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REVIEWS

Modern studies of intramolecular vibrational energy redistribution

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Intramolecular vibrational energy redistribution has been much studied because of the important role it plays in theories of unimolecular reactions and in dictating the feasibility of bond-selective chemistry. In this review we survey some of the more recent experimental studies and hope to provide a general introduction along with some present day conclusions.

1 Introduction

Excited molecules are often a prerequisite to chemical reaction, and as a consequence there has been much interest in their behaviour. When molecules are highly excited they defy our attempts to describe their energy levels with simple expressions and exhibit a phenomenon known as intramolecular vibrational energy redistribution, or IVR. Here, the initial localised energy of an isolated molecule that has been excited by an external perturbation redistributes to reside ultimately in other parts of the molecule. This energy redistribution may be studied by monitoring the evolution of the population in the initially prepared state.

Experimental studies of IVR generally involve the radiative excitation of gas phase molecules. The choice of the gas phase enables the study of truly isolated molecules, and thus of intramolecular dynamics that are not complicated by solvent effects. If a particular superposition of molecular eigenstates (stationary states) with a particular phase relationship is prepared in such gas phase molecules by radiative excitation it is commonly known as a bright state. Similarly, those superpositions which are not radiatively coupled to the ground state are labelled dark states. The initial phase relationship of the eigenstates forming the bright state may, for example, correspond to predominantly the motion of a single excited bond in the molecule. The differing phase dependence of each of these eigenstates causes the bright state to be nonstationary, *i.e.* to evolve in time. This evolution causes the molecule to behave more like a classical oscillator, with certain bonds stretched or compressed at certain times. If enough eigenstates form the superposition then the initial phase relationship (*e.g.* as above, single bond stretched) will never be recovered and the excitation energy will appear to be randomized after some time known as the IVR lifetime.

Because the forms of the true molecular eigenstates are often unknown, and because most experiments are unable to resolve eigenstates, the bright and dark states are usually expressed in terms of basis functions that are orthonormal in some reasonable first approximation Hamiltonian. These functions correspond to excitation in a set of independent normal modes. Articles on IVR therefore often refer to the coupling between these basis functions by anharmonic or Coriolis interactions in the true Hamiltonian as causing IVR, rather than the cause being phase evolution of the true molecular eigenstates, but either language can be adopted. Here, for the most part, we use the former.

The existence of IVR as a ubiquitous rapid process is central to the 1952 Rice–Ramsperger–Kassel–Marcus (RRKM) theory of unimolecular reactions.[1] In this theory, it is assumed that any initial energy of excitation is redistributed across the whole molecule so rapidly that if the original excitation were localized, a rupturing bond would display no memory of this localization. Clearly, in a small molecule with well-separated energy levels there will be instances where RRKM theory will be inappropriate as there is no mechanism by which the energy can flow, but in a large molecule, energy levels are closely spaced and RRKM theory often provides a good description of reaction rates.

Following the initial formulation of the RRKM theory there have been many experimental studies of IVR designed to test the predictions of the theory and to search for systems that display non-RRKM behaviour. The first experimental evidence of the existence of IVR was provided by Butler *et al.*[2] in 1960 and the first direct measurement of an IVR rate was provided by Deutsch *et al.* on SF_6 in 1977.[3] The interest in non RRKM systems and IVR rates stems from the long dreamed of possibility of bond-selective (or mode-selective) chemistry in which bond rupture would predominantly occur in the bond where excitation was initially localised. This possibility has led to a quest for molecules which display redistribution rates that

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are slow compared with the interval between molecular collisions.

Despite the wealth of experimental data on IVR, some of which can be found in Table 1, its description has for the most part eluded theoreticians and in many respects it remains poorly understood. A number of simple models have been developed that seem to provide good explanations for some molecules in some states, but none has so far proved universal. There have been many attempts to rationalise IVR rates in terms of the number of the molecular eigenstates per unit energy, or density of states, but these have not been entirely successful (see Section 4).

Table 1 Representative IVR lifetimes in the ground electronic state of various molecules. All measurements were made by infrared spectroscopy in the frequency domain except where indicated, and the FWHM lifetimes are given. Where the number of vibrational quanta is not given, the lifetime pertains to the fundamental vibration.

Molecule	Vibration	Ref.	Lifetime
$HC{=}CC{=}CH$	CH stretch, v = 2	12*a*	165 ps
	$(\nu_1 + \nu_2)$		2.7 ns
$HC{=}CC{=}CD$	CH stretch, v = 3	12*a*	50 ps
$(CH_3)_3CC{\equiv}CH$	Acetylenic CH, v = 1	24	200 ps
	Acetylenic CH, v = 2		110 ps
$(CH_3)_3SiC{\equiv}CH$	Acetylenic CH, v = 1	24	2000 ps
	Acetylenic CH, v = 2		4000 ps
$CHSi(C{\equiv}CH)_3$	Acetylenic CH, v = 1	12*e*	350 ps
	ν_{13}		490 ps
$(CF_3)_3CC{\equiv}CH$	Acetylenic CH, v = 1	12*c*	60 ps
	Acetylenic CH, v = 2		1 ps
$(CD_3)_3CC{\equiv}CH$	Acetylenic CH, v = 1	12*c*	40 ps
	Acetylenic CH, v = 2		< 20 ps
$(CD_3)_3SiC{\equiv}CH$	Acetylenic CH, v = 1	12*c*	850 ps
	Acetylenic CH, v = 2		140 ps
$CH_3C{\equiv}CH$	Acetylenic CH, v = 1	12*b*	110 ps
	Acetylenic CH, v = 2		320 ps
	$\nu_1 + 2\nu_6$		3.2 ns
Ethanol	OH stretch	21	25 ps
	Methyl CH		123 ps
$CF_3C{\equiv}CH$	Acetylenic CH	29	2 ns
$HC{=}C{=}CH$	$2\nu_1 + \nu_5$	25	210 ps
	$2\nu_6$		180 ps
But-1-yne	Acetylenic CH	27	285 ps
	Methyl CH		320 ps
Pent-1-yne	Acetylenic CH	27	241 ps
	Methyl CH		< 40 ps
Prop-2-ynyl alcohol	OH stretch[a]	27	110 ps
	Acetylenic CH	27	250 ps
But-1-ene	Methyl CH	27	37 ps
Butane	Methyl CH	27	18 ps
Methyl formate	Methyl CH	27	70 ps
trans-But-2-ene	Methyl CH	27	132 ps
tert-Butylacetylene	Acetylenic CH	27	200 ps
2-Fluoroethanol	Methyl CH	27	565 ps
1,2-Difluoroethane	Methyl CH	27	490 ps
Isobutane	Methyl CH	27	< 177 ps
trans-1-Chloro-2-fluoroethane	Methyl CH	27	No Decay
$SF_5C{\equiv}CH$	Acetylenic CH, v = 1	14	3 ns
	Acetylenic CH, v = 2		1.5 ns

[a] Time resolved measurement

A common theme in IVR that is related to the density of states is the existence of different regimes of excitation which give rise to qualitatively different IVR dynamics.[4] Within this description, a very slow rate (or long lifetime compared with the inverse of the average energy spacing) would correspond to the population of a single eigenstate in a sparse region [Fig. 1(*a*)]. Conversely, a short lifetime compared with the inverse of the average energy spacing would correspond to a rapid statistical redistribution mediated by a very high density of states. In this fast regime of IVR, energy is redistributed to parts of the molecule distant from the region initially excited too rapidly for any recurrence to be possible. This redistribution is usually an extremely rapid exponential decay of energy but may take the form of a biexponential with fast and slow components [Fig. 1(*c*)]. In between these two, a region exists in which there is a partial recurrence of the population of the initially prepared state at certain well-defined times [Fig. 1(*b*)]. This phenomenon is known as quantum beats and is analogous to vibrational wavepacket motion with the recurrence time giving an indication of the level spacing.

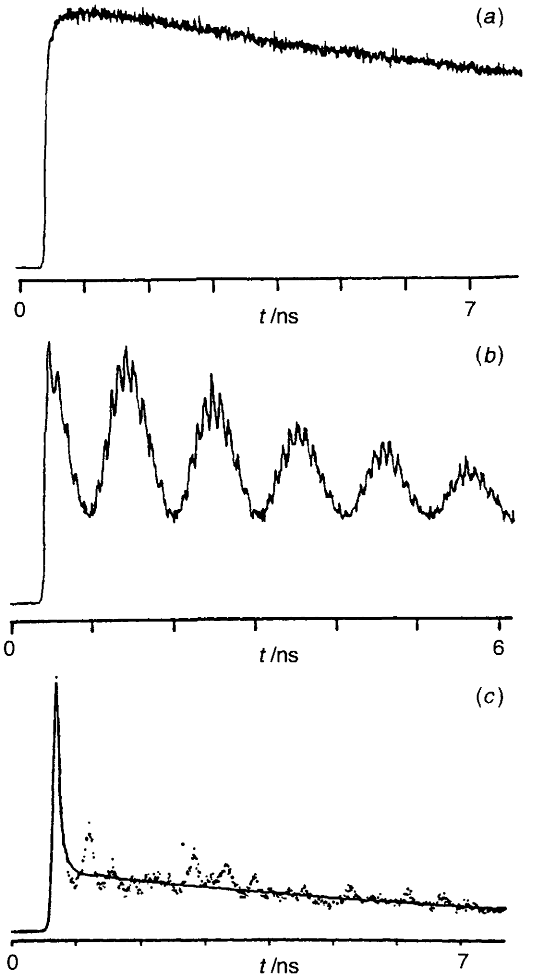

Fig. 1 Fluorescence decay of anthracene in its S_1 electronic state at vibrational energies of (*a*) 390 cm^{-1}, (*b*) 1420 cm^{-1} and (*c*) 1792 cm^{-1} with corresponding densities of states of (*a*) 10, (*b*) 25–40 and (*c*) 120 per cm^{-1}. Clearly there is little redistribution of energy in (*a*), the emergence of quantum beats in (*b*) at a higher density of states and a rapid biexponential decay in (*c*). (Adapted from P. M. Felker and A. H. Zewail, *J. Chem. Phys.*, 1985, **82**, pp. 2961 with kind permission of the American Institute of Physics).

This review is intended to serve two purposes: (*i*) to survey, collate and attempt to rationalise some of the mass of experimental observations and (*ii*) to extract measured IVR lifetimes from a number of sources in the hope of finding an underlying pattern, and systems that display particularly long lifetimes. It is organised as follows: experimental techniques used to probe IVR are reviewed and the origin of IVR is discussed. Possible rationalisations of IVR lifetimes are considered in terms of the density of states and simple models that have been developed. Finally, a brief section focuses on the possibility of mode-selective chemistry.

2 Experimental techniques

Numerous spectroscopic methods are employed to probe IVR in polyatomic systems, in both excited and ground electronic states. Furthermore it is possible to investigate IVR in both frequency-resolved and time-resolved domains. The use of supersonic jet-cooling causes spectral simplification. This has revolutionised IVR studies and provides the basis of most recent experiments. Here, brief details of some relevant techniques will be presented which indicate the scope of information obtainable and limitations where appropriate. The techniques discussed will be referred to in the following sections.

2.1 Excited state

Although IVR in the electronic ground state is of most chemical interest, IVR was first studied in electronically excited states of molecules. The main reason for this was the availability of powerful, tunable light sources, primarily lasers, operating in the visible region of the spectrum. These light sources enabled the preparation of states in a well-defined energy range, and a built-in clock was provided by the radiative lifetime of the electronic state. These advantages have meant that excited state studies continue to be actively pursued. In principle, it is possible to prepare any vibrational level in a mode that is of a symmetry that can be accessed, but the probability of preparing each level is governed by Franck–Condon factors (vibrational overlap integrals) that usually make the higher levels inaccessible.

Typically, the excitation laser prepares a bright state (see Section 1) in the first electronically excited state (where the electronic states are labelled S_0 and S_1 for ground and first excited singlet states, respectively). The extent of IVR can be deduced from either the width of the absorption profile, or the appearance of spectral congestion in emission. The full width at half maximum (FWHM) of the absorption band reflects the reciprocal of the IVR lifetime, however there are some disadvantages in attempting to extract this: (*i*) a known mathematical function must be fitted to the band, and (*ii*) the broadening of the band may not be entirely IVR related as Doppler and collisional broadening can also occur, both of which would imply a faster IVR process than the true one.

It is also possible to resolve the bright state in the time domain by observing the fluorescence at differing time delays following excitation, enabling the evolution of the population of the bright state to be monitored with time. If fluorescence is detected at differing time delays then IVR is manifested by the appearance of spectral congestion at longer time delays. It is possible to monitor only the bright state population by passing the fluorescence through a monochromator and selecting the frequency corresponding to bright state emission. This direct population monitoring is invaluable to IVR studies since it provides a direct probe of how the energy is redistributed and provides a clear indication of whether IVR is in the sparse, intermediate or statistical regime. This type of information is not always inferable from time integrated studies. The lifetime of the bright state can be extracted as the l/e point of a fitted exponential decay curve of the bright state.

Time-resolved studies of this nature require manipulation of the time delay between excitation and observation of the fluorescence. Parmenter and coworkers pioneered a method called chemical timing which is a classic way of imposing picosecond timing by reducing the S_1 fluorescence lifetimes with an added quencher gas, usually oxygen.[5] In the absence of quencher gas the lifetime will be the inherent radiative lifetime. As the pressure of quencher gas is increased, collisions with activated molecules relax them enabling only the fluorescence in a time 'gate' between activation and collisional relaxation to be observed. Because the bright and dark states are collisionally relaxed at the same time and rate, the fluorescence will indicate IVR through the emergence of unstructured emission as the pressure of quencher is decreased. Chemical timing has one substantial disadvantage: because not all molecules are quenched at precisely the same time there is a distribution of lifetimes. This will manifest itself as congestion in the spectrum because the molecules that are quenched later will show enhanced unstructured emission as IVR is more complete, compared with molecules that are quenched earlier. Chemical timing was developed for the purpose of providing quantitative data for IVR processes in systems where IVR is the dominant relaxation pathway, and an estimate of the IVR lifetime can be gained from the ratio of the intensity of structured to unstructured emission. An accurate determination of lifetime however requires mathematical modelling and involves the assumption of either statistical or intermediate IVR. Thus, chemical timing is an excellent way to reveal the presence of IVR but limited in its ability to readily provide accurate lifetimes.

The advent of ultrafast lasers was a great redeemer as changing the time delay between pump and probe pulses allows controllable time resolution. However, it is not unusual for these lasers to have pulse widths of the order of femtoseconds which severely limits their frequency resolution. This inherent problem makes it difficult to probe sufficiently few selected levels, especially high in the vibrational manifold where there is a high density of states. Although time-resolved studies and lineshape analysis should provide complementary information, discrepancies have arisen when comparisons have been performed between the two methods. Zewail and coworkers, the pioneers of 'real time' measurements, have used picosecond molecular beam techniques to record the fluorescence spectra of a number of aromatic molecules such as alkylanilines. They found that for large and complex molecules of this type spectral broadening does not necessarily indicate the rate of energy redistribution. This is especially important at high excitation energies where dispersed fluorescence spectra of different bands tend to be similar in appearance and it may be misleading to infer the dissipative nature of an IVR process by consideration of low resolution frequency-resolved spectra alone. Felker and Zewail studied jet-cooled anthracene using both frequency and time resolution to illustrate this point.[6] The dispersed fluorescence of unrelaxed and relaxed vibrational states in S_1 were separated with a monochromator. Fig. 2 illustrates that the differences are more apparent in the time-resolved results than in the frequency-resolved spectrum.

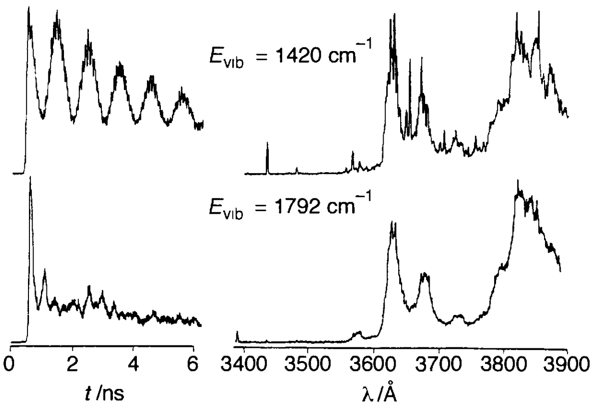

Fig. 2 Unrelaxed time-resolved (left column) and frequency- resolved (right column) spectra of anthracene for two different S_1 vibrational levels. The time-resolved spectra show much clearer differences between the two levels with quantum beats appearing at 1420 cm^{-1} and an exponential decay at 1792 cm^{-1}. (Adapted from P. M. Felker and A. H. Zewail, *Chem. Phys. Lett.*, **108** (4). Direct picosecond time resolution of IVR in isolated molecules, p. 303, 1984 with kind permission of Elsevier Science, NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands).

A relatively new technique has been named time-resolved fluorescence depletion spectroscopy (TRFD) and was pioneered by McDonald and coworkers.[7] Two laser pulses of identical wavelength and duration are used to create and stimulate emission from a vibrational state in S_1. Stimulated emission intensity is measured as a function of the delay between the two pulses, and by monitoring the efficiency with which the second pulse can stimulate emission the evolution of the prepared state can be followed. IVR occurring during the delay causes the prepared state to evolve and reduces the ability of the second pulse to stimulate emission, with the resolution only depending upon the bandwidth of the laser pulse. Thus, there is a large decrease in fluorescence intensity if IVR has occurred. The resulting lineshapes are fitted to an empirical form to deduce the overall IVR lifetime. The technique can also reveal quantum beats which are inferred from the appearance of undulations associated with the band.

Excited state IVR may also be studied by ionization using a technique based upon photoelectron spectroscopy. The ZEKE (zero kinetic energy photoelectron spectroscopy) method involves the ionization of a molecule in its S_1 electronic state with the selective detection of those electrons that carry no kinetic energy. A pump pulse prepares an intermediate state in S_1 and the probe pulse is tuned to a vibronic feature in the cation. The zero kinetic energy electrons are extracted by a voltage applied 1–2 μs after the probe laser excitation. By tuning the probe laser to a specific vibrational band within S_1, population monitoring can be achieved from the observation of the ZEKE signal at different pump-probe delay times. Because IVR occurring during the delay will depopulate the S_1 vibronic bright state, a decrease in the ZEKE signal will be observed. This enables a real-time study of IVR and the method has been used to study a variety of molecules including *p*-difluorobenzene.[8] The resulting spectra are similar to those obtained with the time-resolved studies described previously, and indicate statistical and intermediate IVR at different excitation energies.

2.2 Ground state

Historically IVR studies concentrated on electronically excited states, but it is within the electronic ground state that real chemical interest lies. IR spectroscopy is the most obvious method of studying IVR in the ground state. In its crudest form, applying IR spectroscopy to IVR studies involves standard spectrometers and lineshape analysis similar to that described previously. Conventional IR spectroscopy, however, provides restricted resolution, and until good sources of tunable IR radiation were available the study of IVR in the ground state was somewhat limited. The rectification of this has led to extensive ground state IVR studies in the frequency domain by the direct pumping of low vibrational states and the use of detectors that monitor absorption. An advantage of this is that the spectroscopic resolution is limited only by the bandwidth of the exciting laser, whereas excited state studies often rely on collecting dispersed fluorescence with a monochromator. A disadvantage of IR spectroscopy is the severe harmonic selection rule, $\Delta v = \pm 1$, which means that higher vibrational levels are difficult to populate by direct photon absorption.

This problem has been overcome by a technique known as stimulated emission pumping (SEP) which involves promoting the molecule to an excited electronic state and subsequently stimulating it down to a high vibrational level in the ground electronic state. The accompanying selection rules place fewer restrictions upon the vibrational levels accessible in the ground electronic state. This technique is thus an extremely powerful method of studying IVR in the electronic ground state at differing levels of excitation. Knight and coworkers used this method to study high lying vibrational levels in *p*-difluorobenzene;[9] the level of interest was prepared by SEP and the populated level probed by laser-induced fluorescence. The study of very high lying levels is of great chemical significance, especially if their energies are above a dissociation limit. Geers *et al.* performed just such a study on the CH_3O radical.[10]

The detection of molecular ions in the gas phase can be accomplished relatively easily and accurately, for example by mass spectrometry. This provides the basis for an alternative method to study ground state IVR known as stimulated emission ion dip (SEID).[11] Here the number of molecular ions produced by sequential excitation with two differing laser frequencies is monitored as a function of the second laser frequency ν_2. However, the second laser can also stimulate emission to a vibrational level in the S_0 state if its frequency coincides with an energy gap. Hence, there is a depopulation of the S_1 state and a dip in the ionization spectrum. If IVR is significant the second laser cannot induce pumping back to S_1 leading to a large dip. IVR rates can be derived from the extent of the dip and appropriate rate equations.

A technique which has recently become possible is double-resonance infrared excitation as demonstrated by Gambogi *et al.*[12] Here, a vibrational state in S_0 is prepared by sequential excitation by two IR photons. For example, the transitions $1 \leftarrow 0$ and $3 \leftarrow 1$ were excited within the ν_3 mode of diacetylene to avoid the 'more forbidden' character of $3 \leftarrow 0$ compared with $3 \leftarrow 1$.[12a] This provides considerable advantages: (*i*) the spectrum can be recorded with less overall power because the transition probability will be greater when Δv is small, (*ii*) it is possible to reach states not accessible by one photon absorption *e.g.* symmetric stretches within a molecule with a centre of inversion, and (*iii*) because the rotational angular momentum quantum number, J, is selected in the first absorption step the number of accessible rotational states is reduced compared with those accessible by direct photon absorption, aiding a full assignment of spectra.

Double-resonance IR spectroscopy is often used as a method of 'eigenstate-resolved spectroscopy', *i.e.*, using high resolution IR radiation to resolve the rotational fine structure of vibrational bands. The resolution enables coupling strengths of the bright state to nearly isoenergetic states to be deduced, and since the spectra are eigenstate-resolved the perturbing states can be identified. As an illustration the first overtone C–H stretching vibration of diacetylene was studied using this method.[12a] The spectra revealed three strong lines for each transition of the P and R branch at low rotational angular momentum quantum number, J, with the emergence of a fourth line at higher J indicating a further perturbing state. The perturbing states were deduced to be bending and other stretching vibrations of the molecule, although the exact modes responsible were not determined. An important application of eigenstate resolution is the determination of the density of states which can be 'counted', and would otherwise need to be calculated. This quantity is important for the considerations of IVR and will be discussed later. The double-resonance IR technique has provided a large source of data on IVR lifetimes to date (see Table 1).

IVR in the electronic ground state has also attracted considerable theoretical attention but full quantum calculations are only, as yet, possible for rigid molecules. Classical trajectory calculations are often applied to IVR dynamics and rely upon using classical mechanics to calculate the distribution of energy at desired time delays using a set of initial conditions, an appropriate potential energy surface and spectroscopic data. Full details are beyond the scope of this review but interested readers are directed to a series of papers by Budenholzer and coworkers.[13]

3 Origins of IVR

3.1 Mode specificity in IVR

The basis functions corresponding to excitation in independent normal modes (see Section 1) will in general be coupled by anharmonic interactions. Because potential energy functions are totally symmetric, anharmonic interactions will only couple eigenstates that are of the same vibronic symmetry. However, anharmonic coupling is enhanced through the weak interactions of near degenerate states of differing vibronic symmetry, even though they are in principle forbidden, and it is likely that extensive weak interactions of this nature are important for the rapid statistical IVR reached in large polyatomic molecules. These symmetry controlled interactions lead to the possible transfer of vibrational energy between the coupled states, which is manifested in vibrational spectra by the appearance of bands which would otherwise be dark. For example, Lehmann, Scoles and coworkers studied the CH stretch in SF$_5$CCH using eigenstate-resolved IR spectroscopy.[14] The fundamental absorption revealed five bands of which two could only be attributed to dark states that had borrowed intensity from the bright state and so must have been anharmonically coupled to it. The perturbation was thought to be a CCH bending mode, and it is a general observation that the CH chromophore in acetylenic compounds couples the CH stretch and CCH bend. This coupling was shown to be very important in diacetylene with a second overtone lifetime of 165 ps which upon deuteration of CCH increases to 500–600 ps.[12a] This suggests that the removal of the CCH group was accompanied by the removal of a very important IVR channel. A similar observation for acetylenic molecules was made by Nesbitt and coworkers.[15]

CH stretches excited in other structural environments are also observed to couple to bends involving motion of the same CH unit. Examples of molecules that exhibit this behaviour are CHY$_3$ where Y = F or CF$_3$, and CHFZ$_2$ where Z = Cl or CH$_3$.[16] This coupling of a stretch and bend involving a fundamental and an overtone vibration is known as a Fermi resonance and has been observed for many other sp^3 alkyl chromophores such as toluene[16] and trideuteroacetaldehyde.[17] A general phenomenon of mode specificity, *i.e.* the preferred coupling of the bright state to specific dark states is thus illustrated by trideuteroacetaldehyde and the other molecules above. In trideuteroacetaldehyde coupling was observed between the CH stretch and the CH in-plane bend, but not between the stretch and CH out-of-plane bend. It was also observed that there was no coupling between the CO and CH stretches which to a certain extent provides validation of the 'doorway state' model considered in section 4.2. This mode specificity was thought to be important for modes which possess appreciable anharmonicity, for instance vibrations within a methyl group. An IR study of methyl glyoxal revealed a mode specific coupling between the CO stretching mode and bending modes of the methyl group, suggesting that removal of this group would decrease the IVR rate.[18] The C–C skeletal torsion was also thought to be significantly anharmonic but no evidence of mode specificity involving this channel was observable.

The fact that coupling depends upon the vibrational nature of the dark states was also shown by Philips and coworkers in an eigenstate-resolved infrared study of 2-fluoroethanol in the CH stretching region.[19] Clusters of peaks were observed in the spectrum, with each peak corresponding to a rovibrational state and each cluster corresponding to a bright state. The molecule displayed a large variation in the degrees of coupling within a single cluster of peaks, which could not be explained by the usual random fluctuations in coupling matrix elements. This suggested that the bright state interacts most strongly with specific dark states. This work also illustrates the importance of rotational resolution in identifying coupling pathways.

3.2 Effect of molecular rotation

Molecular rotation can also induce vibrational state mixing. As a molecule rotates it experiences a Coriolis force which can couple vibrational modes. For example, in a triatomic molecule rotation couples the antisymmetric stretch and one component of a doubly degenerate bending mode. Such Coriolis coupling manifests itself in eigenstate-resolved spectra through the dependence of coupling strengths or rotational linewidths upon the rotational quantum number, J; the greater the angular momentum the greater the molecular distortions and hence coupling induced. Lehmann, Scoles and coworkers studied three quanta in the acetylenic CH stretch of propyne using infrared double resonance spectroscopy and illustrated the effect of rotational angular momentum.[12b] The time evolution of the bright state was calculated from frequency-resolved spectra and revealed quantum beats at low J which were not significant at high J. This suggests that Coriolis coupling can be important in mediating IVR.

Coriolis coupling is an important consideration for experiments employing supersonic jet-cooling. Jet cooling vastly reduces the number of rotational levels populated which may increase the lifetime of extensively Coriolis coupled vibrational modes. Infrared jet-cooled studies of dimethyl ether and 1,4-dioxane showed that the CH stretch displayed limited coupling at a rotational temperature of 2 K compared with 20 K, where there was considerable coupling.[20] Similarly, Felker and Zewail found that the decay rates of quantum beat envelopes of jet-cooled anthracene increased significantly as the rotational quantum number increased.[4] McDonald *et al.* made a direct study of the effect of rotational temperature on the lifetime of a vibrational state.[7] TRFD scans of four bands of *p*-cyclohexylaniline were taken with rotational temperatures ranging from 8–110 K by using differing He backing pressures in a molecular beam. The results clearly indicate a decreasing lifetime with increasing rotational temperature which is likely to be caused by more extensive Coriolis coupling (see Fig. 3).

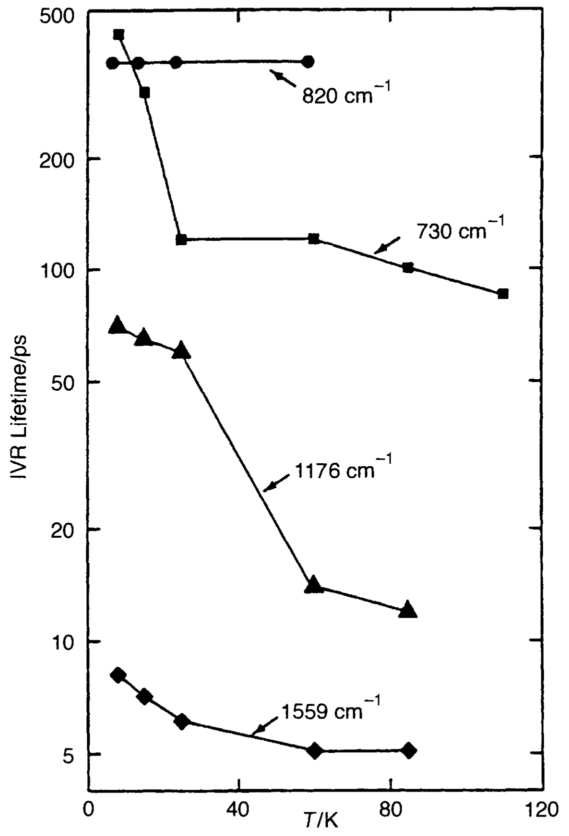

Fig. 3 Data from time-resolved fluorescence depletion (TRFD) scans of four bands of *p*-cyclohexylaniline with rotational temperatures ranging from 8 to 110 K illustrating the resulting change in IVR lifetime. (Adapted from P. G. Smith and J. D. McDonald, *J. Chem. Phys.*, 1990, **93**, 6350 with kind permission of the American Institute of Physics).

The overall IVR lifetime can also indicate whether Coriolis coupling is mediating IVR. For example, the frequency-resolved jet-cooled spectrum of the OH stretch in ethanol displayed a FWHM lifetime of 25 ps which is faster than the overall rotation of the molecule at low J.[21] It was concluded therefore that anharmonic coupling must be dominant. Thus, states with fast IVR rates are likely to be extensively anharmonically coupled.

4 Rationalisation of IVR

A natural consequence of experimental work is the attempt to rationalise any trends that may appear and to propose a model which can be applied generally. IVR studies are no exception with explanations based on principles that involve knowledge of coupling pathways and the general energy level structure of the molecule, through to models based purely on structural features.

4.1 Density of states

Due to its central importance in RRKM theory, the density of rovibronic states is the most commonly used factor to rationalise IVR (see Section 1). A change in the density of states affects the number of dark states that are sufficiently near degenerate with the bright state to couple to it. On these grounds an increase in density of states would imply a corresponding increase in the rate of energy redistribution. Thus, the density of states is generally accepted to be responsible for the existence of a threshold energy for the onset of IVR. However, it has been found that excitation to a vibrational level embedded in a higher density of states does not necessarily produce a faster IVR rate, especially when comparing excitations in different molecules (see below).

Work that confirms the expected trend in IVR rate with density of states is provided in a series of three papers by Smalley and coworkers who carried out an extensive study of jet-cooled alkylbenzenes excited to their S_1 electronic state.[22] Their fluorescence study revealed increasing unstructured emission with increasing alkyl chain length indicating enhanced IVR with increasing density of states. In addition a picosecond time evolution study of the bright state revealed that early members of the series displayed intermediate case IVR with insufficient density of states to permit any dynamical IVR process to occur on a subnanosecond timescale. This time-resolved work also revealed that the longer chains possessed a sufficient density of states to enable complete randomisation of energy within a nanosecond.

Further excellent illustrations of the expected effect of density of states stem from the fluorescence study and an independent time-resolved study of jet-cooled anthracene. Fig. 4(*a*) illustrates an increase in linewidth with vibrational energy while Fig. 4(*b*) indicates a decrease in lifetime with increasing density of states. The latter time-resolved study adds weight to the idea of IVR approaching the statistical regime with increasing density of states. The authors found that up to 1200 cm^{-1} of excitation the vibrational levels were almost eigenstates with little evolution of energy, while intermediate case IVR occurred between 1380 and 1520 cm^{-1}, with a lifetime of 200 ps. At energies greater than 1520 cm^{-1} statistical IVR was observed with a fast component of 22 ps and a slow component of 6.4 ns. This fast component of IVR can be extremely rapid at high vibrational energies which is usually explained as being a consequence of the very high density of states. For example, the sixth overtone of the CH stretch of benzene in its S_1 electronic state which is embedded within a continuum of vibrational and rotational states, displays a lifetime of 50 fs.[23] This trend is also observed for IVR in ground electronic states where it is generally observed that the onset of IVR occurs at a density of states of *ca.* 100 per cm^{-1}. This value predicts the onset in many molecules and is independent of molecular structure.[24] However, the term onset of IVR must be interpreted with care since it is open to discussion at which point energy redistribution is fast enough to be classed as true IVR, and it should not be assumed that IVR is absent below a tabulated threshold.

Using threshold values and calculated densities of states to predict whether IVR will be rapid is not on the whole reliable, because the observed density is often significantly different from that calculated. For example, the eigenstate-resolved infrared spectrum of allene revealed 27 vibrational states per cm^{-1} for one of the combination bands compared with the calculated value of 12,[25] while the high resolution spectrum of $\mathrm{Bu^tC{\equiv}CH}$ suggested a lower limit of 7.8×10^3 per cm^{-1} compared with the estimated theoretical value of 1.7×10^2.[12c]

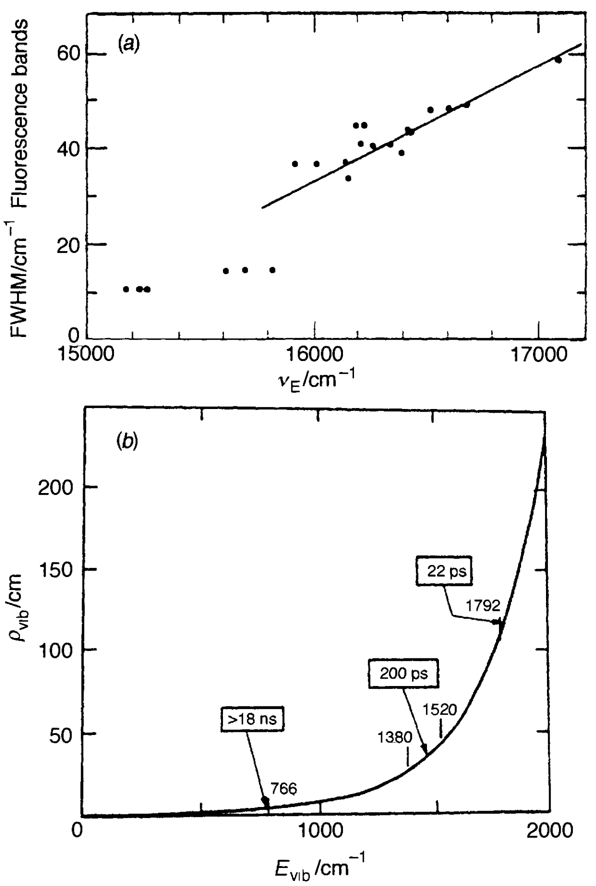

Fig. 4 Illustrations of the effect of density of states on the rate of IVR, as it would usually be expected. (*a*) Linewidth increasing with vibrational energy and hence density of states. (*b*) Calculated density of states vs vibrational energy in anthracene. In (*b*) experimental IVR lifetimes in the sparse (18 ns at 766 cm^{-1}), intermediate (200 ps at *ca.* 1450 cm^{-1}) and statistical (22 ps at 1792 cm^{-1}) regimes are shown. (Adapted from P. S. H. Fitch, C. A. Haynam and D. H. Levy, *J Chem. Phys.*, 1981, **74**, 6612 and P. M. Felker and A. H. Zewail, *J. Chem. Phys.*, 1985, **82**, 2961 with kind permission of the American Institute of Physics).

Another discrepancy arose with the high resolution IR spectrum of 2-fluoroethanol.[19] The calculated density of states in the range 2980–2990 cm^{-1} was 63 states per cm^{-1}. Assuming every dark state couples with the bright state this would lead to a minimum spacing of 1/63, *i.e.* 0.016 cm^{-1}. However, the spacing between states in the experimental spectrum was 0.006 cm^{-1} signifying a disagreement between the calculated density of states and the experimental data.

Often trends in lifetimes of vibrational states cannot be explained by considering either calculated or measured densities of states. Lehmann, Scoles and coworkers used high resolution IR spectroscopy to study the CH stretch of a series of alkynes (see Table 2). Fluorination causes a dramatic increase in the density of states compared with the hydrogen and deuterium species, but the fluorinated molecule has a shorter and longer lifetime respectively. A further discrepancy occurs in an IR study of propyne.[12d] Here, when the molecule was excited with three quanta in its acetylenic CH stretch the prepared state displayed a lifetime of 310 ps while excitation of a combination band gave rise to a lifetime of 3.2 ns. The respective densities of states were 150 and 107 states per cm^{-1} and this difference was considered to be too small to explain such a dramatic increase in lifetime. An IR study of the second, third and fourth overtone bands of the OH stretch in hydroxylamine provides a more obvious failing of the density of states as a predictor of IVR lifetime (see Fig. 5). The spectra revealed sharp features for the second and third overtones, but the fourth overtone consisted of a very broad band with unresolved P and R branches. The

Table 2 Lifetimes of vibrational levels within the acetylenic CH stretch in various alkynes, compared with the density of states with A_1 symmetry, all taken from Ref. 12[c]

	Molecule	Lifetime/ps	Density of states per cm^{-1}
$v = 1$	$(CH_3)_3CC\equiv CH$	200	4.9×10^2
	$(CD_3)_3CC\equiv CH$	40	2.8×10^3
	$(CF_3)_3CC\equiv CH$	60	4.2×10^6
	$(CH_3)_3SiC\equiv CH$	2000	1.0×10^4
	$(CD_3)_3SiC\equiv CH$	850	1.0×10^5
$v = 2$	$(CH_3)_3CC\equiv CH$	110	6.2×10^5
	$(CD_3)_3CC\equiv CH$	< 20	7.6×10^6
	$(CF_3)_3CC\equiv CH$	5	1.0×10^{11}
	$(CH_3)_3SiC\equiv CH$	4000	2.0×10^7
	$(CD_3)_3SiC\equiv CH$	140	6.0×10^8

calculated density of states increases by a factor of 4 between the second and third overtones with a resulting 30% increase in linewidth. By analogy, a similar increase between the third and fourth overtones predicts a linewidth of 1.2 cm^{-1}, not the 7 cm^{-1} observed. These comparisons suggest that the change in linewidth does not come solely from an increase in the density of states (see later).

Thus, the density of states is a quantity that can occasionally explain the changes in vibrational lifetimes accompanying a structural modification or a change in the vibrational energy within a molecule. It is often applied in a rather contingent manner in an attempt to rationalize experimental observations, but its explicit effect is hard to deduce. However, the density of states is almost certainly a major factor in the division of IVR into sparse, intermediate and statistical regimes and initial qualitative inferences may be drawn from consideration of the region of the vibrational manifold into which the original excitation occurs.

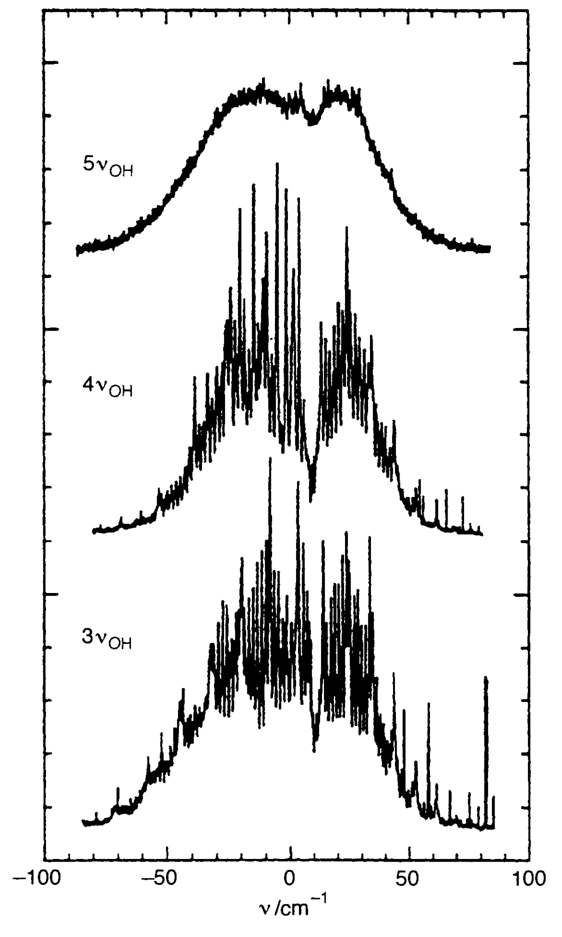

Fig. 5 IR spectra of the second, third and fourth overtone transitions of the OH stretch in hydroxylamine illustrating a large increase in linewidth from the third to the fourth overtone which is not consistent with the small increase in the density of states. (Adapted from J. L. Scott, D. Luckhaus, S. S. Brown and F. F. Crim, *J. Chem. Phys.*, 1995, **102**, 675 with kind permission of the American Institute of Physics).

4.2 Empirical models

The inability of density of states considerations to provide consistency has led to the development of several alternative explanations of relative IVR rates. Perhaps the most promising is the proposed existence of a doorway state by Lehmann, Scoles and coworkers.[24] Within this model mode specific coupling of the bright state to one dark state is a prerequisite to redistribution, and the particular dark state can be considered to be a 'doorway' which exposes the bright state to the full density of rovibrational states available. It is only at this point that the original bright state population becomes fragmented into many eigenstates. Even though the model ignores the relative strength of vibrational state coupling it was successful in explaining the lifetime dependence of diacetylene on the rotational quantum number, J.[12a] The lifetime of this molecule increased with increasing J even though one would expect greater Coriolis coupling with J and a corresponding decrease in lifetime. However, within the doorway model for this molecule, as the energy increases with increasing J there is a larger energy separation between the bright state and the doorway state resulting in a lifetime increase. The doorway state is also central to the tier model proposed by Marcus and Stuchebrukhov.[26] This theoretical model is based upon the assumption that relaxation occurs through a series of 'tiers' of states connected to the bright state. The model assumes the lifetime of a vibrational state is independent of the nature of the states that receive vibrational energy, and determined only by the coupling strength and positions of the levels in the first few tiers. Each 'tier' represents a level coupled to the bright state in a given order, none of which incorporates the total density of available states.

Because it is difficult to apply the above models without some knowledge of the energy level structure, correlations between molecular dynamics and the structural features of molecules are desirable, enabling the prediction of the effects on IVR rates when structural modifications are imposed. Numerous such models exist and it is enlightening to consider three of the more successful ones that have been proposed. It is generally observed that excitation near to a heavy atom produces a relatively long IVR lifetime and this has led to the concept of the heavy atom effect. This effect is essentially proposed to be caused by a heavy central atom impeding the flow of energy across the molecule due to its inherent relative inability to participate in vibrational motion. This results in the removal of those decay channels which involve the heavy atom, causing a slower decay of the optically active state. van der Waals interactions have also been proposed to be important in controlling IVR lifetimes because these interactions naturally lead to state mixing. Thus, a high degree of steric congestion should lead to an enhanced decay rate of the bright state. The flexibility of a molecule has also been used to rationalise IVR rates. Perry and coworkers collected a number of IVR lifetimes and discovered a correlation with molecular flexibility.[27] Essentially it is observed that IVR is faster in flexible molecules when the initially prepared vibration is close to the bond about which groups possess substantial movement as in, for example, *trans-gauche* isomerisation.

Lehmann, Scoles and coworkers have made detailed studies of a whole series of alkynes and substituted alkynes by looking at IR excitation of the acetylenic CH stretch[12,24] (see Table 2). In the course of these studies they have applied the doorway state model and two of the structural models discussed above to rationalise their results. In what follows we illustrate how the principles were applied to these alkynes and how this work ties in with the attempts of other groups to apply these models to their experimental data.

4.2.1 van der Waals model

The van der Waals model is probably the least successful of the structural models but nevertheless provides an explanation for the results of Parmenter and coworkers who compared the fluorescence spectra of *p*-difluorobenzene and *p*-fluorotoluene using chemical timing techniques.[5] The addition of a methyl group clearly accelerated IVR as inferred through the loss of structured emission. The effect observed was thought to be a consequence of an extensive van der Waals interaction between the methyl group and the ring. Although the methyl group couples only weakly to the ring, its low barrier to internal rotation enables this extensive interaction. A study of 1-chloro-2-fluoroethane revealed that torsional motion was responsible for the bright state decay.[28] The *gauche* conformer displayed significantly greater coupling than the *trans* conformer which is consistent with there being reduced interactions between the two methyl groups which are further apart in the latter.

Many of the alkyne studies support the views of Parmenter and coworkers on van der Waals interactions. The increase in the lifetime of an acetylenic CH stretch upon silylation of $(CH_3)_3CC{\equiv}CH$ and $(CD_3)_3CC{\equiv}CH$ (see Table 2) can be rationalised by a reduction of steric congestion between methyl groups, as a consequence of the longer $Si{-}CH_3$ bond. This reduced van der Waals interaction would decrease state mixing leading to a suppressed IVR rate. Similarly, an enhanced van der Waals interaction explains the decrease in lifetime upon deuteration for both silicon and carbon compounds. The same trend is not however observed for the acetylenic CH stretch lifetimes in the pair of molecules $(CF_3)_3CC{\equiv}CH$ and $(CD_3)_3CC{\equiv}CH$. Considering solely van der Waals interactions, one would expect a faster decay of the bright state in the fluorinated molecule, but the corresponding lifetimes are 60 and 40 ps, respectively. Because parameters such as normal mode frequencies and bond lengths are unlikely to remain constant upon fluorination, attempts to rationalise lifetimes based on this simple model may be a little optimistic in this case. The van der Waals model does however lead to the prediction that removal of the trifluoromethyl rotors would lead to a substantial increase in lifetime, which is indeed observed. It is also successful when applied to the IR spectra of trifluoropropyne.[29] Here, insignificant IVR was observed when the fundamental was excited and a lifetime of 2 ns found for the first overtone, consistent with the reduction of van der Waals interactions compared with $(CF_3)_3CC{\equiv}CH$. However this may be fortuitous since the density of states will also decrease and parameters such as the coupling matrix elements are likely to change upon removal of the CF_3 rotors. Further scepticism surrounding this model is apparent on consideration of the lifetime measurements for $CH_3Si(C{\equiv}CH)_3$.[12e] This molecule has only one methyl group but relaxes faster than the structurally similar molecule $(CH_3)_3SiC{\equiv}CH$ that has three (see Table 1). These results suggest that although van der Waals interactions between methyl groups do not dominate IVR, they may be an important initial guide for a qualitative understanding of IVR.

4.2.2 Doorway state model

The alkyne studies also provide some evidence of the existence of a doorway state. $(CH_3)_3CC{\equiv}C{-}H$ and $(CH_3)_3SiC{\equiv}C{-}H$ have acetylenic CH stretch lifetimes of 400 ps and 2 ns, respectively. As the density of states increases when the carbon is replaced with silicon, it was thought that the change in mass and force constants moved some key doorway state out of resonance with the CH stretch. Direct experimental evidence for the existence of a doorway state stems from the infrared studies of a number of substituted toluenes by Sowa *et al.*[16] It was observed that, contrary to density of states considerations, there was line narrowing of the overtone acetylenic CH stretch transition from toluene to penta-fluoro substituted toluenes. Mode specificity between the CH stretch bend was discovered and the coupling thought to fall out of resonance following the modification of the CH stretching frequency in the presence of the fluorine substituents, leading to a longer lifetime as inferred from the decrease in linewidth. It was concluded that this Fermi resonance can be prevented through a judicious choice of substituents suggesting that one can control the vibrational lifetime of an excited CH stretch.

4.2.3 Heavy atom model

The alkyne series probably best illustrates the heavy atom effect. The calculated densities of states show a large increase on going from the fundamental to the first overtone for each compound, and yet $(CH_3)_3SiC{\equiv}C{-}H$ displays a longer lifetime and $(CH_3)_3CC{\equiv}{-}H$ a shorter lifetime in the first overtone. It was also recognised that the carbon compounds displayed considerably shorter lifetimes than the silicon analogues. As this is contrary to density of states considerations it was thought to be a consequence of a heavy atom effect.[12e] The study was extended to the tin analogue of the molecules where a lifetime of 6 ns was obtained for the acetylenic CH stretching fundamental which agrees with the proposed model.[24] However this heavy atom effect is unlikely to be solely due to mass because the bond lengths and vibrational frequencies will also change. The model also fails to explain why a factor of 2.3 mass increase from carbon to silicon increases the lifetime tenfold, whereas from silicon to tin the mass increases by a factor of 4.2 with an accompanying threefold increase in lifetime.

It is revealing to compare these results with other experimental and theoretical studies of the heavy atom effect which were performed prior to the above experiments. Rogers and coworkers studied the reactions of tetraallyl tin and tetraallyl germanium with fluorine atoms.[30] Here, the deduced rate constant was 1000 times larger than that predicted from RRKM theory which suggests that, in this case, the heavy atom blocked the statistical redistribution of energy, which is central to RRKM theory. In contrast, the unimolecular dissociation of activated 4-(trimethylstannyl)-2-butyl and related compounds displayed rates which were consistent with RRKM and suggested that the heavy atom did not block IVR to any significant extent.[31] Lopez and Marcus used classical trajectories to investigate IVR in a system designed to explore the heavy atom effect.[32] They considered a C–C–C–X–C–C–C system (X = Sn, Ge) and found that when the stretches were described by Morse oscillators, Sn inhibits the flow of energy while the Ge does not, which could be due to the greater mass of the tin. However for harmonic stretches both Sn and Ge allowed energy flow across them. This suggests that a purely heavy atom effect is unlikely to predict the changes in lifetime accompanying substitution for a heavier atom, which is further supported by the calculations of Hase and coworkers.[33] Here, a potential energy surface for the tetraallyl system $[Sn({-}C{-}C{=}C)_4]$ was calculated using Morse oscillators to describe all stretches. The energy flow past the Sn atom increased with increasing energy placed in the C=C stretch, but upon substitution of carbon for tin in the same surface there was no significant change in IVR rate. However, when the surface was modified to give potential parameters that were chosen to match experimental frequencies and bond energies of carbon, IVR was found to be almost complete within a picosecond, which suggests the change in mass is not the dominating factor in this system. Nevertheless, both theory and experiment suggest that heavy atom substitution is a promising structural modification to inhibit IVR.

4.2.4 Molecular flexibility model

Molecular flexibility has been used by Perry and coworkers to rationalise IVR lifetimes.[27] The model focuses on CH stretches with the following conditions: (*i*) All stretches are equivalent, with relaxation rates attributed to local identity and not chemical reactivity and (*ii*) proximity to centre of flexibility tends to accelerate IVR in the absence of strong coupling matrix elements. Chromophores in rigid molecules should then diplay longer lifetimes than those in flexible molecules. This flexibility may involve internal rotation, as for example about the C–O bond in ethanol. In but-1-yne the methyl and acetylenic CH stretches have similar lifetimes of approximately 280 ps which is described as a consequence of this molecule having no significant centre of flexibility. However, in pent-1-yne the aliphatic CH relaxes faster than the acetylenic CH which is consistent with the proposed model due to *trans-gauche* isomerisation about the C^2–C^3 bond in pent-1-yne: CH_3–CH_2–CH_2–C≡CH. The enhanced relaxation of the aliphatic CH could be due to the closer proximity of the methyl group to the centre of flexibility.

Fig. 6 illustates the concept of molecular flexibility, indicating how the IVR lifetime varies as a function of the distance from the centre of flexibility. For example the lifetimes of the C–H stretch in three rigid molecules, isobutane, *trans*-but-2-ene and *tert*-butylacetylene are longer than those in three flexible molecules, but-1-ene, butane and methyl formate. This model appears to rationalise IVR lifetimes of C–H stretches quite readily and only requires the structure to estimate the region of the molecule which is likely to retain vibrational energy the longest. However, if the bright state is strongly coupled to the surrounding dark states the model breaks down, and since coupling strengths cannot be deduced from the molecular structure it is difficult to apply this model without experimental data.

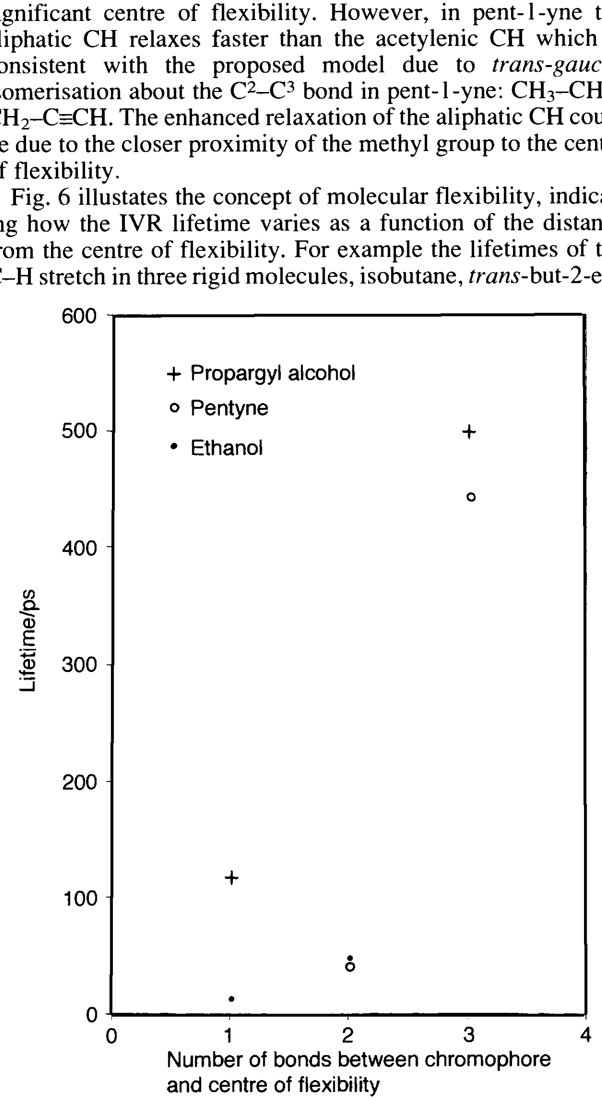

Fig. 6 IVR lifetimes as a function of the number of bonds (n) between a given chromophore and the centre of flexibility. For ethanol the OH chromophore is at $n = 1$ and the methyl chromophore is at $n = 1$. For *trans*-pentyne the methyl chromophore is at $n = 2$ and the acetylenic chromophore is at $n = 3$. For propargyl alcohol the methyl chromophore is at $n = 1$ and the acetylenic CH is at $n = 3$. The IVR lifetime increases as the distance from the centre of flexibility increases. (Adapted from G. A. Bethardy, X. L. Wang and D. S. Perry, *Can. J. Chem.*, 1994, **72**, 652 with kind permission of the National Research Council of Canada).

Although at present correlations between IVR rates and the structure of molecules are purely qualitative they still prove invaluable since they may aid the design of molecules that exhibit significantly slow intramolecular dynamics. This is particularly relevant to mode-selective chemistry since such modifications can have dramatic effects on the lifetimes of vibrational states, which in turn may permit selective reactions.

5 Mode-selective chemistry

IVR is not only important for unimolecular dissociation (RRKM theory) but also for the consideration of bimolecular collision induced reactions, where mode-selective chemistry may be possible if the retention of energy within a specific mode is longer or comparable to the time between bimolecular collisions in the gas phase. Bimolecular mode-selective chemistry has been achieved with deuterated water, HOD.[34] When HOD reacted with fast hydrogen atoms there was a preference for breaking either the OH or OD bond when the respective bond contained quanta of stretching motion. However, this is the only true example of mode-selective chemistry reported to date and was thought to be possible because of the small size and low density of states of HOD.

With obvious synthetic applications in mind, it is desirable to extend mode-selective chemistry to larger polyatomic molecules. The inherent problem with this is that large polyatomic molecules possess a greater density of states, especially high up in the vibrational manifold, which promotes the rapid randomisation of localised energy. Furthermore, to ensure facile bond breakage it would be necessary to work at these high excitation energies where the enhanced IVR rate could lead to the formation of alternative products, rendering mode-selective chemistry in such species impossible to control. Thus, to accomplish mode-selective chemistry, a compromise is required between the energy needed to ensure a selective reaction and an excitation energy which exhibits slow IVR. To ascertain whether mode-selective chemistry is possible it is necessary to determine if the rate of bimolecular collisions is faster than the rate of IVR. Simple collision theory gives an approximate collision interval at room temperature and pressure of 1 ns. The IVR lifetimes listed in Table 1 reveal that only acetylenic CH stretches and combination bands have so far exhibited IVR lifetimes close to this benchmark value. The energy in combination bands however is distributed over several bonds so, although energy is retained in specific parts of the molecule for the duration of a collision any one of several bonds could break leading to a mixture of reaction products. Thus, the attention must be focused on the acetylenic compounds, and especially on the acetylenic CH stretch itself. Mode-selective chemistry with these compounds has not yet been reported, although many authors have stated it to be possible with, for example, trifluoropropyne, which possesses a first overtone lifetime of 2 ns. Lehmann, Scoles and coworkers recently published a paper stating their intention to study the effect of 'heating the bath' of vibrational modes which ultimately receive the vibrational energy in the IVR process in an attempt to extend the lifetimes of molecules.[14]

Mode-selective chemistry may be achievable in relatively small polyatomic molecules such as the alkynes listed in Table 1, but in other molecules it appears to be only a distant possibility. The structural modifications discussed previously may be an aid to mode-selective chemistry, if the modification suppresses IVR. The structural modification could be the introduction of a heavy atom which would allow the selective reaction, and the molecule could be subsequently converted back.

6 Conclusion

In this review we have attempted to give a broad overview of IVR studies highlighting some recently developed experimental techniques, and some attempts to rationalize results. We have concentrated on only a small subsection of the available literature in order to illustrate our arguments. It can be seen that there are still many active workers in the field, and many questions to be answered. A review by Nesbitt and Field which appeared after the manuscript for this article was written confirms the timeliness of a review on IVR.[35] Their article takes a somewhat different approach from ours, being heavily referenced (including mention of a number of earlier reviews) and more rigorous, and is recommended for further reading.

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