

INTRAMOLECULAR DYNAMICS FROM EIGENSTATE-RESOLVED INFRARED SPECTRA

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INTRODUCTION

Understanding intramolecular energy flow in molecules is one of the central goals of chemical physics. Statistical theories [such as Rice-Ramsperger-Kassel-Marcus (RRKM) theory] of unimolecular reaction rates, which assume that the vibrational degrees of freedom rapidly exchange energy, have proved extremely successful (1). Recent work on small molecules has provided rigorous tests of these theories (2). With the success of unimolecular reaction theory, it has become clear that intramolecular vibrational energy redistribution (IVR) is a nearly universal phenomenon when molecules have enough energy to break bonds. However, despite this success, several important issues about the nature of the assumed statistical motion have been left unresolved.

Definitive measurements of the time scale of the IVR process have only recently become possible. Unimolecular reaction theories only require IVR to be faster than the dissociation rate. For most chemical reactions, these

rates are on the order of microseconds, although studies of radical addition to unsaturated hydrocarbons have suggested IVR rates of $\sim 10^{12} \text{ s}^{-1}$ (3). Quack (4) has reviewed the classical literature and concluded that in ordinary tightly bound molecular systems IVR occurs at a rate of 10^{11} – 10^{13} s^{-1} . However, these experiments have relied on rather poorly defined clocks to measure IVR, thereby generating only vague lower limits on the IVR rate.

Freed (5) has argued that most of the classical experiments can be explained by assuming statistical state preparation but no IVR. Furthermore, an assumed statistical character of the vibrational motion appears to conflict with the highly successful normal mode theory of vibrations (6), which indicates that, for small amplitude vibrations, the energy in each normal mode is conserved. How do molecules make the transition from nearly separable motion at low energy to rapid energy interchange at high energy? These and other issues have motivated a range of experiments that seek to determine IVR rates for well-defined initial excitations. Only in the last few years has it become possible to push these experiments to their fundamental quantum limit and determine the IVR rates of single quantum states.

The overwhelming majority of experiments investigating isolated molecule IVR have used frequency domain techniques to measure the decay rate via splittings and broadening of spectroscopic transitions. A handful of experiments have been performed using time-resolved pump-probe techniques (7–13). For an ideal measurement, both time and frequency domain techniques contain the same information. However, in gas-phase studies of larger molecules, the absorption spectrum (or the free induction decay signal for a time-resolved measurement) also contains contributions from inhomogeneous structure. In these cases, IVR rates can be overestimated unless the inhomogeneous contributions can be determined (14, 15).

In this review we consider cases where spectroscopic techniques have been used to determine the homogenous IVR dynamics. When the homogeneous structure cannot be resolved in the single-photon spectrum, two-photon techniques (whether they be frequency-domain double resonance methods or time resolved pump-probe techniques) can dramatically reduce inhomogeneous broadening. The great advantage of frequency-resolved techniques is the ability to measure the rotational state-dependence of the homogeneous IVR rates. By contrast, time-resolved techniques usually measure IVR rates that are averages over a range of rotational and other quantum states. The increased level of detail provided by frequency-domain methods produces a more complete picture of the vibrational energy redistribution process, thereby invalidating frequently made claims that time-domain techniques, being more direct, are somehow superior.

There are now a large number of molecules for which quantitative IVR rates have been determined. For molecules large enough to show energy redistribution, the rates range from 10^8 – 10^{13} s^{-1} , with $\sim 3 \times 10^9$ s^{-1} being typical. These IVR rates are much faster than most unimolecular reaction rates but slower than previously inferred from chemical activation and other experiments (3). Still, the measured rates may be sufficiently slow to permit mode-selective chemistry in some systems. Small, vibrationally excited molecules, which are exempt from energy redistribution, show greatly enhanced rates for bond-selective, bimolecular reactions with H or Cl atoms (16–18).

Achieving laser-induced bimolecular chemistry may be easier than controlling unimolecular dissociation reactions. For gas-phase samples at standard conditions, the gas-kinetic collision rate is $\sim 10^{10}$ s^{-1} , and thus, many vibrationally excited molecules will undergo one, or perhaps several, collisions while the excitation is bond localized. If the localized vibrational excitation can induce a reaction with a stable, abundant species at near gas-kinetic rates, then mode-selective chemistry is a likely result. From a chemical point of view, bimolecular reactions may be more interesting because they can be used to build molecular structures.

In this review we concentrate on experimental studies of intramolecular vibrational energy redistribution of isolated molecules in their ground electronic state, aimed at measuring fully quantum-state-resolved spectra. These molecular eigenstate spectra provide the most complete information available for a quantum mechanical system from a single-photon spectrum. However, as discussed in the next section, molecular eigenstate spectra can only be interpreted once they have been rotationally assigned. Recent developments in double-resonance spectroscopy make rapid and accurate assignments for these complex spectra possible. Several of these powerful techniques are highlighted here. Finally, the general picture of the IVR process emerging from these types of studies and the outlook for future experiments is presented.

The reviewed area of research forms only one part of current efforts in understanding intramolecular dynamics. Space does not allow treatment of many closely related topics. In particular, areas that have been reviewed previously, including intramolecular dynamics in excited electronic states (19–21), vibrational dynamics on the subpicosecond time scale (22), stimulated emission pumping measurements of high-lying vibrational states (23, 24), and IVR in condensed phases (25, 26) are not represented. Additionally, discussion of the vast array of theoretical methods used in IVR studies is limited. The theoretical techniques of IVR have been reviewed recently (27, 28). Theoretical issues covered here relate directly to experimental results.

BACKGROUND THEORY

Dynamics from Frequency-Resolved Spectra

In this section we discuss some issues concerning the dynamical interpretation of a fully resolved, frequency-domain measurement. The past few years have seen a rapid increase in the use of time-domain techniques in chemical physics (29). Results from these studies are often described as real-time measurements. It should be realized, however, that quantum mechanics ensures a correspondence between time- and frequency-domain measurements. High-resolution spectroscopic studies of IVR are equivalently real-time techniques: The time evolution of a well-defined and easily prepared superposition state can be rigorously calculated from information contained in the frequency-resolved spectrum. More complete discussions of calculating vibrational dynamics from frequency-domain measurements have appeared in several places (30–32).

The standard interpretation of frequency-domain studies of IVR is

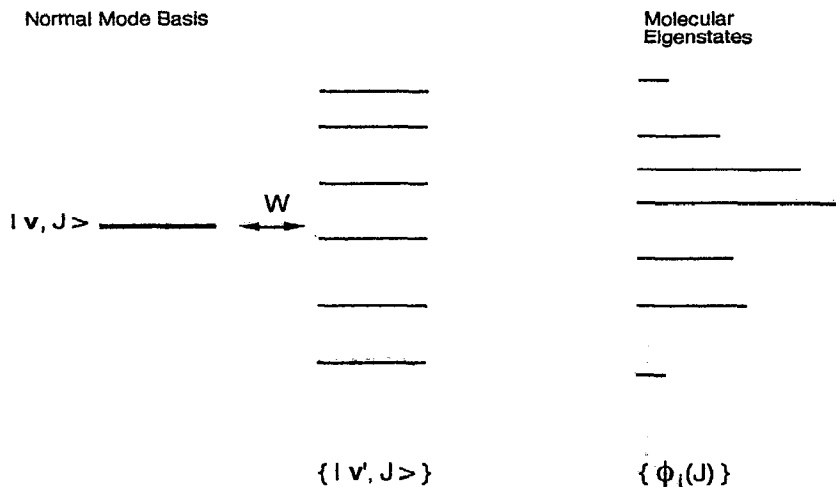


Figure 1 This figure shows the standard interpretation of IVR in the frequency domain. There is a single rotational state in an excited anharmonic normal-mode vibrational state that is assumed to carry all of the oscillator strength in this energy region. This is the so-called bright state. The bright state is coupled to the near-resonant vibrational bath states through higher-order terms in the rovibrational Hamiltonian. This coupling results in molecular eigenstates that mix the character of the zeroth-order rovibrational states. As a result, the bright-state oscillator strength is distributed among these states. The width of the distribution of intensity is a measure of the time scale of energy localization in the bright state. The center-of-gravity of the IVR multiplet is preserved at the original position of the bright state.

illustrated in Figure 1. Here a single, rovibrational, zeroth-order quantum state, the bright state, carries oscillator strength from the ground vibrational state. This state is immersed in a bath of other zeroth-order rovibrational states that are not optically accessible from the ground state (the dark states). All of these rovibrational states are eigenfunctions of the standard Hamiltonian used in the analysis of rovibrational spectra at lower energy (33). This Hamiltonian contains a vibrational part, corrected by perturbation theory for nonresonant anharmonic interactions, and a rotational part, which is the distortable rotor Hamiltonian. Also included are the rovibrational perturbation terms that give the effective rotational constants for different vibrational states.

Even with the inclusion of these perturbation terms in the zeroth-order Hamiltonian, a large number of higher-order interactions have been neglected. These additional rovibrational couplings (anharmonic, Coriolis, and centrifugal couplings) are grouped together in a perturbation term to the zeroth-order Hamiltonian, W . These additional interactions induce population transfer to the near-resonant bath states giving rise to the IVR process. In the frequency-resolved spectrum, the manifestation of IVR is the fragmentation of the single, expected transition to the bright state into transitions to a set of molecular eigenstates. This set of eigenstates, arising from a single bright-state parent, forms an IVR multiplet. From the eigenstate-resolved spectrum, the transition frequencies and intensities to each eigenstate of the multiplet are obtained. The sum of the intensities of the multiplet is fixed by the bright-state transition strength. Knowledge of the ground-state rotational energies permits the transition frequencies to be converted to energies relative to the ground state of the molecule ($J = 0$ of the ground vibrational state).

Although it is true that exact quantum mechanical predictions are independent of the chosen, complete basis set, it is also true that some basis sets are physically more appropriate. The choice of the zeroth-order Hamiltonian traditionally used in molecular rovibrational spectroscopy is motivated by several issues. This Hamiltonian nearly diagonalizes the vibrational problem. Therefore, the perturbation terms included in W are typically small (on the order of 10 cm^{-1}). One extremely important benefit of this basis set is that standard spectroscopic theory provides the correspondence between the vibrational normal modes and specific motions in the molecule (i.e. bond stretches and bends) (6). Lastly, the optical selection rules between the basis functions are simple and typically known from the IR spectrum. In short, the formalism developed over the past 60 years for the interpretation of vibrational spectra provides the most convenient framework for discussing IVR dynamics.

Using first-order, time-dependent perturbation theory, it is easy to show

that a short-pulsed excitation creates an initial state that is the bright state of the zeroth-order Hamiltonian. To create this bright state as the initial state, the entire IVR multiplet must be excited with a nearly equal electric field strength (given by the Fourier transform of the pulse shape). This type of excitation occurs when the pulse duration is much faster than the IVR dynamics so that state creation and evolution are on well-separated time scales. Following its creation by pulsed excitation, the bright state will have a nontrivial time evolution because it is composed of the superposition of several eigenstates. Calculation of the population decay of the bright state requires only the eigenstate energies and relative intensities, which is precisely the information contained in the frequency-resolved spectrum (31).

The major advantage of frequency-resolved studies is that quantum-state-specific IVR dynamics can be investigated, providing truly homogeneous dynamical information. Using traditional methods of spectroscopic assignment (such as ground state combination differences), the molecular eigenstates are assigned to their parent zeroth-order bright state. These bright states are individual rotational levels of the excited vibrational state and, therefore, provide a full specification of the quantum numbers. Additional insight on the vibrational dynamics, such as the role played by rotationally mediated (Coriolis) coupling mechanisms in IVR, is possible when the results are quantum state-resolved. Furthermore, the fully resolved studies give information on the fluctuations of the properties of the spectrum. Fluctuations in eigenstate spacings and intensities carry important information on the global dynamics of the quantum system (34). By contrast, a time-resolved study will often prepare an ill-defined ensemble of bright states. As a consequence, only average values of the dynamical quantities remain accessible.

It has been argued that shaped laser pulses may be used to modify the full molecular Hamiltonian to suppress IVR (35, 36) or to excite specific target bonds (37, 38). Such proposals are based on the creation of special superpositions of the molecular eigenstates. To design such coherent control pulse shapes, the position of each eigenstate must be known to better than their average spacing; the vibrational make-up of the eigenstates must be known as well. In the region of the acetylenic C-H stretch fundamental of 3,3,3-trifluoropropyne [which displays trivial IVR dynamics (39) compared to most of the molecules considered in this review], this will require the calculation of the rotational structure of vibrational bands that are about the 30,000th vibrational eigenfunction of the full Hamiltonian with a precision of better than a few parts per million. Theoretical calculations to this precision are currently impossible and unlikely in the foreseeable future. Judson & Rabitz (40) have suggested that adaptive

feedback control through a sequence of pump-probe experiments may provide a means to get around the need for a detailed knowledge of the field-free Hamiltonian. The applicability of these ideas has yet to be demonstrated; on the other hand, it is possible that through eigenstate-resolved spectroscopy of the type discussed in this review, combined with double-resonance probes of the vibrational character of the eigenstates, this type of information will become available. Characterization of the field-free dynamics of the molecule is a prerequisite to attempts to rationally modify the vibrational motion using external fields. High-resolution spectroscopy provides the best methods for accomplishing this task.

Current Issues in IVR Theory

Perhaps the major goal of IVR theory is to calculate the measured relaxation rates. As is discussed below, measured rates span a wide range (50 fs to 10 ns) and strongly depend on molecular structure. IVR on sub-ps time scales is largely driven by strong, low-order resonances, and the theory of such effects is largely understood (22). The calculation of IVR rates for large molecules (more than 10 atoms) and longer times has succeeded only recently (41–44). Most of these computations assume some form of a tier model for the energy redistribution. The empiricism that appears in these models through assumptions of the intramolecular potentials is presently being removed by dramatic developments in *ab initio* gradient methods that allow direct computation of anharmonic force fields (45). Therefore, theory and experiment are positioned for a very fruitful collaboration. Experiment can provide IVR rates to check the force fields and examine the assumptions of the energy redistribution models, thus allowing fine tuning of the calculational approach. Theory can provide a much more detailed understanding of where the energy goes and how it gets there.

A second direction of recent theoretical work involves understanding how subtle features of the dynamics are encoded in an eigenstate-resolved spectrum. These studies are applications and extensions of random matrix theories initially developed in nuclear physics (46). The statistical properties of the eigenstate positions and intensities give information on the global nature of the dynamics, such as whether or not they are chaotic (47). Recently developed hierarchical methods of spectral analysis (48) are designed to extract the characteristic time scales of the dynamics (49). This should allow the determination of hidden bottlenecks in the energy redistribution process. The ever-improving quality of eigenstate-resolved spectra will spur the further development of these and related methods, as spectroscopists strive to extract as much insight as possible about the dynamics encoded in the spectrum.

EXPERIMENTAL METHODS

General Requirements

In a frequency-resolved study of vibrational dynamics, it is necessary to measure and assign complex rovibrational spectra. In these measurements two normally dichotomous experimental parameters, resolution and sensitivity, must be simultaneously maximized. In terms of investigating vibrational dynamics, the resolution determines the long time limit over which the dynamics may be followed. The ultimate goal, therefore, is to fully resolve all of the rovibrational transitions in the spectrum as this covers the full time of nontrivial quantum dynamics (50).

At the same time, it is necessary to maintain high sensitivity. The signature of IVR is the fragmentation of a single rovibrational transition into a number of components that make up the IVR multiplet. However, the total transition strength of the multiplet is fixed by the bright-state transition moment. As more vibrational states become involved in the dynamics, either through a faster IVR rate that increases the distribution width or, for larger molecules, through an increase in the state density, the peak absorption strength of the largest component becomes increasingly weaker.

In the next two sections we discuss several techniques that have been applied in the study of IVR of larger molecules. Single-photon techniques are presented first. Double-resonance techniques, which offer very powerful assignment capabilities for analyzing complex rovibrational spectra, are presented in the following section.

Single-Photon Techniques

GAS-PHASE TECHNIQUES The study of the vibrational dynamics of small polyatomic molecules plays an important role in IVR investigations. In small molecules the connection with theory can be made more easily since few-atom systems can be treated rather precisely with current theoretical methods (45, 51). The spectra of small molecules in regions of low state density often show the strong, low-order anharmonic couplings that can lead to sub-ps energy exchange between specific modes (such as between a CH stretch and its own bend) (22). Similar low-order, but nonresonant, couplings are also believed to play an important role in determining the much slower IVR rates found in many larger molecules (41).

One of the most powerful techniques of gas-phase vibrational spectroscopy is high resolution Fourier transform infrared spectroscopy (FTIR). The main advantage of FTIR is the ability to scan wide spectral regions, which yields a global view of the vibrational spectrum (52–55). Modern FTIR instruments have achieved resolution well below typical

room temperature Doppler widths, thereby surpassing all but the highest resolution laser systems (56, 57). Analysis of FTIR spectra comprises a large body of literature in spectroscopy. Space limitations prevent us from covering these results.

Several gas-phase techniques have been developed to obtain spectra of highly vibrationally excited molecules with very high sensitivity. One broadly applicable method is to measure the spectrum of the molecules within a resonant cavity. When the cavity includes a laser gain medium, the technique is called intracavity laser absorption (ICLAS) (58). The exponential sensitivity to cavity losses (i.e. molecular absorptions) makes this a very sensitive technique. The molecules can also be placed in an external cavity coupled to a pulsed laser. The decay time of the cavity, the so-called ring-down time, is again exponentially sensitive to cavity losses (59, 60). Very weak absorptions ($< 10^{-9} \text{ cm}^{-1}$) can be measured (61).

Indirect spectroscopic methods are often extremely sensitive. For gas-phase spectroscopy, photoacoustic (62, 63) and photothermal (64) effects have been used to obtain spectra with high sensitivity. In both cases, the signal is proportional to the excited state population. Small transition cross-sections can be compensated for by the use of increased laser power.

Lastly, four-wave mixing techniques have been developed in recent years that have shown high sensitivity (65–68). Perturbed spectra of highly vibrationally excited states accessed through a stimulated emission pumping (SEP) scheme have been measured (PH Vaccaro, private communication). One limitation of these methods is the scaling of the signal with the square of number density and an even higher power of the transition strength. In highly perturbed spectra, where small transition moments prevail, this scaling could limit the applicability of the technique.

MOLECULAR BEAM TECHNIQUES For larger polyatomics containing more than three heavy atoms, rotational resolution of the gas-phase spectrum is hampered by the large value of the rotational partition function. The large number of populated rotational states increases the demand on sensitivity and leads to extensive rotational congestion, which increases the resolution requirements. To overcome these limitations, seeded supersonic expansions can be employed to reduce the rotational temperature to the 1–50 K range (69).

The earliest molecular beam infrared measurements directed toward understanding IVR used IR fluorescence detection following pulsed excitation in the region of the hydride stretch fundamentals. In a series of IR fluorescence experiments (70, 71) with resolution down to about 0.006 cm^{-1} (72), McDonald and coworkers (71) showed that IVR in isolated molecules was a nearly universal occurrence. These experiments showed

that the threshold value of the rovibrational state density for the observation of IVR is 10–100 states/cm⁻¹; these studies provided the basis for much of the high-resolution work that has followed.

Direct absorption of laser radiation using a pulsed-jet source to obtain eigenstate-resolved spectra of a large molecule in an IVR regime was first reported by deSouza, Kaur, & Perry (73). Using a pinhole expansion, with Ar as the carrier gas, the resolution was Doppler-limited to 150 MHz (73, 74). Later, the University of Akron group showed that the Doppler broadening in a free-jet expansion can be reduced to 12 MHz by using a sliced-jet technique (75). Nesbitt & McIlroy (76, 77) demonstrated an improvement in both resolution (~ 50 MHz) and sensitivity by employing a slit-jet expansion. These slit-jet studies used a tunable IR difference frequency laser, which allowed them to cover the entire 2000–4000 cm⁻¹ region. A difference frequency laser system that covers the C-H stretching overtone region was later developed for use in the slit-jet spectrometer (78, 79).

A great advantage of absorption spectroscopy is that a low power (~ 1 μW) laser can be used. Lasers with sufficient power for direct absorption measurements exist in many spectral regions. For wavelengths longer than 4 μm, direct absorption of lead salt diode laser radiation has been extensively used to obtain molecular spectra in a jet. However, these spectrometers have yet to be employed to obtain the extensively perturbed spectra characteristic of the IVR process largely because of the poor characteristics of these laser sources. Recently, narrow band, difference frequency sources have been developed in the 4–9 μm region that hold great promise for IVR studies (80). Efforts to achieve more complete frequency coverage have focused on using FTIR instruments to detect absorption in a jet expansion (81–85). At present the sensitivity of these spectrometers has not allowed the measurement of highly perturbed spectra. Although all of these absorption methods are expected to extend IVR studies to vibrations other than hydride stretches, the low power of the excitation sources will not permit adoption of some double-resonance schemes.

A limitation of direct absorption techniques is that the signal depends on the relative attenuation of the laser power. In order to measure spectra with weaker absorption cross-sections, such as overtone vibrations, it is necessary to improve the amplitude stability of the laser, the length of the absorption path, and the noise level at the detector. All three of these quantities have to be pushed near their limits to measure highly fragmented spectra of fundamentals.

As in gas-cell spectroscopy, the adoption of indirect detection techniques, which scale with the excited-state population, appear to be advan-

tageous because the reduction in absorption strength can be compensated by increasing the laser power. Hineman et al (86) have demonstrated the use of thermal lensing for the detection of overtone bands of acetylene in a free-jet expansion. The main difficulty in this technique is that it requires molecular collisions to form the thermal lens. Therefore, the spectrum must be measured in the early part of the expansion where rotational cooling is incomplete and the residual Doppler broadening is still great.

Energy-deposition, optothermal (bolometer) detection offers the advantage of a technique where the signal is proportional to the laser power (87). Collimated molecular beam, optothermal spectrometers coupled with color-center lasers have been used to sensitively measure the fundamental (39, 88, 89) and first-overtone (39, 90) hydride stretch spectra of a number of molecules with 8 and 16 MHz resolution, respectively. The technique can be used in any frequency region where reasonably powerful continuous wave (CW) lasers are available. In the case of the fundamental and first-overtone studies, similar sensitivities are achieved in both frequency regions because the higher power of the 1.5 μm laser partly compensates the reduction in oscillator strength for overtone excitation. Spectra of the third overtones of the hydride stretches in small molecules via direct excitation with a tuneable dye laser have also been obtained using this technique (91). However, no highly fractionated spectra have yet been measured in this way (92).

A variation of the optothermal method involves the addition of a state-focusing assembly of quadrupolar symmetry (93). In this electric resonance, optothermal spectrometer (EROS), the signal is proportional not only to the transition dipole moment, temperature factors, and Hönl-London factors, but also to the state-focusing characteristics of the rovibrational states involved. One benefit of this method is that spectra in lower frequency regions can be obtained with high sensitivity (94, 95). Spectra of the hydride stretch fundamentals have been obtained with an order of magnitude improvement in signal-to-noise ratio over the normal optothermal technique (96).

One potential problem with the EROS technique is that, because the signal strength depends on the focusing strength of the states involved in the transition, it might not be possible to obtain the true relative intensities of an IVR multiplet. However, in regions of high state density, the effect of near degeneracies on the molecular Stark effect causes the molecules to travel through the inhomogeneous electric field without deflection (96, 97). As a result, the upper states are all observed to be nonfocusing, and relative intensity information within an IVR multiplet is preserved.

Most applications of optothermal techniques have been limited to the use of CW laser sources owing to the slow time response of common

semiconductor bolometers. However, a pulsed laser and a fast, superconducting bolometer have been used to measure the second- and third-overtone bands of the C-H stretches of benzene in a collimated molecular beam (98, 99). The resolution of these initial studies was limited to 0.2 cm^{-1} by the laser employed. However, single-mode, $\sim 10 \text{ ns}$ pulsed lasers can provide $\sim 50 \text{ MHz}$ laser linewidths. This resolution is only about a factor of two larger than the residual Doppler broadening expected in the second and third overtones of hydride stretches in the collimated molecular beam. Further development of this method could provide many interesting studies of IVR in the higher overtones.

Double Resonance Techniques

Double-resonance (DR) techniques have long been employed in molecular spectroscopy to simplify and assign complex spectra. When studying highly perturbed spectra where transitions frequently overlap, DR methods are often the only way to obtain accurate assignments. In addition, the use of two (or more) photons allows the study of vibrations that cannot be accessed in single-photon work.

DR techniques for spectroscopic assignments require the two spectral sources to share a common vibrational level. In most implementations, one of the frequency sources is tuned within a previously assigned, unperturbed spectrum. The second source is then scanned through an unassigned spectrum. DR signals transfer the spectroscopic assignments from the known spectrum to the spectrum of interest. IR-IR double-resonance techniques have the added advantage of allowing access to overtone and combination states with reduced power requirements.

MICROWAVE-INFRARED TECHNIQUES *The lower vibrational level is the shared level* Microwave-infrared techniques in which the ground vibrational state is the shared level offer several advantages for obtaining and assigning complex infrared spectra. The pure rotational spectrum of a molecule is frequently known; with the EROS technique the pure rotational spectrum can be measured directly in the same spectrometer used for the infrared measurement (94). At low temperatures, assignment of the rotational transitions is usually straightforward, and DR allows one to obtain the IR spectrum of one rotational quantum state at a time. However, molecules with high barrier internal motions, such as the three-fold rotation of methyl tops, frequently do not show resolved tunneling splittings, thus leaving this ambiguity in the upper state.

In cases where the infrared and microwave transitions can be saturated, large signal modulations ($\sim 40\%$) can be achieved (100). However, in regions of extensive IVR fragmentation, the IR transition dipole moment

may be too weak to saturate. In the absence of saturation, signal modulation comes from the thermal population difference of the two rotational levels. Even at the low temperatures achieved in molecular beam experiments, a modulation of only about 3–10% of the infrared signal is achieved when using microwaves in the 14–40 GHz range. Using the EROS configuration, it is possible to circumvent this limitation and achieve very large (> 100%) signal modulations, as demonstrated by the assignment of the highly fragmented O-H stretch of *trans*-ethanol (101). In addition to the EROS measurements, infrared-radio frequency DR of small molecules has been performed in a traditional electric-resonance spectrometer (102, 103).

The upper vibrational level is the shared level For the purpose of investigating vibrational dynamics, we only discuss here microwave measurements made in perturbed vibrational states. Microwave spectra originating from excited vibrational states are often able to access new states not observable in single-photon spectra. For example, in a two-state interaction the vibrational states are often resonant at a single (or only a few) rotational levels. The vibrational mixing at these rotational levels causes the dark states to acquire intensity at the isolated crossing point. Once entry into the dark state has been obtained through the IVR dynamics, its spectroscopy can be investigated through pure rotational transitions within the dark manifold. This type of dark-state rotational spectroscopy has been performed for a few molecules to establish the symmetry and rotational constants of the interacting vibrational state, which can lead to a unique assignment when the density of states is low (104).

The general principles of this experiment can be extended to more complex coupling cases where the infrared laser prepares a highly mixed vibrational eigenstate. Because of the rapid tuning of near-resonant perturbations, the spectrum could be very complicated, including rotational transitions to several eigenstates in other IVR multiplets. At the other extreme, if the resonances do not tune so that the vibrational perturbation structure is nearly the same in sequential rotational states, the spectrum may be very simple because of strong propensity to stay within the diagonalized vibrational state. One of the first infrared-microwave double-resonance measurements (conducted with a Zeeman-tuned rare gas laser) showed anomalous microwave spectra (105). Transitions between nominally different, highly excited vibrational levels (which are forbidden in zeroth order) were found to be of similar strength as pure rotational transitions. However, because the full single-photon infrared spectra was not obtained and assigned (because of the minimal tunability of the laser), quantitative interpretation was not possible.

INFRARED-INFRARED TECHNIQUES *The ground-state vibrational level is shared* When one of the infrared lasers operates at low frequency, it typically pumps an unfragmented spectrum. In this case, the IR-IR measurement presents the same advantages as those discussed for microwave-infrared techniques. In addition, any tunneling degeneracy associated with high barrier internal motions is usually lifted in the infrared spectrum because of nonresonant coupling to background states containing a few quanta of excitation in the large amplitude coordinate (106). Level shifting without fragmentation makes it possible to use these spectra to make complete assignments of the higher lying vibrational state.

Even when both lasers are tuned within the same highly perturbed band, DR can be used to establish connectivity in the spectrum [as in two-dimensional, nuclear magnetic resonance (2D-NMR)], and ultimately unravel the spectrum. One difficulty with this technique is that in highly fragmented spectra, where DR is most important, the dilution of the oscillator strength makes it much harder to reach saturation. The necessity of saturating weak transitions in a fragmented spectrum is a common problem for employing DR techniques in the study of complex spectra. The use of build-up cavities (formed from high-finesse etalons) promises to allow saturation of these weak transitions (92, 107). Recently, saturation of the weak $\nu_3 + 2\nu_2^0$ transition in propyne, which receives 2% of the intensity of the acetylenic C-H stretch through an anharmonic interaction, has been achieved showing the promise of this technique (DS Perry, private communication).

Schemes in which the induced transition by the second laser originates in the upper vibrational level of the first transition Several variations of infrared-infrared double-resonance are possible when the shared level is not the vibrational ground state. First of all, the second laser can either excite the molecule to a final vibrational state with energy higher than the shared common state or to a vibrational state of lower energy. [This latter process can be considered a vibrational stimulated emission pumping (SEP) method.] Additionally, the shared vibrational state can either be unfragmented or can show extensive perturbations characteristic of the IVR process. All of these variations can provide new and interesting information about the molecular vibrational dynamics.

To date, the only variation that has been reported is the case where the shared vibrational state is unfragmented and the second laser excites the molecule to a higher energy vibrational state. In many cases the higher energy state cannot be reached by single-photon transitions. The single-photon limitation can result from either symmetry restrictions or very weak absorption cross sections from the ground vibrational state (as in the case of combination bands or high overtones).

Using two 3.0 μm color center lasers in direct absorption, several vibrational states of propyne around 6000 cm^{-1} have been studied with excellent sensitivity (107, 108). Included in these vibrations is the combination band of the acetylenic C-H stretch and a methyl C-H stretch. The dynamics in these combination bands are important in the context of energy relaxation models. In tier models of IVR, low-order combination states are believed to provide virtual intermediate states in the relaxation of overtone states. Measurement of the relative IVR rates of overtones and near-isoeenergetic combination bands can provide stringent tests of such models.

Spectra of molecules in vibrational states near 9000 cm^{-1} have been obtained using sequential excitation with 3.0 μm and 1.5 μm color-center lasers in an optothermal spectrometer (109, 110). Again, these measurements allow for the investigation of vibrational states that are inaccessible through single-photon studies.

The combination of a Ti:sapphire laser with either of the two color-center lasers mentioned above has allowed observation of the *gerade* local-mode states of the C-H stretches of acetylene in the $v = 5$ and $v = 6$ region. This two-step excitation is able to saturate unfragmented transitions to states with ~ 50 kcal of vibrational energy, enough energy to induce isomerization and cleavage of weak bonds (JE Gambogi, private communication).

INFRARED-VISIBLE TECHNIQUES *The ground electronic and vibrational level is shared* Infrared-visible DR techniques in which the shared vibrational state is the ground state can be used as a basis for sensitive detection of the infrared spectrum. In these experiments, a signal is derived from a fixed, electronic-state excitation. A dip in this signal is observed when the infrared frequency is tuned through a resonance. When fluorescence from the electronic state is monitored, the technique is a fluorescence dip method. Resonance-enhanced, multiphoton ionization through an excited electronic state can also be used. Ionization dip spectra of the fundamental and the first and second overtones of the jet-cooled benzene have been obtained using this technique by Page et al (111, 112). The experiments employed relatively broad band lasers that resolved the vibrational, but not the rotational, structure. Measurements of the first overtone have been repeated at 120 MHz resolution of the IR laser, thus allowing the resolution of individual eigenstates (113). Unfortunately the resolution of the UV probe was insufficient to provide definite rotational assignments of the transitions.

Other schemes For shared upper vibrational states, it is possible to excite first with the visible laser, or first excite with the infrared source. In the

latter case, if electronic absorption of the visible laser only occurs when the vibrational state is populated, then a background-free, fluorescence-appearance technique is possible. One highly successful implementation of this technique (called vibrationally mediated, photodissociation spectroscopy), uses excitation from the vibrationally excited state to a dissociative state, followed by laser-induced fluorescence (LIF) detection of the products (114–116).

This method has been extended and enhanced by using two resonant vibrational excitation steps to reach the dissociative state (which is monitored by LIF). These enhancements have increased the rotational resolution by using an initial IR excitation of a low-lying, unperturbed vibrational state (such as the O-H stretch fundamental, in the case of HOOH) (117, 118). By using different vibrational states in this rotationally selective initial step it has been possible to study the vibrational dynamics for states with delocalized excitation (119–121). When the second laser excitation step moves the molecule from a highly vibrationally excited state to a dissociative state, the spectrum of this statistically relaxed excited vibrational state is measured (122–124). These measurements provide new information on the nature of the vibrations participating in the IVR process.

Another variation of the visible-followed-by-infrared method has been developed by Settle & Rizzo (125) to allow beam spectroscopy of high overtones of polyatomic molecules. In this technique, molecules excited to high overtones are selectively dissociated by an intense CO₂ laser pulse. The selectivity comes from two factors. First, anharmonicity shifts the IR absorption of overtone pumped molecules substantially to the red of the ground-state absorption so that the CO₂ laser can be tuned to a region of negligible ground-state absorption. Second, following IVR, the overtone excited molecules are well into the quasicontinuum, and thus will dissociate at much lower IR fluences than ground state molecules, which need to be pumped through the bottleneck region. The fragments of the dissociation are then probed by LIF.

VISIBLE-VISIBLE TECHNIQUES *Shared upper state* In an IVR context, only shared upper state, visible-visible double-resonance studies have appeared. The most prominent are those based on the SEP technique (23, 24). The shared upper state in this technique is a low-lying vibrational state in an excited electronic state. With high resolution visible lasers, this electronic spectrum can be accessed with rotational resolution, permitting full assignment in the double-resonance step. Highly vibrationally excited states of the ground electronic state manifold are probed by tuning a second visible laser and observing a fluorescence dip, or some other signal, when a

Franck-Condon active vibration is resonant. The SEP technique has been extensively reviewed, and we mention here only a few differences between these studies and the direct IR excitation that is the focus of this review. The Franck-Condon accessible states carry their initial excitation in bending vibrations and stretching modes of chemically unsaturated bonds. In contrast, hydrogen stretching vibrations (which are dark in SEP) have dominated IR studies because a significant amount of energy can be pumped into the molecule with only one or two quanta of vibration. Another difference is that most SEP studies have been carried out with pulsed lasers with > 1 GHz linewidth, more than two orders of magnitude worse than the best IR studies.

An experiment similar to the one discussed at the end of the previous section has been successfully used to study a few molecules and roughly falls into the visible-visible DR category. In these experiments, the visible laser excites a high overtone of a molecule that can dissociate. Following dissociation, a product fragment, such as OH or NH, is probed by LIF. For smaller molecules, like HOOH (126) and HN_3 (127, 128), the resolution available with pulsed lasers is sufficient to fully rotationally resolve the spectrum. These measurements not only provide information on the IVR, but also on how IVR and dissociation processes compete and interact with each other.

INFORMATION ON THE IVR PROCESS FROM FREQUENCY-RESOLVED STUDIES

In this section we present the basic picture of the IVR process that has emerged from frequency-resolved studies of complex spectra. We concentrate on what we believe to be generic features of IVR. Of course, in some instances there are special case molecules that go against the accepted rules. These exceptions are indicated. The discussion presents a phenomenological view of the IVR process and considers the structural dependence of the vibrational dynamics.

Basic Issues in the Phenomenology of the IVR Process

A traditional point of reference in discussing IVR dynamics is Fermi's Golden Rule, and this has led to numerous discussions about the role of the density of states in determining IVR rates. Fermi's Golden Rule states that the lifetime-imposed linewidth is proportional to the product of the mean-squared coupling of the bright state with the bath states and the density of states: $\Gamma = 2\pi\langle W^2 \rangle \rho$. However, it is the lifetime that is the important physical quantity. Frequently this proportionality of lifetime and the density of states (for fixed mean-squared coupling matrix

elements), is interpreted as implying that an increase in the state density would cause a proportional increase in the IVR rate. However, if one adds new states that are weakly coupled to the dark states, but not to the bright-state, to a Hamiltonian model, the density of states will increase but the mean-squared coupling will fall commensurately. Thus, the IVR lifetime of the bright state remains unchanged (129).

Frequency-resolved determinations of IVR lifetimes show that the total state density and the IVR rate are largely uncorrelated. For example, the lifetimes of the acetylenic C-H stretch and the state densities for a series of molecules of the form $(\text{CY}_3)_3\text{X}-\text{C}\equiv\text{CH}$ (130–132) are presented in Table 1. Clearly the IVR lifetime does not decrease with increasing state density. In all of these molecules, the frequency of the band origin and other spectroscopic constants related to the vibrational potential, are very similar, which indicates the similarity of the initially excited vibrational motion in these molecules.

One objection to the argument that the previous data set illustrates an independence of the IVR lifetime on the density of states is that too many vibrational frequencies have changed to make a comparison meaningful, in spite of the fact that the nature of the bright state (the acetylenic C-H stretch) is preserved. However, three further results show the lack of

Table 1 Experimental IVR lifetimes and state densities for the acetylenic C-H stretch in molecules of the form $(\text{CY}_3)_3\text{XCCH}$

Molecule	Level of excitation	Density of states ^a (cm)	Lifetime (ps)	Reference
$(\text{CH}_3)_3\text{CCCH}$	$\nu = 1$	4.9×10^2	200	130
	$\nu = 2$	6.2×10^5	110	130
$(\text{CD}_3)_3\text{CCCH}$	$\nu = 1$	2.8×10^3	40	131
	$\nu = 2$	7.6×10^6	< 40 ^b	131
$(\text{CH}_3)_3\text{SiCCH}$	$\nu = 1$	1.0×10^4	2000	130
	$\nu = 2$	2.9×10^7	4000	130
$(\text{CD}_3)_3\text{SiCCH}$	$\nu = 1$	1.0×10^5	830	131
	$\nu = 2$	6.0×10^8	140	131
$(\text{CH}_3)_3\text{SnCCH}$	$\nu = 1$	1.0×10^6	6000	130
	$\nu = 2$	1.0×10^9	> 1000 ^c	^d
$(\text{CF}_3)_3\text{CCCH}$	$\nu = 1$	4.2×10^6	60	132
	$\nu = 2$	1.0×10^{11}	< 40 ^b	132

^a The state densities (states/cm⁻¹) are for vibrational bath states of A₁ symmetry, which can couple via anharmonic interactions.

^b Upper bound to the lifetime. The overtone absorption was unobservable, despite observation of the fundamental.

^c Lower limit to the lifetime. The Q branch structure was too sharp to obtain an estimate of the Lorentzian wing. Other inhomogeneity (either isotopes, torsional, or K structure) was also present.

^d ERTh Kerstel, KK Lehmann, TF Mentel, BH Pate, and G Scoles, unpublished results.

importance of the state density in determining the IVR rate. First, let us consider that, for the same molecule, the IVR lifetime can be determined at different energies by studying the vibrational overtones. Indeed, for a few molecules, the IVR lifetimes in the fundamental and first overtone have been determined. These results are also shown in Table 1. Again, no obvious correlation between the lifetime and the total density of states is found.

Another indication that the state density is not a major factor in determining the IVR rate comes from studying molecules with multiple chromophores (79, 101, 133, 134). Molecules with different types of hydride stretches have been examined in the region of the fundamentals between 3000 and 3600 cm^{-1} . In such a narrow energy interval the density of states is nearly constant. However, several molecules show significant differences in IVR rates depending on the mode initially excited. These results are presented in Table 2.

Finally, the IVR rates of a number of structurally similar acetylenic compounds have been investigated. These molecules are of the form $(XYZ)C-C\equiv CH$, where X, Y, and Z are the three substituents on the third carbon down from the acetylenic C-H stretch. These molecules have widely different vibrational-state densities at the acetylenic C-H stretch fundamental, as indicated in Table 3. However, the IVR-observed lifetimes are all very similar.

Taken as a whole, frequency-resolved IVR studies clearly indicate that total state density is not a primary factor in determining the IVR rate. However, one qualification should be placed on this statement: The obser-

Table 2 Experimental IVR lifetimes of fundamental bands for molecules with multiple chromophores

Molecule	Vibrational band	Lifetime (ps)	Reference
1-butyn	acetylenic C-H	269	77, 133
	<i>asym</i> methyl stretch	270	133
<i>trans</i> 1-pentyne	acetylenic C-H	442	77
	methyl stretches	< 40 ^a	77
<i>gauche</i> 1-pentyne	acetylenic C-H	241	77
	methyl stretches	< 40 ^a	77
<i>trans</i> ethanol	O-H stretch	25	101
	<i>asym</i> methyl stretch	59	134
prop-2-yn-1-ol	acetylenic C-H	500	172
	O-H stretch	110	^b

^a Upper limit to the lifetime based on lack of rotational structure in the vibrational band despite the ability to measure the acetylenic C-H stretch band.

^b GT Fraser & BH Pate, unpublished results.

Table 3 Experimental measurements of lifetimes for the acetylenic C-H stretch of molecules of the form (XYZ)C-CCH

Lifetimes for the $\nu = 1$ level

Molecule	Density of states (cm) ^a	Lifetime (ps)	Reference
1-butyne	22	269	77, 133
<i>trans</i> 1-pentyne	2.4×10^3	442	77
<i>gauche</i> 1-pentyne	2.4×10^3	241	77
prop-2-yn-1-ol	20	500	172
propynylamine	50	450	^b
(CH ₃) ₃ CCCH	490	200	130
(CD ₃) ₃ CCCH	2.8×10^3	40	131
(CF ₃) ₃ CCCH	1.0×10^{11}	60	132

^a State densities (states/cm⁻¹) are given for the vibrational states that can couple through anharmonic interactions.

^b AM Andrews, GT Fraser, and BH Pate, unpublished results.

Lifetimes in higher overtones

Molecule	Level of excitation	Density of states ^a (cm)	Lifetime (ps)	Reference
CF ₃ CCH	$\nu = 2$	1000	2000	39
(CH ₃) ₃ CCCH	$\nu = 2$	6.2×10^5	110	130
(CD ₃) ₃ CCCH	$\nu = 2$	7.6×10^6	<40 ^b	131
CH ₃ CCH	$\nu = 3$	150	320	110

^a Density of states (states/cm⁻¹) that can couple by anharmonic interactions

^b Upper limit to the lifetime. Overtone was not observed.

vation of IVR requires a vibrational bath. As discussed by Heller (135), quantum dynamics has an effective cut-off time that is proportional to the density of states. If the natural IVR lifetime, as determined by the Golden Rule expression, is longer than this break time, then no relaxation will occur and the population will remain forever in the bright state. Thus, there is an onset dependence of IVR on the state density. However, for a fixed lifetime, once the state density is large enough to provide a vibrational bath for the redistribution, it no longer plays a significant role in the vibrational dynamics.

Surprisingly, the IVR rate is largely independent of the identity of the bath states that ultimately receive the population. Experimental determinations of the vibrational bath-state density from fully-resolved spectra indicates that all energetically accessible vibrational states (of the correct symmetry) will couple to the bright state. In other words, the calculated and measured state densities are usually in excellent agreement (39, 79,

133, 134). The errors are typically less than a factor of two which can easily be accounted for by fluctuations and anharmonic corrections. In most cases, the hydride-stretch bright-state has a rotational constant similar to the ground state. However, most bath states have multiple quanta in bending modes that result in very different (usually larger) rotational constants (39). The resonant dark states at high- J values are most likely to be completely different from the ones coupled at lower J values because of the $BJ(J+1)$ rotational dependence of the state energy. Despite the wildly varying make-up of the vibrational bath, the lifetimes remain nearly constant.

These results suggest that the IVR lifetime is determined by strong couplings to nonresonant vibrational states. These vibrational states can couple to the bright state through low-order terms in the vibrational potential energy surface and thus will have the biggest anharmonic coupling matrix elements. In terms of Fermi's Golden Rule, these strong couplings dominate the average squared-coupling out of the bright state and hence control the IVR rate. The states coupled by low-order resonances comprise a small fraction of the total vibrational bath and are typically separated by tens of cm^{-1} . Because these states, which are often called doorway states, are separated by much more than the homogeneous width of the bright state, they act as virtual states in the relaxation, i.e. they are never significantly populated. Due to the large band origin detunings of these doorway states, the small relative energy shifts induced by differences in rotational constants become a small effect. Independence of the IVR rate on rotational state is consistent with the presence of strong, nonresonant anharmonically coupled states.

In widely used tier models of IVR, vibrational energy redistribution proceeds through the low-order coupling of the doorway states to a larger set of states (but still small compared to the full state density) that form the second tier of states (41, 136, 137). This second tier is, in turn, coupled to another tier, and so on, with the state density increasing with each tier. In most molecules that have been studied, one must go to at least the fifth tier to achieve a state density high enough to form a resonant bath for the relaxation of the bright state (41). It should be emphasized that it is not just the number of low-order couplings possible to the bright state that determines the IVR rate, but also how the states in this first tier are coupled to other tiers. Therefore, the low-order paths may face a bottleneck, resulting in longer vibrational excitation lifetimes.

These ideas have been beautifully illustrated by the calculation of the IVR lifetimes of $(\text{CH}_3)_3\text{SiC}\equiv\text{CH}$ and $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$ carried out by Stuchebrukhov & Marcus (41, 42). This calculation used a Hamiltonian model with only cubic and quartic interactions, which were fixed by the

force fields of smaller molecules. The harmonic frequencies were taken from experiment. No parameters were adjusted to fit the observed lifetimes. It can be seen in Table 4 that the calculated IVR rates are in good agreement with the experimental results. In particular, the theory has reproduced the observed increase in the lifetimes of the silicon containing species, as well as the reduced lifetimes of the CD₃ containing molecules. Both effects are found to arise from changes in the structure of the low-order tiers.

The calculation has been performed with a variable number of tiers. Calculated by the Golden Rule, lifetimes converge when about six tiers are included in the model. At this point, the density of coupled states is still sparse compared to the IVR width, so that true relaxation cannot yet occur. Adding tiers fills in the near Lorentzian lineshape given by the Golden Rule expression. This result provides justification for the empirical observation that the IVR lifetime is independent of the exact identity of the states receiving the excitation.

In summary, the IVR rate is controlled by the strong couplings to nonresonant states that can interact with the bright state through low-order terms of the intramolecular potential energy surface. Furthermore, for fast energy redistribution, it is necessary that these states are in turn well coupled to additional states, thereby preventing a bottleneck in the energy flow. At present, very accurate ab initio determinations of the potential energy surface, and the third- and fourth-order anharmonic constants, are possible for small molecules (45). These methods will continue to develop along with computing resources. For larger molecules, efficient searches, based upon artificial intelligence algorithms, can be used to identify key resonances and to incorporate them in the dynamics (138,

Table 4 Comparison between observed and calculated IVR lifetimes in the acetylenic CH stretch fundamental and overtone

Molecule	Level of excitation	Experimental lifetime (ps) ^a	Calculated lifetime (ps) ^b
(CH ₃) ₃ CCCH	v = 1	200	260
	v = 2	110	90
(CD ₃) ₃ CCCH	v = 1	40	35
	v = 2	< 40 ^c	50
(CH ₃) ₃ SiCCH	v = 1	2000	> 52,000
	v = 2	4000	1300
(CD ₃) ₃ SiCCH	v = 1	830	260
	v = 2	140	170

^a From Ref. 131.

^b From Ref. 41.

^c Upper limit to the lifetime.

139). The results of Stuchebrukhov & Marcus (41) suggest that the age of true ab initio theory of IVR, as opposed to phenomenology, will soon be here.

As we have seen, because only a small subset of the total vibrational state density controls the dynamics, the IVR rate does not strongly depend on the total state density. This is encouraging because it establishes that long-lived (> 1 ns) vibrational excitation does exist for larger, properly structured or properly controlled, molecules. The chemical importance of this statement is quite clear.

Structural Aspects of IVR

The general phenomenological aspects of IVR presented in the previous section have been clarified during the course of several studies designed to elucidate the structural dependence of vibrational energy redistribution. Three main questions have been pursued: (a) Is there a chromophore dependence of the lifetimes? (b) Can simple structural changes be used to rationally modify the IVR rate? (c) Do large amplitude motions such as methyl or skeletal rotation cause enhanced IVR rates? These questions are, in many cases, still open, and here we present the results to date.

CHROMOPHORE-DEPENDENT DYNAMICS The rationale behind expecting chromophore-dependent dynamics is that the most strongly coupled states are expected to have excitation in modes that involve motion of a common or proximate atom (or atoms). The best-studied example of chromophore-dependent dynamics is the overtone dynamics of the methyl-like C-H stretch. Several studies have shown that the most strongly coupled states involve overtones of the C-H bend (22). The first overtone of the C-H bend is nearly resonant with the C-H stretch and couples through a large third order anharmonic term in the potential (k_{sbb}). The early time (< 1 ps) dynamics involve sequential removal of one quantum of C-H stretch from the n C-H stretch overtone and coupling into the combination vibration [$(n-1)$ C-H + 2 C-H bend]. The ability to assign the polyads in the overtone region to these states supports this mechanism of energy redistribution. Quack (140) has found that for high overtone levels, the IVR rate for CH stretches depends largely on the degree of saturation of the carbon atom, with the fastest rate corresponding to saturated carbon atoms, and the slowest to acetylenic CH bonds.

With these overtone studies as a basis, different hydride stretches have been investigated in several molecules to search for chromophore dependent behavior in the slow (> 1 ps) IVR that has been observed in the fundamentals and first overtone bands. As shown above in Table 3, structurally similar acetylenic compounds have similar IVR lifetimes. However,

there are counter examples to the trend. For example, the IVR lifetimes of $(\text{CD}_3)_3\text{CC}\equiv\text{CH}$ (131) and $(\text{CF}_3)_3\text{CC}\equiv\text{CH}$ (132) are much shorter than those of the other compounds listed in Table 3.

While acetylenic compounds form the largest data set, a few lifetimes of other types of C-H stretches and O-H stretch fundamentals have also been determined and are given in Table 5. In general, both of these hydride stretches show faster IVR rates than the acetylenic C-H stretches. This is true even when both acetylenic and methyl or hydroxyl stretches are in the same molecule. This, therefore, indicates that the acetylenic C-H stretch may be more resistant to IVR. A similar conclusion was reached based upon IR-fluorescence measurements (71). At this point, however, the notion of a chromophore-dependent lifetime can only be regarded as tentative because, with the exception of the acetylenic C-H stretch, IVR lifetime data for other chromophores are still very limited.

CHANGING THE IVR RATE BY STRUCTURAL MODIFICATION A minimum requirement for laser-directed chemistry is that the nonstatistical nature of the excitation should survive long enough for the desired reaction to occur. In the case of bimolecular chemistry, this requires the energy localization to live for times at least on the order of the mean collision time. One possibility is to use structural substitutions to slow the IVR rate. This pragmatic approach to laser chemistry seeks to use the well-developed methods of synthetic chemistry to engineer molecules with long-lived, bond-localized excitations. In other words, IVR blocking groups would be employed to allow chemistry at a specific site.

Following a suggestion from the chemical activation literature (141,

Table 5 Experimental lifetimes in nonacetylenic C-H stretches and other hydride stretches

Molecule	Vibrational band	Lifetime (ps)	Reference
1-butyne	$\nu = 1$ <i>asym</i> methyl stretch	270	133
<i>trans</i> ethanol	$\nu = 1$ O-H stretch	25	101
	$\nu = 1$ <i>asym</i> methyl stretch	59	134
prop-2-yn-1-ol	$\nu = 1$ O-H stretch	110	^a
1-butene	$\nu = 1$ <i>asym</i> methyl stretch	31	^b
<i>trans</i> 2-butene	$\nu = 1$ methyl stretch	130	^b
HOOH	(4 O-H + O-H) stretch	28	121
	(5 O-H + O-O) stretch	6	119
	$\nu = 6$ O-H stretch	4	126
NH ₂ OH	$\nu = 7$ O-H stretch	0.37	118

^a GT Fraser & BH Pate, unpublished results.

^b A McIlroy & DJ Nesbitt, private communication.

142), the series of structurally similar molecules, $(\text{CH}_3)_3\text{X}-\text{C}\equiv\text{CH}$, with an ever-increasing mass of the central atom were studied (130). The rationale behind the study was that, since the majority of vibrational states involve excitation of vibrational motions of the three methyl groups on the back end of the molecule, substitution at the central atom position might be expected to modify the dynamics. As seen in the data in Table 1, the (perhaps) naive expectation of a longer energy localization for heavier central atoms is born out.

Theoretical studies of the $\text{X} = \text{C}$ and $\text{X} = \text{Si}$ molecules have shown that this lifetime increase is related to the reduced number of low-order relaxation pathways (41, 42). This reduction can largely be attributed to the lowering of the C-X stretch and bend vibrational frequencies, as well as the lowering of the torsional frequencies of the methyl rotors. This effect is still related to the presence of a heavy atom, which results in weaker bond force constants and larger distances between the methyl rotors but is not directly related to the mass of the central atom. In fact, simply changing the mass of the central carbon atom to 28 (that of Si) while keeping the force field constant dramatically increased the calculated rate of IVR (41, 143)! Previously it had also been noted that the relative IVR lifetimes were not in accord with the mass-dependent expectations (130).

ROLE OF LARGE AMPLITUDE MOTIONS IN THE IVR DYNAMICS Since the results of Walters et al (144) and Parmenter & Stone (145, 146) indicating enhanced IVR rates in molecules with methyl rotors, there has been much interest in the role of large amplitude motions in the vibrational energy redistribution process. A major problem in this work is the relative lack of molecules that do not have internal rotors but still have a sufficient state density to show IVR. A comparison as clear as the one of Parmenter & Stone (145) has yet to be made.

Vibrational states with large excitation in the rotor without a doubt participate in the dynamics since the experimental densities of states are nearly equal to the calculated values. The torsional motion is usually the lowest frequency vibration, so the typical near-resonant bath state will have a multiple quanta of torsional excitation. What is still not clear is whether this causes an increased IVR rate. In other words, it is not known whether the coupling matrix elements to these states are stronger than those to states without torsional excitation.

One indication of strong coupling due to the torsional motion is the observation of widely different centers of gravity for different torsional tunneling symmetries of the molecule. This spectroscopic signature indicates a strong coupling to an excited torsional state, which exhibits a large

tunneling splitting. For most vibrations, tunneling splittings are expected to be small in the absence of such couplings because the vibrational motion is not strongly coupled to the torsional potential. For small molecules, this differential coupling has been observed in several cases. The difference in the centers of gravity for the highly perturbed acetylenic C-H stretch in propargyl amine is on the order of 100 MHz for all rotational levels, thus suggesting that a nonresonant torsionally excited state plays a prominent role in the dynamics of this molecule (AM Andrews, GT Fraser & BH Pate, unpublished results). An isolated torsional resonance in 1,1-difluoroethane has also been observed with a matrix element of 0.01 cm^{-1} (147). This matrix element is slightly larger than those typically observed in IVR, which are on the order of $0.001\text{--}0.003 \text{ cm}^{-1}$. These results suggest that large amplitude motions play an important role in the dynamics.

Several experiments have looked for changes in IVR rates when the methyl groups are modified. In their room temperature FTIR study of acetaldehyde and acetone, Walters et al (144) found that deuteration of the methyl group resulted in more rotational structure in the vibrational spectrum, which was interpreted as a consequence of a decreased IVR rate. Given the extensive inhomogeneous contributions to these spectra, these results must be viewed as tentative at best. In contrast, deuteration of the methyl groups in the $(\text{CH}_3)_3\text{X-C}\equiv\text{CH}$ molecules results in faster IVR in all cases examined (138). Furthermore, a successful theoretical treatment of IVR in molecules containing rotor groups treats the torsional modes as harmonic oscillators, thus without internal rotation at all (41). In addition, the fundamental spectrum of $\text{CH}_3\text{Si}(\text{CCH})_3$ has also been examined, for both the A (350 ps) and E (490 ps) symmetry acetylene stretch modes, and the IVR rate was found to be faster than for $(\text{CH}_3)_3\text{Si-CCH}$, which has three methyl groups (148). Thus, the available evidence from high-resolution studies indicates that, although rotor modes participate in the IVR process, the presence of a methyl group does not accelerate the IVR for hydride stretches.

Part of the discrepancy between the high-resolution results and those of the previous studies may be related to the nature of the vibrational mode being studied. The methyl rotor may have a larger effect on the dynamics of more proximate vibrations such as the carbonyl stretches (144) or benzene ring modes (145). In fact, a strong coupling to a torsionally excited vibrational state, evidenced by an effective 7 cm^{-1} tunneling splitting in the spectrum, has been found in the high-resolution spectrum of the carbonyl stretch overtone of acetaldehyde (149).

Stronger evidence exists for an accelerating effect of skeletal torsional modes. McIlroy & Nesbitt (150) found the CH stretch IVR lifetime (~ 130 ps) of *trans*-2-butene (which has no skeletal torsion) to be much longer

than that for the corresponding mode in 1-butene, which they estimate at ~ 31 ps (150). Li, Ezra & Philips (151) have proposed a vibrationally induced rotational axis switching (VIRAS) model for IVR, where rotational axis reorientation as a function of a skeletal torsional coordinate provides additional coupling to nearby rovibrational states. The Cornell group has seen evidence of coupling to the torsional coordinate in halogen substituted ethane molecules (89, 147). Bethardy et al (152) have reviewed the evidence for such skeletal torsional motions contributing to IVR and concluded that there is a correlation of IVR rate with distance (defined by the number of intervening bonds) of a XH chromophore with nonthreefold internal rotors (152). However, this correlation is largely chromophore dependent. For example, an O-H stretch will always lie near the X-O torsional coordinate. Similarly, the acetylenic C-H stretch is necessarily at least three bonds away from the torsion. This correlation makes it difficult to separate the torsional-proximity-effect from other chromophore dependent mechanisms. We believe that the existing evidence is suggestive, but the issue is far from resolved.

OTHER ISSUES OF MODE-DEPENDENT IVR RATES: CORIOLIS COUPLING AND THE DYNAMICS OF DELOCALIZED VIBRATIONS For an isolated gas-phase molecule, rotational motion opens up new couplings that result from Coriolis and centrifugal forces. However, in the majority of spectra reported to date there appears to be little or no rotational dependence of the IVR lifetime. This indicates that anharmonic couplings provide the dominant contribution to the mean-squared coupling out of the bright state (and hence to the IVR rate). Despite the general lack of rotational dependence of the IVR lifetime, Coriolis coupling is indicated in several spectra by a strong increase in the coupled-state density with increasing rotational quanta (108, 110). For lower rotational levels, where the sensitivity is still high, effective densities proportional to $(2J+1)$, as expected for a complete K mixing, have been observed.

The increased coupled-state density, without an increased IVR rate, indicates a hierarchy of coupling strengths in the isolated-molecule dynamics. The bright state undergoes IVR through anharmonic couplings. This step defines the overall Lorentzian width of the IVR multiplet. The dark rovibrational states are then further mixed by Coriolis or centrifugal couplings, as evidenced by the state density increase (74). Numerical simulations by Perry have shown that one can in principle determine the strength of the dark-dark couplings if one observes a saturation of the effective density as a function of J or K (153).

The development of infrared-infrared double-resonance methods now makes it possible to prepare combination bands involving vibrations that

are spatially separated. The dynamics of these states can be compared to that of states of similar energy where the excitation is localized in a single bond. The IVR dynamics of delocalized vibrational states are especially important in energy flow models because they often form the tier levels that are important in the redistribution from overtone-localized vibrations.

For HOOH, distributing the excitation resulted in slower IVR compared to placing all of the excitation in one of the O-H bond stretches (119, 120). Similarly for propyne, the strength of bright-state and dark-state coupling in the combination band composed of one quantum of acetylenic stretch (ν_1) and one quantum of methyl stretch (ν_6) is significantly smaller than for either the $2\nu_1$ or $2\nu_6$ states (108, 109). Also it was found that the IVR rate is faster for the $3\nu_1$ than $\nu_1 + 2\nu_6$ (109, 110).

The total anharmonicity of the excitation, which is less for a combination band than for an overtone of similar energy, apparently plays a major role in the vibrational dynamics (109). These results on large molecules contrast with earlier work on smaller molecules [C_2H_2 (154), HFCO (155)], where it was found that initial states with the excitation localized in a single mode, so-called extreme motion states (156), have the slowest rates of IVR. Results from these and future studies of distributed states will provide stringent tests of theoretical models for energy flow and will increase the contact between studies of IVR and statistical theories of chemical reactions.

OUTLOOK

Experimental progress in frequency-resolved studies of IVR can be expected to continue in a number of directions. Extension of recent double-resonance work, particularly infrared-infrared techniques, will provide a much better understanding of energy flow in molecules as different kinds of vibrational states are investigated. At the same time, these techniques will enable eigenstate-resolved IVR measurements at ever-higher energies, moving towards smaller molecules and towards energies significant for chemical reactions. Combined with progress in complementary frequency-resolved techniques such as SEP and progress in the a priori calculations of force fields and couplings, a much more complete picture of intramolecular vibrational dynamics will emerge.

Progress in laser technology will, of course, directly impact IVR studies. The development of high-power, tunable CW lasers in new frequency regimes continuously widens the array of vibrational motions that can be excited. At the same time, progress in narrow bandwidth pulsed lasers provides an opportunity to access higher energy vibrations through direct overtone excitation and allows direct pumping of weak bands, such as

combinations and overtones of heavy atom motions. These sources, coupled with fast detection techniques, (including fast bolometers or other detection methods such as thermal tensing) will greatly improve our understanding of the dynamics of larger molecules at higher energy. The development of double-resonance schemes in these experiments to produce homogeneous spectra will be an important advance.

The development of nontraditional double-resonance techniques holds great promise for providing new types of information about the vibrational dynamics. For example, techniques are being developed to measure the IR spectrum of highly vibrationally excited molecules (122–124, 157). Such measurements, which are related to earlier infrared fluorescence measurements (72), will give information on the exact vibrational motions of a relaxed molecule. Additional developments can be expected in the wedding of frequency-resolved and time-resolved techniques. Using a narrow bandwidth laser, a single rovibrational state can be prepared. Coherent excitation of this state with a short laser pulse can then prepare a single, homogeneous state for which the dynamics can be studied without inhomogeneous effects.

Several issues concerning the IVR dynamics of molecules will also be addressed in the next few years. As discussed above, there is still much work to be done to understand the mode dependence of the IVR rate. The questions in this area that have been attacked experimentally, such as chromophore dependent IVR and the role of large amplitude motions of the dynamics, are yet to be resolved. Hopefully, the continued development of theoretical techniques will provide a more quantitative understanding of these phenomena by providing realistic models that can be tested experimentally.

To achieve the goals of laser controlled chemistry, it will be necessary to manipulate IVR lifetimes to allow for long-lived, bond-localized excitation. Two approaches to this problem have been put forth. In one case, the molecule is engineered using the techniques of synthetic chemistry. The other approach that has received much recent attention is to engineer the laser pulse (or pulses) to modify the vibrational dynamics (35–38, 158). The synthetic approach is the more pragmatic of the two. In particular, it does not require a detailed understanding of the full molecular Hamiltonian and instead relies partly on chemical intuition. The latter approach is still in an early stage of development, both experimentally and theoretically.

In the past few years, the study of weakly bound (or Van der Waals) complexes has moved towards issues of intramolecular vibrational energy redistribution (159–161). The study of perturbed spectra of weakly bound complexes (159, 162–165) brings several new issues into play. The inter-

action of intramolecular and intermolecular dynamics needs to be addressed. For example, in most of the complexes studied so far, which are comprised of two monomer units too small to show IVR fragmentation by themselves, spectral perturbation requires coupling to vibrational modes localized on both monomers or to vibrations of the large amplitude van der Waals surface. The mechanisms and strengths of these couplings lie at the heart of energy exchange and relaxation in condensed phases systems (such as a molecule in solution) (26).

Finally, with the experimental techniques now available, it is possible to study the physical properties of molecules excited to individual, highly mixed, eigenstates. Because chemical reactions occur in regions of high state density, the physical properties of mixed states are important for understanding the details of reactions of medium- to large-sized molecules. A fundamental issue is, What is the spectrum of a statistically mixed eigenstate? Due to the complex state-mixing in regions of high state density, interference effects in the spectra are expected. The final states reached from a highly perturbed, intermediate level can be strongly dependent on the exact eigenstate excited. Preliminary investigations of the microwave spectra of eigenstates show that interference effects can cause strong propensity rules for pure rotational transitions (JE Gambogi, private communication). Similar interference effects can operate in the infrared spectra of an eigenstate and are important in an understanding of multiphoton excitation.

The presence of a high-density bath also affects the way highly excited molecules interact with static electric fields. The molecular Stark effect in these regions reveals both shifting of levels and further fragmentation of the spectrum when the electric field strength is increased (166). The high density of rovibrational bath states rapidly results in a case of multiple overlapped avoided crossings which affect the vibrational dynamics (167, 168). Many of the observed effects are similar to those found in the study of highly excited atoms in external fields (169–171). Excitation to regions of high state density can have observable physical effects and is responsible for the lack of deflection of eigenstate-excited molecules by inhomogeneous electric fields (96, 97).

While much work remains to be done, it is evident that molecules in regions of high state density, where extensive spectral fragmentation characteristic of the IVR process occurs, respond in qualitatively different ways to static and oscillating electric fields. Because response to electric fields is the basis of intermolecular interactions, it is reasonable to expect new types of behavior for molecules excited to a single molecular eigenstate. The frequency-resolved techniques discussed here, originally developed to characterize the IVR process of molecules, can now be

extended to permit the study of the new physical properties of highly excited molecules at a level of precision that permits qualitative and quantitative elucidation of the dynamics.

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