calculations to experimental measurements stems from the former having access to a much larger amount of information, typically limited only by computational power. While experiments can only access states that are permitted by spectroscopic selection rules, calculations can be made for any type of state. On the other hand, for those states that are accessible by experiment, the

measured results provide a critical test of the calculated results. It is only in recent years that advances in computational methods and computation power have allowed reaching a fully quantum state resolved level. Moreover, the HOCl problem is particularly challenging because of the exceedingly small dissociation rates, putting extreme demands on both the accuracy of the numerical method used and of the potential energy surface itself.

One major, and initially unexpected, finding of these studies[35,37] is that the large deviations of the observed rates from the prediction of statistical theories are the norm. Hauschildt *et al.*[35] find that 'HOCl exhibits a pronounced state specificity which results in an unexpectedly broad distribution of rates comprising seven orders of magnitude at threshold'. Eventually, this range narrows down to 3–4 orders of magnitude at energies of several thousand of cm^{-1} above the threshold. Analysis of the wavefunctions helps clarify the connection between the broad distribution of rates and the dynamics of vibrational energy redistribution. Many of the resonance states have 'regular' wavefunctions that can be assigned an approximate set of zeroth-order quantum numbers, implying correspondingly regular intramolecular dynamics. The calculated potential energy surface suggests that the weak coupling of the three vibrational modes arises from the separability of the surface along the corresponding coordinates. When combined with the sizable mismatch of the three vibrational frequencies—3609, 1239 and 724 cm^{-1} respectively for the OH stretching, bending and OCl stretching—this gives only a weak mixing among the zeroth-order states. Only at high energy does the situation change, as the anharmonicity of the potential brings the bending and OCl stretching into a 2 : 1 Fermi resonance that mixes the two modes, but the OH stretching remains weakly coupled to the two other coordinates. When viewed in a time dependent frame, this finding implies that vibrational energy does not flow freely among all coordinates, particularly when the OH stretching is involved, which explains the extreme state specificity of the dissociation rates.

These same theoretical studies go one step further to investigate the experimentally observed fluctuations in dissociation rate of a given vibrational state with rotational quantum numbers J and K. Although one cannot expect to reproduce quantitatively the observed patterns, the calculated rates exhibit qualitatively the same sharp, seemingly random state-to-state fluctuations. The theoretical results indicate that sharp increases of the dissociation rate correspond to increased mixing of the bright state with fast dissociating bath states. Mixing between any two states depends on their separation in energy and the strength of their coupling, and the former changes slightly with the rotational state (J, K) due to slightly different rotational constants. Because the coupling is weak, states that are significantly mixed for a given value of J and K may not be so at a slightly different value. The apparent randomness of the rate fluctuations is then a consequence of the extreme dependence of the rates on the fine details of the Hamiltonian. An extraordinarily accurate calculation would be needed to reproduce exactly each of the individually observed rates.

5.3 A tier model for IVR limited unimolecular dynamics

In the attempt to understand the mechanisms that regulate HOCl dynamics, it may be beneficial to relax the expectation of exactly reproducing the experimental observations and instead find a simple model that is qualitatively correct while at the same time being computationally tractable. While the success of statistical models for other small molecules is an encouragement to seek similar descriptions of HOCl dynamics, a blind transposition of those models to the present case is likely to be inadequate. In the case of formaldehyde, for example, strong vibrational coupling ensures that the initially prepared state is well described by a random mixture of zeroth-order states. In HOCl, on the other hand, coupling is weak, and the initially prepared state consists mostly of OH stretching character. While statistical models are convenient for their conceptual and computational simplicity and often represent the most honest description of a system when no *a priori* knowledge is available, when this knowledge is available it may be advantageous to adapt the approach accordingly. Our approach to describe HOCl unimolecular dynamics is to use the information gained from spectroscopic observations and *ab initio* studies to find the simplest, yet quantitatively correct model.

A good starting point is the zeroth-order approximation that vibrational motion is separable in the OH stretching, OCl stretching and HOCl bending coordinates. It is precisely the breakdown of this approximation by coupling between vibrational modes that makes dissociation of molecules initially excited in the OH stretch possible. Both our spectroscopic analysis and the regularity of the potential energy surface provide a good indication that this breakdown can be conveniently described in the framework of perturbation theory. In this case, the molecule is still described by the same set of oscillators but, because of couplings, energy in the form of vibrational quanta can flow back and forth among them. The propensity of such energy exchange generally decreases exponentially with the total number of quanta exchanged, and there is no reason to expect HOCl to behave otherwise. On the contrary, there is experimental and theoretical evidence to suggest that any interaction involving a total exchange of more than four quanta can be safely neglected, or in other words, that only couplings of order four or less give a significant contribution to the dynamics of HOCl at the energy investigated. When combined with the idea that exchange of vibrational energy is most effective for states that lie nearby in energy (*i.e.*, quasi-resonant coupling), this simplification gives an intriguing insight into the mechanisms that regulate the intramolecular dynamics. Since one OH stretch quantum is roughly equivalent in energy to 2–3 quanta of bend vibration or 4–5 quanta of OCl stretch, low-order quasi-resonant coupling can only connect states that differ by at most one quantum of OH stretch. It is natural then, to arrange the states in a given energy range into tiers, sorted by their number of OH quanta, as shown in Fig. 6. Within this picture, vibrational energy is initially deposited in the leftmost tier, the (6,0,0) state, and must flow to the rightmost tier to dissociate the molecule, since at energies near the dissociation threshold, all the energy initially deposited in the OH stretch is required to break the chemical bond. It should be noted that early tiers (on the left) are sparser than late ones (on the right), and thus states in the former are more likely to be far apart in energy than those in the latter. As a consequence, we can expect that the degree of vibrational mixing increases along the progression of tiers, starting from very weak in tier 6 and 5 and possibly ending up quite strong in tier 1 and 0. We introduce one further approximation, justified by analysis of computer-calculated wavefunctions,[39] that tiers 6 to 2 are only weakly mixed and tiers 1 and 0 are completely mixed. We also assume that in the zeroth-order picture, only states from tier 1 and 0 are directly coupled to the continuum (dissociative), while all others are infinitely long lived (non-dissociative). In this way, we can separate the specific role of early and late tiers and link it with the changes in observed rates for different rotational quantum numbers—that is, upon slightly 'tuning' the energies of vibrational states by using their differences of rotational constants. The early tiers determine the observed spectroscopic features, since the preparation laser can prepare efficiently only states with significant content of the (6,0,0) bright state. Because the early tiers are sparse and weakly coupled, small changes in the rotational quantum number produce no major change in the spectroscopic character of the initially prepared

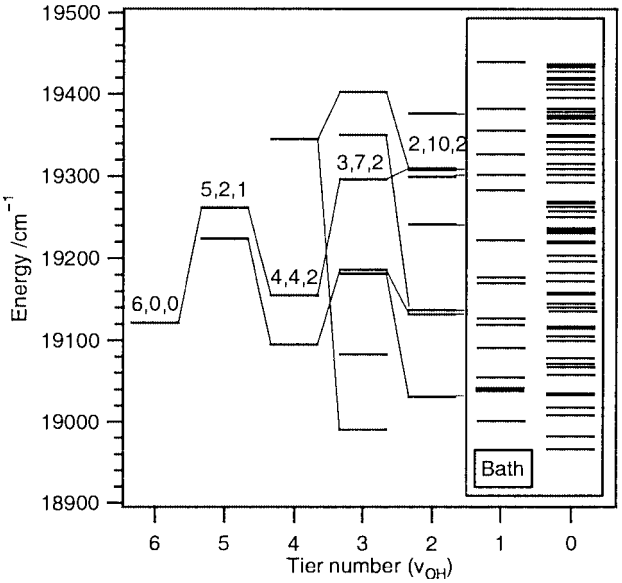


Fig. 6 Tier model of HOCl vibrational Hamiltonian in the region near the (6,0,0) state. Vibrational states, represented by horizontal lines, are sorted by their number of OH stretch quanta. Diagonal lines connecting two states represent anharmonic vibrational coupling of order four or less. States in tiers 1 and 0 are strongly coupled with one another; hence, in this model they are treated as a bath of highly mixed states. Direct coupling to the dissociative continuum (not shown in the picture) is assumed to occur only from tiers 1 and 0.

states. It is only by following a long progression of rotational states that one can detect a smooth evolution in bright state character. On the other hand, the dissociation rate is determined by minute amounts of 'dissociative' states from tiers 1 and 0 that mix into the initially prepared state. This, in turn, depends both on a dissociative state being sufficiently close to the bright state and on the presence of a suitable path of intermediate states connecting the two. The presence of a suitable coupling path depends on the positions of the energy levels in the early tiers, and this is only a weak function of the rotational quantum number. The presence or absence of a dissociative state suitably close to the bright state, however, is a condition that can change rapidly with rotational quantum number, since tiers 1 and 0 are much denser. In this case, even a small change of rotational quantum number can be sufficient to present the bright state with a quite different configuration of these tiers. The rotational dependence is further enhanced by the fact that the less energy one state has in the OH stretching coordinate, the more it is likely to have in the OCl stretching coordinate, whose elongation mostly determines the *B* rotational constant. Thus, the more tiers separate any two states, the faster they are likely to change their relative energy with *J*. In the light of this, what at first appear to be random state-to-state fluctuations of the dissociation rates most likely arise from states in the late tiers tuning into and out of resonance with the bright state. In fact, if *J* were a continuously adjustable parameter instead of a discrete quantum number, one would probably observe a clear pattern of sharp, smooth peaks in the dissociation rate each time a state tunes into and out of resonance with the bright state.

It is unrealistic to expect that this simple model could reproduce exactly the pattern of dissociation rates measured across the range of *J* and *K* states investigated. On the other hand, it should be reasonable to use the model to reproduce the ensemble properties of the entire set of measured rates, as long as the set is reasonably large. The basic assumption is that even if we ignore the exact form of the Hamiltonian, the data set is sufficiently large to explore *all* possible realisations of a suitable model Hamiltonian, which we can then study by numerical methods. The structure of this Hamiltonian is already defined by the tier model. In order to keep the number of adjustable parameters to a minimum we make the following approximations.

(1) Only a single path connects the bright (6,0,0) state with the bath of dissociative states. This allows one to cast the Hamiltonian in the following matrix form:

$$\mathbf{H} = \left(\begin{array}{ccccc|c} E_6^0 & W_{65} & & & & \\ W_{65} & E_5^0 & W_{54} & & & \\ & W_{54} & E_4^0 & W_{43} & & \\ & & W_{43} & E_3^0 & W_{32} & \\ & & & W_{32} & E_2^0 & W_{2b} \\ \hline & & & & W_{2b} & \\ & & & & & \mathbf{B} \end{array}\right)$$

where we have separated the early tiers from the tiers 1 and 0, the latter being represented collectively by sub-matrix **B**.

(2) The upper-left side of the matrix does not change significantly with *J* and *K*; hence, we consider it as constant.

(3) The bath states are all strongly coupled, and our dataset explores all possible realisations of a strongly coupled random-matrix (**B**).

In the limit of weak coupling, perturbation theory gives for the decay width of the initially prepared state

$$\Gamma_6 = \sum_j \Gamma_{6j}$$

where each Γ_{6j} is the partial width acquired by the bright state as the result of the interaction with a single bath state, described by the 2×2 matrix

$$\mathrm{H} = \begin{pmatrix} E_6^0 & W_j^{\mathrm{eff}} \\ W_j^{\mathrm{eff}} & E_j^0 - i\dfrac{\Gamma_j^0}{2} \end{pmatrix}$$

and the coupling through the intermediate tiers has been collapsed into a single effective coupling W_j^{eff}. This treatment, albeit approximate, has the important advantage of isolating the main parameter of the problem, the average strength of the effective coupling between bright state and bath, which we keep as an adjustable parameter.

The result of applying this model to our HOCl experiments is shown in Fig. 7, where we compare the observed distribution of dissociation rates with the predictions of both our tier model and the predictions of the pure statistical approach, as applied in the case of formaldehyde. Clearly, the pure statistical approach does not do a good job of reproducing the observed distribution, while the adapted tier model works reasonably well. The picture that emerges from this analysis confirms that the main features of the observed HOCl dynamics have all the same origin—an initially prepared state that is weakly coupled to the dissociation coordinate and corresponding dissociation rates limited by the slow redistribution of vibrational energy. Because it assumes random coupling among all states, the pure statistical model cannot reproduce results such as these that are limited by dynamical constraints.

5.4 Towards the statistical limit: HOCl at v = 7 and 8

Part of the motivation of this work has been to examine the assumptions of standard statistical theories and determine their limits of applicability. The results and modelling discussed above for the (6,0,0) level of HOCl indicate that energy transfer

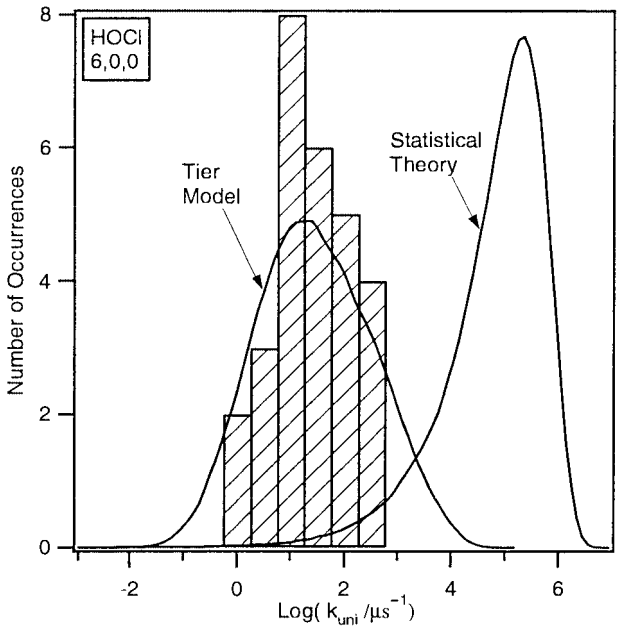


Fig. 7 Distribution of unimolecular dissociation rates of HOCl excited with 6 quanta of OH stretch vibration. Filled boxes give the number of dissociation rates experimentally observed in each respective interval. The two solid curves show the prediction of a pure statistical theory and of the adapted tier model discussed in the text and in Ref. 25.

out of the initially prepared OH stretch mode serves as a bottleneck for unimolecular dissociation and, hence, standard statistical approaches are not at all appropriate. While our restricted tier model seems to capture the essential physics of the dissociation process in a computationally tractable manner, it is important to assess the validity of the model and its limits of applicability. If the weak coupling that characterises the dynamics of (6,0,0) arises from the particular choice of the initially prepared state and the regularity of the potential energy surface, it should persist, at least to some extent, as one goes to more highly excited OH stretching states. One might expect the weak coupling approximation to eventually break down under the combined effects of the increased density of states and the greater anharmonicity of the regions of the potential energy surface accessed at higher energies. Reaching these highly excited states becomes increasingly difficult and requires correspondingly greater care in the optimisation of the experimental conditions and the choice of the excitation scheme.[26] Aside from these technical aspects, the main conceptual difference is that the dissociation rates are expected to be faster for higher excited states, possibly too fast to measure directly with our finite time-resolution. In this case, however, lifetime broadening of the spectroscopic transitions is sufficiently large that it can be measured in the frequency domain with our narrowband pulsed lasers. From the lifetime-broadened linewidth, Γ, the decay rate can be deduced using the relationship $k = \Gamma/\hbar$ as long as there are no overlapping transitions.

Representative spectra of the (7,0,0) and (8,0,0) energy regions are shown in Fig. 8. In the (7,0,0) region the spectra show no visible signs of perturbations and this conclusion is confirmed and reinforced by the same quantitative spectroscopic analysis that was used in the (6,0,0) region. This implies that the average coupling remains small compared to the average level spacing, that the initially prepared state still largely maintains its pure OH stretching character, and that unimolecular dynamics is still limited by the slow IVR rate. As we push to still higher excitation in the OH stretch to the region of (8,0,0), we observe the emergence of several extra features in the spectra, indicating that coupling of the bright state to nearby bath states has become more extensive. Even in cases when the perturbing states themselves do not appear in the spectrum, their presence can be inferred from displacements of the energy of the bright state from its expected value, often by several cm^{-1}. Consistent with this increase of vibrational coupling, the average dissociation rate increases, and the state-to-state fluctuations become less pronounced in magnitude and vary more smoothly as a function of *J*, as shown in Fig. 9. Recall that a strong increase in the dissociation rate of the bright state occurs when it comes into resonance with a fast dissociating state as the rotational quantum number is changed. There are two ways that the increased coupling at this higher energy makes the rates vary in a smoother fashion. First, on average, a larger number of dark states are in resonance with the bright state and contribute to determining its dissociation rate; hence, extremely slow dissociation rates become unlikely. Secondly,

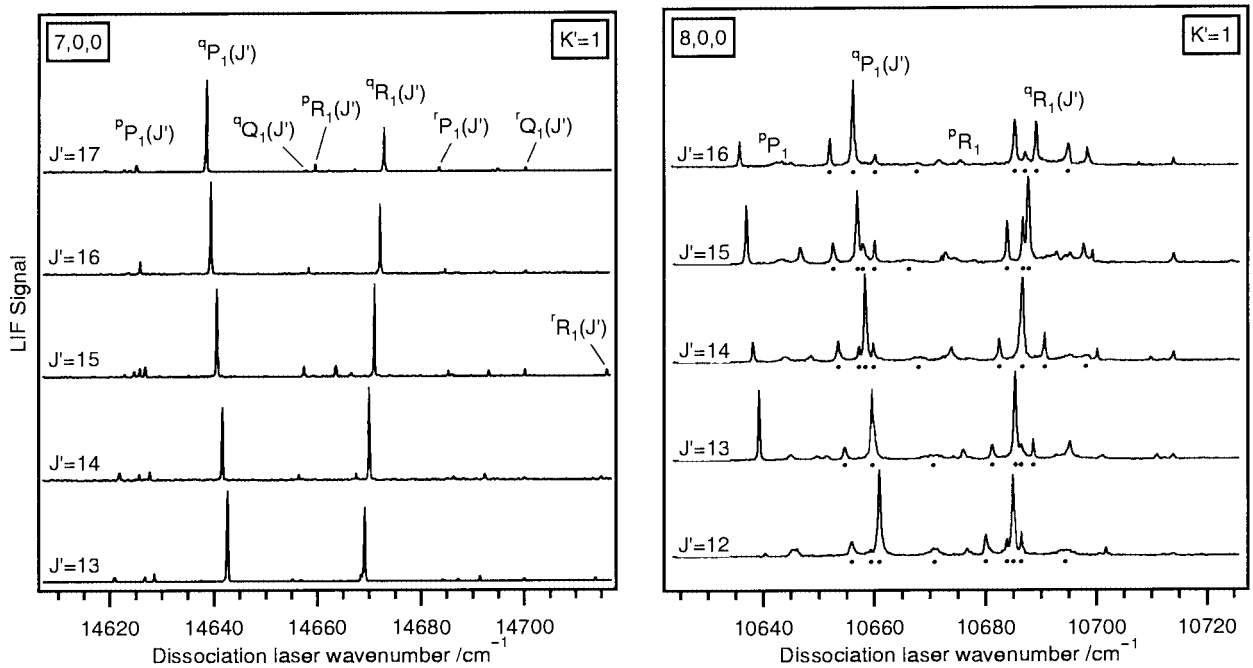


Fig. 8 Sample double-resonance spectra of the HOCl $7\nu_1 \leftarrow 2\nu_1$ and $8\nu_1 \leftarrow 4\nu_1$ bands. Each spectrum in the plot originates from a selected (*J'*, *K'*) rotational state, as indicated in the figure. In the $7\nu_1 \leftarrow 2\nu_1$ spectra no splitting arising from coupling to perturbing states is visible. In the $8\nu_1 \leftarrow 4\nu_1$ spectra peaks arising from coupling of the bright state with nearby dark states are marked with a dot.

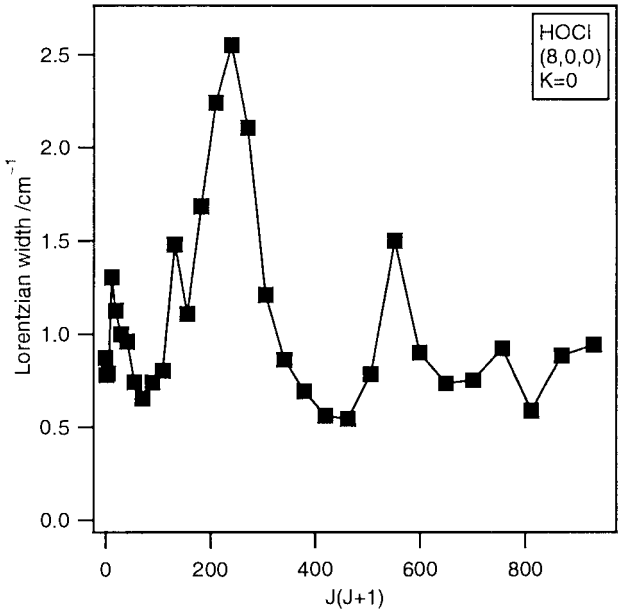


Fig. 9 Rotational dependence of the dissociation width of HOCl excited with 8 quanta of OH stretch vibration and rotational quantum number J = 0–30, K = 0.

with stronger coupling matrix elements, one must tune the interacting states further in energy to affect their mixing to the same degree, and this requires a larger change in J. The end result is that the effect of dark states tuning into and out of resonance with the bright state is clearer in the (8,0,0) region than in the (6,0,0) region (compare Figs. 5 and 9).

Plotting our measured rates for the entire energy range investigated as a function of v_{OH}, as shown in Fig. 10, reveals an

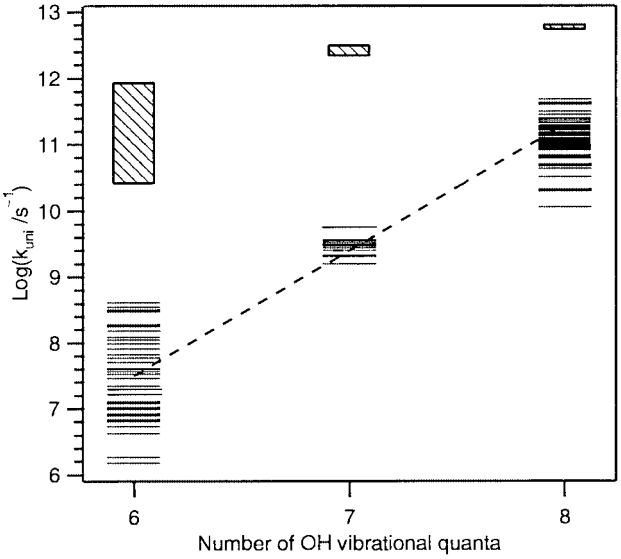


Fig. 10 Vibrational dependence of the distribution of dissociation rates of HOCl prepared in highly excited states of the OH stretching mode. Each horizontal line corresponds to the measured dissociation rate of an individual rovibrational state. Filled boxes show the distribution range expected under the assumption of completely ergodic dynamics. The dashed line serves to emphasize the trend of an 80-fold rate increase for each quantum of OH stretch.

almost 100-fold increase of the average rate for each additional quantum of OH stretch in the initially prepared state. It is interesting to compare, in the same figure, the distribution of the observed rates with that predicted by a pure statistical theory (*i.e.*, for a completely ergodic system). One can see that although at (6,0,0) they are 2–3 orders of magnitude slower than statistical predictions, the observed rates rapidly approach, but do not reach, the statistical limit as the number of OH vibrational quanta in the initially prepared state increases. It is important to determine the origin of this sharp increase in dissociation rate, as this helps us in determining the limits of applicability of simplified models such as ours. Since the dissociation rate is limited by the slow IVR rate, and this in turn is given by Fermi's golden rule $k_{IVR} = 2\pi w^2\rho/\hbar$, we know that the two important factors are the density of states involved, ρ, and the strength of their average coupling w. The former increases relatively slowly with energy,[26] going from 0.17 states per cm^{-1} at v_{OH} = 6 to 0.36 and 0.6 states per cm^{-1} respectively at v_{OH} = 7 and 8, that is, about a factor of two for each additional quantum of OH stretching. The largest contribution must then come from the increase of the average coupling strength, which in turn scales with energy according to the order of the anharmonic terms in the potential that are responsible for it. In the tier model used for explaining the dynamics at (6,0,0), we had considered only coupling up to fourth order to be significant, and this would result in vibrational coupling matrix elements that scale at most as the 3/2 power of the OH stretch quantum number. Since this would not nearly be sufficient to explain the observed increase, we must consider the contribution of higher order couplings.

Inspection of the potential energy surface[40] provides a clue as to the origin of such couplings, as well as an explanation of why they could safely be neglected at (6,0,0). The regular appearance of the potential energy surface in the R_{OCl}–R_{OH} plane indicates that direct coupling between these two coordinates is not very strong, even at the very high energies investigated. On the other hand, a cut in the R_{OH}–θ plane indicates that at low energy the surface is regular, but at energies above 55 kcal mol^{-1}, significant distortion is apparent in the range R_{OH} = 2.3–3 Bohr and θ = 50–70 degrees where the pathway to the HClO isomer is located. The energies of the v_{OH} = 6, 7 and 8 levels are, for this two-dimensional oscillator, about 61.6, 69.0 and 75.8 kcal mol^{-1} respectively, above the potential minimum, so one can expect the distorted region to play an increasingly important role in the stretch–bend energy redistribution. It thus appears that the strength of stretch–bend coupling could be the key controlling factor that regulates IVR and, hence, the unimolecular dissociation rate, in HOCl. The range of energies explored experimentally and theoretically encompasses a broad range of behaviour, starting from extremely regular IVR dynamics and eventually approaching the statistical limit. Extrapolation of the observed trend suggests that this limit would be reached at v_{OH} = 9 or 10. It would be interesting, in this respect, to focus future experimental and theoretical work on defining even further this transition from regular to ergodic unimolecular dynamics.

6 Conclusions and outlook

We have summarized the results of recent studies of unimolecular reaction dynamics at the state-resolved level and discussed how these studies have changed the general understanding of the role of vibrational energy redistribution in the dissociation process. Even in the comparatively small number of cases and sizes of molecules investigated thus far, one finds a variety of different behaviours, ranging from dissociation driven by completely ergodic dynamics, to somewhat mode-specific, to extremely mode-specific dissociation. We have focused our attention on HOCl dissociation from highly excited OH stretching states as an extreme case of IVR-limited unimolecular dynamics. The extensive amount of recent experimental and theoretical work on this molecule makes it a textbook case for this class of problems. We have demonstrated that the combination of different, often complementary techniques can give a picture of the mechanisms involved in the intramolecular dynamics with unprecedented clarity. On the experimental side, spectroscopic analysis gives details on the

nature of the initially prepared state and the mechanism of vibrational energy redistribution from that state, while time-resolved measurements give the resulting unimolecular dissociation rates. Both types of data provide essential benchmarks for numerical calculations. On the theoretical side, highly accurate *ab initio* calculations that are tested by comparison with experiment give access to information that would be virtually impossible to obtain experimentally. We have also demonstrated the value of simple approximate models to complement exact *ab initio* calculations. While it is clear that these models cannot give the same precise detail as exact methods, they provide a valuable tool for extracting the essential physics of the problem that can be applicable to a broader class of systems.

The picture that emerges in the case of HOCl is that the dissociation dynamics at the level of individual states is extremely sensitive to the finest details of the Hamiltonian. On the other hand, at the ensemble level, where we are interested in the *probability* of finding a certain dissociation rate for a given state, only a small number of parameters play an important role, leaving open the possibility that the results can be generalized into a unified treatment of state-resolved unimolecular dynamics. Perhaps the most important ingredient necessary to make this happen is the continued fruitful cooperation between theory and experiment.

7 Acknowledgements

It is a pleasure to acknowledge the help and collaboration of many people. Those who worked with us to make possible the experiments described on this paper: Mike Wedlock, Julia Rebstein, Remy Jost, John Muenter, Roman Schmied, Patrice Theulé, and the many colleagues that shared their knowledge, in particular the groups of Reinhard Schinke and Joel Bowman. Financial support from EPFL and the Fonds National Suisse is gratefully acknowledged.

8 References

1 In this article we give only a brief review of the issues relevant to the discussion; the interested reader can find a review of the broader field in Refs. 2–6 and the papers cited therein.
2 T. Baer and W. L. Hase, *Unimolecular reaction dynamics: theory and experiments*, Oxford University Press, 1996
3 K. A. Holbrook, M. J. Pilling, S. H. Robertson and P. J. Robinson, *Unimolecular reactions*, Wiley, 1996
4 R. Schinke, C. Beck, S. Y. Grebenshchikov and H. M. Keller, *Ber. Bunsenges. Phys. Chem.*, 1998, **102**, 593.
5 W. H. Green, C. B. Moore and W. F. Polik, *Annu. Rev. Phys. Chem.*, 1992, **43**, 591.
6 S. A. Reid and H. Reisler, *Annu. Rev.Phys. Chem.*, 1996, **47**, 495.
7 M. Quack and J. Troe, *Ber. Bunsenges. Phys. Chem.*, 1974, **78**, 240.
8 P. Rogers, D. C. Montague, J. P. Frank, S. C. Tyler and F. S. Rowland, *Chem. Phys. Lett.*, 1982, **89**, 9.
9 F. F. Crim, *Annu. Rev. Phys. Chem.*, 1984, **35**, 657.
10 K. K. Lehmann, G. Scoles and B. H. Pate, *Annu. Rev. Phys. Chem.*, 1994, **45**, 241.
11 M. Quack, *Annu. Rev. Phys. Chem.*, 1990, **41**, 839.
12 D. J. Nesbitt and R. W. Field, *J. Phys. Chem.*, 1996, **100**, 12735.
13 T. Uzer, *Phys. Rep.*, 1991, **199**, 73.
14 A. Sinha, M. C. Hsiao and F. F. Crim, *J. Chem. Phys.*, 1991, **94**, 4928.
15 O. V. Boyarkin, L. Lubich, R. D. F. Settle, D. S. Perry and T. R. Rizzo, *J. Chem. Phys.*, 1997, **107**, 8409.
16 B. R. Foy, M. P. Casassa, J. C. Stephenson and D. S. King, *J. Chem. Phys.*, 1990, **92**, 2782.
17 F. Reiche, B. Abel, R. D. Beck and T. R. Rizzo, *J. Chem. Phys.*, 2000, **112**, 8885.
18 X. Luo, P. R. Fleming and T. R. Rizzo, *J. Chem. Phys.*, 1992, **96**, 5659.
19 A. Geers, J. Kappert, F. Temps and J. W. Wiebrecht, *J. Chem. Phys.*, 1994, **101**, 3634.
20 Y. S. Choi and C. B. Moore, *J. Chem. Phys.*, 1992, **97**, 1010.
21 W. F. Polik, D. R. Guyer and C. B. Moore, *J. Chem. Phys.*, 1990, **92**, 3453.
22 C. Stock, X. N. Li, H. M. Keller, R. Schinke and F. Temps, *J. Chem. Phys.*, 1997, **106**, 5333.
23 J. D. Tobiason, J. R. Dunlop and E. A. Rohlfing, *J. Chem. Phys.*, 1995, **103**, 1448.
24 A. Callegari, J. Rebstein, J. S. Muenter, R. Jost and T. R. Rizzo, *J. Chem. Phys.*, 1999, **111**, 123.
25 A. Callegari, J. Rebstein, R. Jost and T. R. Rizzo, *J. Chem. Phys.*, 1999, **111**, 7359.
26 A. Callegari, R. Schmied, P. Theulé, J. Rebstein and T. R. Rizzo, *Phys. Chem. Chem. Phys.*, 2001, **3**, 2245.
27 G. Dutton, R. J. Barnes and A. Sinha, *J. Chem. Phys.*, 1999, **111**, 4976.
28 A. Geers, J. Kappert, F. Temps and J. W. Wiebrecht, *J. Chem. Phys.*, 1994, **101**, 3618.
29 S. A. Reid, D. C. Robie and H. Reisler, *J. Chem. Phys.*, 1994, **100**, 4256.
30 S. A. Reid and H. Reisler, *J.Phys. Chem.*, 1996, **100**, 474.
31 W. H. Miller, R. Hernandez, C. B. Moore and W. F. Polik, *J. Chem. Phys.*, 1990, **93**, 5657.
32 S. Skokov, J. X. Qi, J. M. Bowman, C. Y. Yang, S. K. Gray, K. A. Peterson and V. A. Mandelshtam, *J. Chem. Phys.*, 1998, **109**, 10273.
33 R. Schinke, *Photodissociation dynamics: spectroscopy and fragmentation of small polyatomic molecules*, Cambridge University Press, 1993.
34 When referring to vibrational states of HOCl, we use the notation (n_1, n_2, n_3,) to indicate the number of quanta in the OH stretching, HOCl bending and OCl stretching modes respectively. We use J, K_a, and K_c to label rotational states, although since HOCl is nearly a symmetric top, simply J and K (= K_a) are often sufficient.
35 J. Hauschildt, J. Weiss, C. Beck, S. Grebenshchikov, R. Duren, R. Schinke and J. Koput, *Chem. Phys. Lett.*, 1999, **300**, 5.
36 S. Skokov, J. M. Bowman and V. A. Mandelshtam, *Phys. Chem. Chem. Phys.*, 1999, **1**, 1279.
37 S. Skokov and J. M. Bowman, *J. Chem. Phys.*, 1999, **111**, 4933.
38 J. Hauschildt, J. Weiss and R. Schinke, *Z.Phys. Chem.*, 2000, **5**, 609.
39 M. Joyeux, D. Sugny, M. Lombardi, R. Jost, R. Schinke, S. Skokov and J. Bowman, *J. Chem. Phys.*, 2000, **113**, 9610.
40 S. Skokov, K. A. Peterson and J. M. Bowman, *J. Chem. Phys.*, 1998, **109**, 2662.