Controlling the quantum numbers in chemical reactions

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Reactivity and energy transfer of highly vibrationally excited molecules

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This review covers research into the quantum state specific preparation and characterization of highly vibrationally excited molecules, a field of research that has moved into a very exciting period where many new laser techniques can be used to prepare molecules with extremely large quantities of vibrational energy and with exquisite control over the kind of vibrational motion excited. This field gives a foreshadowing of the future, where control of reactant quantum numbers may become as important to the chemist as control of macroscopic reaction conditions such as temperature and pressure. Laser directed chemistry has already been realized in 'demonstration of principle' experiments. Many of the unresolved questions relevant to the expanded usefulness laser-directed chemistry will be covered. These include such issues as: (1) control of chemical identity in isomerization reactions, (2) laser-directed photochemical and bimolecular reactions, (3) restriction of intramolecular vibrational redistribution, (4) collisional energy transfer of highly vibrationally excited molecules, (5) atmospheric sightings of highly vibrationally excited molecules and (6) molecular beam scattering of highly vibrationally excited molecules.

1. Introduction

The study of highly vibrationally excited molecules is intimately related to the investigation of the microscopic world of elementary physical and chemical rate processes. Indeed, it is in this area of research, perhaps more than in any other, that the spectroscopist and the kineticist begin to see eye-to-eye. The reason for this lies in the fact that the 'average, run-of-the-mill molecule' which engages in chemical or photochemical reactivity either as a reactant or a product, contains 'chemically significant' quantities of vibrational energy. When one considers an exothermic reaction, such as $F + H_2 \Rightarrow HF(vib) + H$ for example, it is very common to find highly vibrationally excited products. Another important aspect of the situation is photochemistry, which on a very fundamental level is simply the process of converting ultraviolet photon energy into photo-product energy, often vibrational energy. For example, it now appears clear that stratospheric ozone photodissociation,

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$O_3 + h\nu \Rightarrow O_2 + O$, the very process that protects us from skin cancer, is an efficient means for producing vibrationally excited O_2 in quantum levels as high as $v = 22!!$ The atmospheric implications of this are presently a very exciting area of on-going research.

The role of highly vibrationally excited molecules is also important to endothermic chemical reactions, which are often strongly enhanced by vibrational excitation. In fact, it is quite easy to see how control of vibrational excitation, especially in endothermic reactions, might be equivalent to control of chemical reaction rates and/or branching ratio's. As we will soon see, we are *already* living in an age where, at least for some small molecules, it is possible to control the outcome of reaction through control of the 'microscopic reaction conditions': the reactant's own quantum numbers. This suggests new and unprecedented levels of understanding and control over chemical reactivity may be possible in the near future!

There is also increasing evidence that chemically significant amounts of vibrational excitation can remain localized in one part of even a relatively large polyatomic molecule, such as propynal, $HC\equiv C-CHO$. This is a prerequisite to chemical control and remains one of the basic areas of research in this field. So, one begins to see the possibility of controlling chemical reactivity by local bond excitation for a large class of molecules and not just for di- and tri-atomics.

But the story does not end here. Completely stable, closed-shell molecules may undergo chemical isomerization when enough vibrational energy is available. This means that even the *chemical identity* of a molecule might be controlled by state specific control of a molecule's vibrational excitation. For example, it has been demonstrated that vibrational excitation of HCCH can lead to a totally chemically distinct isomer $H_2CC:$. The same is true for $HCN \Rightarrow CNH$ and $HCP \Rightarrow CPH$.

For many years, a major area of research for physical chemists has been in the area of determining the pathways of energy flow in exothermic and photochemical reactions and it has been found that vibrational excitation of the products is a ubiquitous channel. Now we are fully into the era where we are trying to understand the special properties that these highly energetic molecules may possess. Central to this area of investigation is a need for experimental data on the collisional relaxation of such highly vibrationally excited molecules, information that has remained very elusive. Very recent studies suggest that brand new mechanisms for collisional-vibrational relaxation may be possible for such highly vibrationally excited molecules. This is due to the fact that molecules with many quanta of vibrational excitation may spend a great deal of their time sampling parts of the potential energy surface where their electronic structure is much different than that of their equilibrium structure. Such electronic rearrangement due to vibrational excitation appears to lead to much different interactions with collision partners, resembling 'transient chemical bond formation'. We are just barely scratching the surface of this intriguing topic and there is still much to learn, but there is no doubt that the future holds many surprises.

Since the advent of lasers in the 1960s, laser spectroscopy has made an immense contribution to our understanding of molecular structure and dynamics, especially for molecules near their equilibrium configurations. With the recent development of new laser techniques that combine the dual features of high selectivity and high efficiency for the preparation of highly vibrationally excited molecules, it has become possible to systematically study the vibrational dependence of chemical reactions and vibrational energy transfer. In this article, we will review the many excellent studies that have been performed with an aim towards understanding the chemical reactivity and the relaxation properties at extremely high vibrational excitation. All of these studies, and

many that have escaped inclusion in this article, have contributed to a better understanding of the dynamics of highly vibrationally excited molecules.

The article is organized as follows. First, a general description of present and promising future technologies for quantum state specific preparation of highly vibrationally excited molecules is given. Then recent investigations of chemical reactions of highly vibrationally excited molecules are presented. The topic of 'isomerization as a problem in high resolution spectroscopy' is then presented. Several examples of unimolecular dissociation (H_2O, HOD, H_2O_2 etc.) are also presented. This is followed by recent work on vibrational relaxation of highly vibrationally excited molecules. NO and OH are discussed in detail. Finally concluding remarks are given.

2. Methodology

There are many ways to prepare molecules in high vibrational states. The simplest and most common method is performed every time a chemical sample is heated or burned: thermal heating. Of course, this produces a broad Boltzmann distribution of vibrationally excited states and may not be a useful way to solve problems in chemical physics, but it is important to mention this 'technique' if only to drive home the point that vibrationally excited molecules are extremely common. Early on, exothermic chemical reactions were used to create highly vibrationally excited species, whose properties could then be studied. The very well known and pioneering work of Rabinovitch and his co-workers led to the first experimental estimations of the rate of intramolecular vibrational redistribution (IVR) in medium sized molecules with enough vibrational energy to react (Chan *et al.* 1970, Lin and Rabinovitch 1970). Electric discharges have been used, for example with CO, followed by Treanor-Tear energy pooling collisions, which when monitored by infrared emission, showed very high levels of vibrational excitation (Teare 1966, Treanor *et al.* 1968, Teare *et al.* 1970). The advent of high-power CO_2 lasers led to the field of infrared multiphoton pumping (Bloembergen and Yablonovitch 1978, Cantrell *et al.* 1979, Schultz *et al.* 1979, Ashfold and Hancock 1980). The major disadvantage of these techniques was that none of these methods have proved to be very successful in terms of depositing the vibrational energy into a specific bond or mode of the molecule.
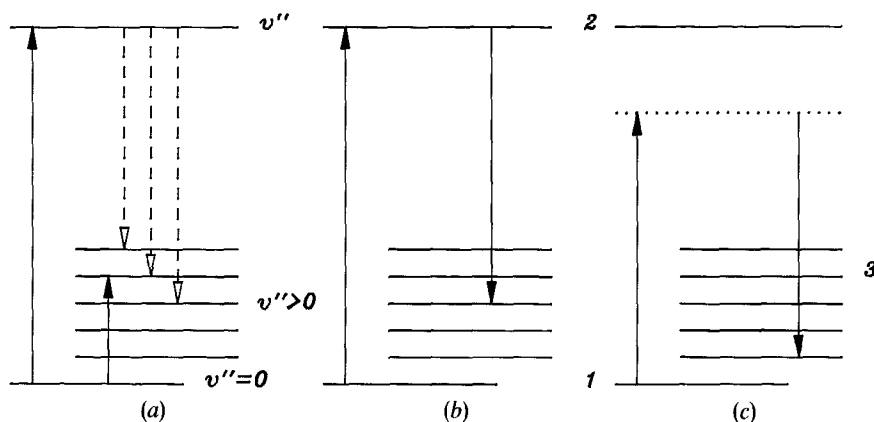

Figure 1. Schemes for most of the experimental techniques that prepares molecular species at high vibrational excitation. (*a*) OP and FCP, (*b*) SEP and STIRAP, (*c*) SR.

Within the last decade, laser-based methods have been developed for producing vibrationally excited species with exquisite selectivity. Figure 1 shows the experimental schemes for most of the presently available techniques. So far, overtone pumping (OP) and stimulated emission pumping (SEP) have been the 'methods of choice' for studying the spectroscopy and dynamics of highly vibrationally excited molecules. Other possibilities are Franck–Condon pumping (FCP) and the stimulated Raman (SR) method, which can both be used as a way to prepare molecules in a high vibrational state. One of the most intriguing methods is that of stimulated Raman scattering involving adiabatic passage (STIRAP). These modern state specific techniques will be discussed in detail.

2.1. Franck–Condon pumping

Many molecules, when going from the ground electronic state to an excited electronic state or vice versa, experience a large geometric change. For example, HCN, is linear in the ground electronic state and is bent in the first excited electronic state. These systems have good Franck–Condon factors over a large range of vibrational quantum number, in this example especially for the bending vibrational quantum number. These molecules can be prepared in very highly vibrationally excited levels by exciting them to an excited electronic state, which will subsequently radiate spontaneously back to the ground state. The final population distribution in the ground state is determined solely by the product of the Franck–Condon factors and the cube of the emission frequency. The method has the advantages of requiring only a single laser and providing large quantities of vibrational excitation. However, this method is not completely state selective and the total population in highly vibrationally excited states can be very low because spontaneous emission is weighted by the cube of the emission frequency, which favours lower vibrational levels.

2.2. Overtone pumping

In a perfect harmonic oscillator, the vibrational transitions obey a very strict selection rule, $\Delta v = 1$. But in reality, molecular vibrations are not perfect harmonic oscillators, especially for hydride bonds, e.g. O–H, C–H, N–H. In this case, the vibrational selection rules are not strictly obeyed. Powerful pulsed lasers have made efficient direct overtone pumping to very high vibrational states possible. Direct overtone pumping up to $\Delta v = 7$ is now quite common (Crim 1984). The applicability of OP to hydride bonds is due to two factors: the potentials are not parabolic and the light mass of the H atom allows the quantum mechanical wavefunction to sample a much larger amplitude of vibrational motion in the classically forbidden region than is possible for a heavier atom. Again only one laser is required and this adds the advantage of simplicity. The limitation of this method for many systems comes from the fact that for bonds that contain two heavy atoms, the vibrations are typically much more harmonic and the amplitude of vibrational motion is much smaller. Consequently, for these kinds of molecular motions, overtone transitions are too weak for even the most powerful lasers.

2.3. Stimulated emission pumping

One of the most successful methods is that of stimulated emission pumping. Many molecular systems have allowed electronic transitions with long progressions in their spontaneous emission spectra. SEP was developed in the early 1980s (Kittrel *et al.* 1981, Reisner *et al.* 1984) and utilizes this special advantage to achieve a high level of state

specificity and very high vibrational excitation. SEP is essentially a variant of optical–optical double resonance in which one laser (the PUMP) is used to transfer molecules from an initially thermally populated level to an excited electronic state and a second laser (the DUMP) stimulates emission back to a high vibrational level of the ground electronic state. This method has already been applied to many molecules including: I_2 (Ma *et al.* 1991), C_2H_2 (Abramson *et al.* 1984, 1985), CH_2O (Vaccaro *et al.* 1983, Reisner *et al.* 1984), HCO (Zhao *et al.* 1990, Houston 1992), CH_2 (Xie *et al.* 1988, 1990), $C_2H_2O_2$ (Frye *et al.* 1986, 1988), NO (Yang and Wodtke 1990), HCN (Yang *et al.* 1990), HCP (Chen *et al.* 1990), HC≡CHO (Rogaski *et al.* 1992), CH_3CHO (Price *et al.* 1992), CH_3O (Geers *et al.* 1990a, b), HFCO (Choi *et al.* 1990, Choi and Moore 1991), C_3 (Rohlfing and Goldsmith 1989, 1990, Northrup and Sears 1990, Northrup *et al.* 1991), SiC_2 (Butenhoff and Rohlfing 1992), CS_2 (Zhang *et al.* 1992) and $CH_3(CO)_2H$ (Reid *et al.* 1990). Van der Waals molecules have also been studied in molecular beam SEP experiments, for example, OH · Ar (Berry *et al.* 1991), $C_2H_2O_2$ · Ar (Frye *et al.* 1988) and $C_2H_2O_2$ · Ar_2 (Frye *et al.* 1990). From this list one can get a feeling for the popularity of the method and its quite wide applicability. Much of the work with SEP has been in the area of two-laser spectroscopy but a growing number of three-laser experiments have been done, where SEP is used as a preparative method and laser induced flurorescence is used to probe energy transfer, for example. Extremely high levels of vibrational excitation and high efficiency population transfer are possible. For example, more than $440 \, kJ \, mol^{-1}$ of vibrational energy can easily be deposited into NO with quantum state specificity, saturating both PUMP and DUMP transitions with unfocused lasers (Yang and Wodtke 1990).

There are a number of considerations one must know when it comes to SEP. First, the excited electronic state must have a reasonable spontaneous emission quantum yield. A general rule of thumb that has proven very useful is that if you can see the spontaneous fluorescence with a monochromator, you will be able to see the SEP signal. This important limitation will be overcome when pico-second and femto-second lasers are applied to SEP problems, an area of research that is as yet untapped and promises a great deal of excitement. Another consideration is that the method requires two lasers and adds to the complexity of any experiment. However, it is often possible to pump two dye lasers with a single pump laser, recovering some simplicity. It must also be pointed out that for the purpose of state specific preparation, state selectivity can be jeopardized by simultaneous Franck–Condon pumping (FCP).

The flurorescence dip method is the usual way to detect SEP. By monitoring the laser induced fluorescence from the intermediate state at an angle 90° with respect to the axis of the overlapped lasers, an SEP transition is observed as a loss of the 'side fluorescence'. This makes the SEP spectrum similar to an absorption spectrum of the prepared excited rovibronic level. Consequently, all intermediate state loss processes that are induced by the second laser appear in the fluorescence dip spectrum and one must be careful to distinguish between absorption and stimulated emission processes.

Recently, a new probe technique for detecting SEP has been demonstrated that can enhance the signal-to-noise ratio of the SEP signal by two orders of magnitude or more (Zhang *et al.* 1992). This so-called 'zero-background SEP' relies on the resonantly enhanced degenerate four-wave mixing that can occur when a laser is tuned to an SEP transition. By using the phase matching conditions of the nonlinear process, one can arrange for the coherently generated signal beam to emerge from the apparatus as a coherent beam and it can be brought over a long distance to a remote PMT (photomultiplier tube). A variation of this method has already been applied to SEP of

SiC_2 created by laser ablation in a molecular beam (Butenhoff and Rohlfing 1992), and it is becoming clear that these new zero-background methods are of general importance. These are very promising techniques that will likely lead to a new generation of SEP experiments.

2.4. *Stimulated Raman pumping*

Stimulated Raman pumping resembles stimulated emission pumping in many ways except that SR pumps molecules to excited vibrational states via a virtual state, whereas SEP uses a real molecular eigenstate. Stimulated Raman pumping has been used for many spectroscopic and collisional dynamical studies, for example, Na_2 (Shimizu *et al.* 1985, Becker *et al.* 1987), H_2 (Wolfrum 1987, Kreutz *et al.* 1988, Kliner and Zare 1990) and HCl, N_2. Except for the Na_2 example, most of these studies are involved with low vibrational states. This method is particularly well suited for generation of molecules in $v = 1$. A notable ingenious trick has been applied for the case of H_2. A single laser pulse can be passed through a high pressure H_2 Raman cell to generate the Stokes light. Both frequencies are then passed into the experimental sample, naturally at exactly the correct wavelengths to induce the SR pumping of H_2. Complete state specific preparation can be accomplished with a single, fixed-frequency laser!!

2.5. *Stimulated Raman scattering involving adiabatic passage*

As was previously mentioned, SEP occurs simultaneously with FCP, and this cannot be avoided using incoherent laser pulses. Upon saturation of the three-level system, about one third of the molecules will be in each of the three states depending on their degeneracies. After the laser pulses are over, the third that was left in the excited electronic state spontaneously radiates to a number of ground electronic state vibrational levels as in FCP. One consequence of this is that one seldom achieves more than 33% population transfer in SEP. In the last few years a new experimental method has been developed which greatly resembles SEP but has the advantages of complete vibrational state specificity, i.e. no accompanying FCP, and 100% transfer efficiency. This method has been dubbed the Stimulated Raman Scattering with Adiabatic Passage method or STIRAP for short (Kuklinski *et al.* 1989, Gaubatz *et al.* 1990, He *et al.* 1990, Coulston and Bergmann 1992).

A molecular three-level system (see figure 1) is exposed to a coherent radiation field consisting of two different frequencies whose frequency difference is the desired vibrational excitation. This problem must be treated with the dressed states approach and has nothing to do with the more well known perturbation theory approach to spectroscopic selection rules. The dressed states can be solved exactly for the three-level system and the three distinct dressed states emerge as time-evolving linear superpositions of the three molecular quantum levels. The amazing result of this quantum mechanical problem is that conditions can be found where one of the three dressed states is a linear superposition of the initial and ground states *only*! Consequently, transitions are possible between the initial and final states without any probability amplitude for the intermediate level. So the properties of the intermediate level are totally unimportant to the process even when the two laser frequencies are adjusted to be on resonance with the intermediate level. Interestingly, it is necessary for the 'DUMP' pulse to *precede* the 'PUMP' pulse! Of course, there is a significant time where they are overlapped. Experimental confirmation of this idea has been obtained for Na_2 as well as Ne metastable atomic three level systems. For example, near unity transfer

efficiency of the pumping process (Na_2, $v = 0 \rightarrow v = 5$) has been achieved (Gaubatz *et al.* 1990). Since truly coherent lasers are presently the exception rather than the rule, the technique is limited by the present level of laser technology. However, STIRAP will almost certainly come to dominate the field, especially when one wishes to prepare high vibrational states for the study of chemical reactions or other processes, when truly coherent laser sources become more readily available in the ultraviolet.

3. Chemical reactions

Studies of the reactivity of highly vibrationally excited species has been focused primarily on two types of elementary processes: unimolecular reactions (including isomerization, and dissociation) and bimolecular reactions.

3.1. *Isomerization: spectroscopy of 'chemical rearrangement'*

Particularly by way of the SEP method, it has become possible to obtain high resolution spectra of molecules with enough energy to undergo chemical rearrangement. Since one is measuring properties associated with the molecular eigenstates, whose square is not time dependent, there can be no notion of a chemical isomerization rate in these experiments. Nevertheless the information contained in the high resolution spectrum of a chemically isomerizing molecule is the most detailed possible experimental information that can be had on a fundamental molecular rate process. This can be seen if one realizes that from the high resolution spectrum it will be possible to determine the actual isomerization potential energy hypersurface. From this, solutions of the Schroedinger equation will lead to any and all possible physically observable properties of the isomerization reaction. In other words, it is possible to view a chemical isomerization reaction as nothing more than a kind of molecular internal rotation. This area of investigation is still at the earliest stages but notable breakthroughs have been made.

One of the simplest isomerizations is that of HCN going to HNC. Both species have been well characterized spectroscopically near the bottom of each well. The isomerization barrier has been calculated (Pearson *et al.* 1975) obtained a barrier height of $17\,000\,cm^{-1}$. While empirical methods (Murrel *et al.* 1982) obtained a full, three-dimensional potential energy surface (the MCH surface by Murrel, Carter and Halonen) that conforms to a large amount of experimental data on HCN and HNC at low vibrational excitation. The barrier on that surface is $12\,000\,cm^{-1}$. A semi-rigid bender Hamiltonian has been used (Ross and Bunker 1983) in order to do calculations with a barrier height based on *ab initio* values (Pearson *et al.* 1975). The transition state is bent resembling more bent HCN than bent HNC.

Recently, SEP has been used to study this system in great detail (Yang *et al.* 1990a, b, c, Yang 1991). HCN is linear in its ground electronic state, but is bent in its first excited electronic state. SEP using the first excited electronic state as the intermediate state allows one to access very high bending vibrational states, which are much more likely to be involved with the isomerization than, for example CH stretch states. Sixty seven vibrational states were observed altogether in the range between 8900 and $18\,900\,cm^{-1}$. Most of the states could be assigned to normal $1 - k = \pm 1$ transitions, while the rest of the states were assigned either to axis switching transitions or perturbed dark states borrowing intensities from bright states (Jonas *et al.* 1992). This most surprising result means that, at least for the case of HCN, very simple and traditional spectroscopic ideas, such as rotation constants and normal mode vibrational coordinates are still valid, *even at chemically significant energies.*
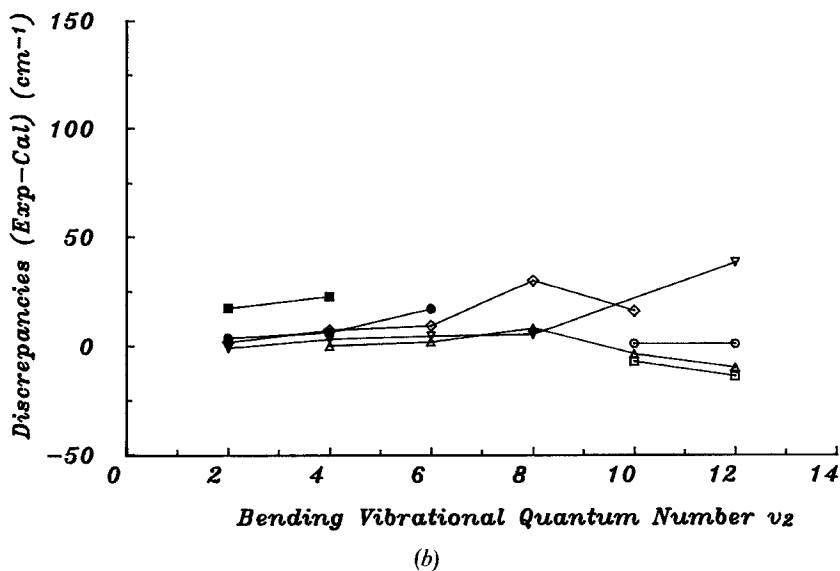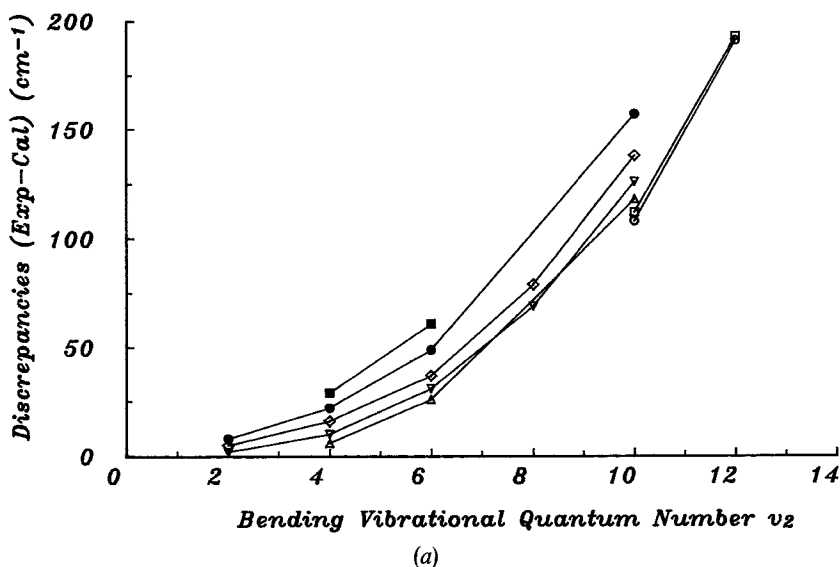
Figure 2. (a) Comparison of the observed and theoretical vibrational term energies on the original MCH potential of HCN as a function of vibrational quanta. Each curve indicates the bending progression accompanying a specific number of C–N stretching quanta. v_3 = 1 ($\bigcirc$), 2 ($\square$), 3 ($\triangle$), 4 ($\triangledown$), 5 ($\diamondsuit$), 6 ($\bullet$) and 7 ($\blacksquare$). Notice that the deviation between theory and experiment grows nonlinearly with increased bending motion, which roughly correlates with the reaction coordinate for the isomerization. (b) Comparison of the experimental and theoretical vibrational term energies on the modified MCH potential of HCN. Notice that no systematic discrepancies exist and the deviation between theory and experiment is much smaller than that in the case (a) at high bending energies.

Full quantum mechanical calculations on the MCH potential surface have been performed (Bentley *et al.* 1989, Bentley and Wyatt 1990). In order to gain knowledge on the quality of the MCH potential, a direct comparison between experimental and calculated energies is necessary. The discrepancies between observed and calculated vibrational energies based on the MCH surface are plotted against the bending vibrational quantum numbers in figure 2 (*a*). Notice that if the number of bending quanta, v_2, is small, the agreement is excellent while as v_2 increases, the disagreement becomes greater and greater. This indicates that the bending part of the MCH surface is definitely too low, which leads to the reasonable conclusion that the predicted isomerization barrier height is too low on the surface. Figure 2 makes very clear how the potential energy surface can be obtained from *assigned* high resolution spectra. The MCH surface was recently modified (Gazdy and Bowman 1991) in order to be consistent with all of the available data including the SEP data and a barrier height of $16\,700\,\text{cm}^{-1}$ was obtained. The comparison of the experimental and the recent theoretical results are shown in figure 2 (*b*). The agreement is much better.

One of the most important aspects of this work is that one can see how a reactive potential energy surface can be optimized with respect to high resolution spectroscopic data. So far, no evidence of delocalized vibrational states, which sample both sides of the isomerization barrier, has been found in the HCN/HNC SEP experiment. This is most likely due to explanations given by Bentley and Wyatt (1989). The vibrational wavefunctions that are delocalized are also systematically much more irregular with many more nodes and wiggles than those localized on the HCN side of the barrier. This means that their Franck–Condon factors with the relatively smooth vibrational wavefunction of the excited electronic state may be quite small. Consequently there is a great deal to be learned from construction of an 'ultrahigh sensitivity HCN SEP experiment'. Work is already underway in this direction in the Santa Barbara laboratory.

HCP is isovalent with HCN, yet their chemical properties are very different in terms of isomerization. For HCN, an isolable HNC isomer exists while for HCP, no stable HPC isomer has ever been detected. Experimental and theoretical studies (Lehmann *et al.* 1985) suggest that HPC resides at a saddle point on the potential energy surface. One may ask the interesting question: could one ever study the chemical properties of the HPC isomer, which is not even a stable point on the potential energy surface. The surprising answer to this question may well be yes. SEP on HCP has been carried out recently (Chen *et al.* 1990). The vibrational structure of this molecule, like HCN, was found to be surprisingly harmonic and vibrational quantum numbers could be assigned. As many as 30 quanta of bending vibration could be deposited into the molecule. The turning point of the bending vibration for such high states was estimated to be approximately $\Theta_{\text{HCP}} \approx 90°$. This suggests that SEP pumping of HCP may be a 'synthetic' means of producing a molecule that is chemically very similar to the 'unisomer' HPC!! This is a very interesting example of the control of chemical identity through vibrational excitation, mentioned in the introduction.

Another important isomerization reaction is the acetylene to vinylidene reaction. Vinylidene(H_2CC:) is the simplest unsaturated carbene. It is particularly important in many organic reactions as a reaction intermediate. Direct photodetachment experiments on the vinylidene negative ion H_2CC: (Burnett *et al.* 1983) confirmed that vinylidene does indeed exist and determined its lifetime of at least 0·01 ps. Theoretical calculations (Gray *et al.* 1981, Osamura *et al.* 1981, Pople *et al.* 1983) shows the reaction barrier, corresponding to the 1, 2 hydrogen shift in the vinylidene–acetylene rearrange-

ment, ranging from 0 to $1400\,cm^{-1}$ above the vinylidene minimum. The exothermicity of the reaction was calculated to be about $15\,000\,cm^{-1}$ and the lifetime of the vinylidene was determined to be 10 ps if the barrier height is $1400\,cm^{-1}$, and 0·2 ps if the barrier height is $700\,cm^{-1}$. High quality SEP experiments were performed on the acetylene molecules up to extremely high vibrational excitation, and above certain vibrational excitation, vibrational and rotational assignment becomes virtually impossible because of the onset of 'quantum chaos' (Abramson *et al.* 1984, 1985). It is worthwhile to point out here that the short time dynamics of this molecule at the highest vibrational excitation achieved, still appear to be regular, but long time dynamical behaviour becomes chaotic (Yamanouchi *et al.* 1991).

Completely different means are required for analysing a spectrum that reflects quantum chaotical motion and a spectral cross correlation (SCC) method was developed (Chen 1988, Chen *et al.* 1989) in an effort to understand the dynamics of the highly vibrationally excited acetylene. If all vibrational states are coupled strongly to one another in the ground electronic state, the chosen vibrational level of the intermediate electronic state will have little influence on the emission spectrum. On the other hand, if there are residual vibrational quantum numbers, there will be a more limited cross correlation between the two high resolution emission spectra coming from different vibrational levels of the excited electronic state. The SCC technique therefore aims to extract dynamical information, the vibrational mode mixing strength between two sets of characteristically different vibrational states prepared by SEP. A group theoretical treatment indicated that this approach could be used to distinguish between vinylidene-like vibrational states and acetylene-like vibrational states. The onset of enhanced coupling as evidenced by increased cross correlation between the acetylene and vinylidene like states could therefore be used to find the isomerization barrier height. In the region between 15 410 and $15\,640\,cm^{-1}$ of acetylene vibrational excitation, the spectral cross correlation index showed signs of the rotational symmetry alternation which is characteristic of acetylene–vinylidene isomerization rather than intra-acetylene Fermi or Coriolis interactions. Thus an upper bound for the vinylidene zero point level of $15\,525\,cm^{-1}$ was inferred from the SCC data. The newly developed SCC approach provides a potentially powerful method for detecting a specific perturbation induced mixing in the energy region where the spectral complexity is beyond the capability of traditional spectroscopic approaches.

3.2. *Vibrationally promoted chemistry*

As was discussed earlier, control of vibrational excitation can be a means of controlling chemical activity. This applies to photochemical activity as well. By selectively pumping the OH or the OD overtones in HOD, followed by u.v. photodissociation it has been found that either molecular bond could be broken selectively (Vander Wal *et al.* 1991a, b). Experimental results show that initial vibrational excitation alters the photodissociation dynamics dramatically. With photolysis wavelengths at 266·0 and 239·5 nm, selective bond-breaking can be controlled. At these two wavelengths, the dominant product of u.v. photodissociation of HOD($v_{OH} = 4$) is OD, where the product branching ratio was at least 40 : 1. When the photolysis wavelength was changed to 218·5 nm, the selectivity was lost. This was explained in terms of the Franck–Condon principle. At longer wavelengths, photodissociation of HOD($v_{OH} = 4$) proceeds only upon excitation to the portion of the repulsive, symmetric excited electronic potential energy surface where the OH bond is extended. From this point on the potential, only one of the two chemical bonds can be

broken. At shorter wavelengths excitation to the portion of the surface with an extended OD bond is also possible.

In a similar experiment on HOH, it was demonstrated how the final product state distribution can be controlled by photodissociating different overtone states (Vander Wal and Crim 1989). In these experiments two different highly excited vibrational states $|0,4\rangle$ and $|1,3\rangle$ were prepared. This notation indicates the number of quanta in each OH local mode. The photolysis of the $|0,4\rangle$ state at 239·5 nm produced no detectable vibrationally excited OH($v=1$), while dissociation from the $|1,3\rangle$ state produced roughly comparable amounts of OH($v=0$) and OH($v=1$). The results were also explained in terms of the Franck–Condon principle. In addition, it appears that the departing H atom does not impart a significant impulsive force to the dissociation partner OH. In other words, the photodissociation is diagonal with respect to the less excited OH local mode. Meanwhile, the $|0,4\rangle$ state has almost all the vibrational energy in one bond which is more extended and will be selectively broken. So, the excess energy will mainly be deposited into relative translation and rotation.

These ideas have even been applied to bimolecular chemical reactions. Recently bond selective reactions for HOD + H and Cl have been observed using vibrational excitation (Crim *et al.* 1990, Sinha *et al.* 1990, Hsiao *et al.* 1991, Crim *et al.* 1992, Sinha *et al.* 1992). The reaction of water with hydrogen atoms, $H_2O + H \rightarrow OH + H_2$ is 62 kJ (mol)$^{-1}$ endothermic and has a calculated barrier of 90 kJ (mol)$^{-1}$. The reaction of water with cholorine atoms, $H_2O + Cl \rightarrow OH + HCl$, is 66 kJ (mol)$^{-1}$ endothermic with an activation barrier of 72 kJ (mol)$^{-1}$. Atomic reactants were generated from diatomics by a conventional discharge or by laser photolysis. In these reactions, the OH molecules were pumped to an excited state $4v_{OH}$, from which state reaction with H or Cl was found to be facile. Energetically, there are two channels available for the HOD + H(Cl) reaction

$$\rightarrow OH + HD(DCl)$$
$$H(Cl) + HOD(4v_{OH})$$
$$\rightarrow OD + H_2(HCl).$$
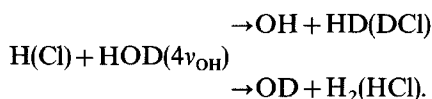
Experimentally the OD product channel was found to be much more favourable than the OH channel. Figure 3 shows the dramatic differences of the OH and OD product signal using LIF detection. The branching ratio OD:OH is greater than 100:1. Recently, this bond selective effect was observed even for the lowest excited vibrational states of OH products were detected by laser induced fluorescence. The larger than 25:1 for H + HOD(001) and smaller than 1:8 for H + HOD(100).

The control of product vibrational energy content was also demonstrated for the $H_2O + H$ reaction (Sinha 1990, Sinha *et al.* 1992). The water molecules were excited to a highly vibrationally excited state using OP. For the $H + H_2O$ reaction, $|0,4\rangle^-$ and $|1,3\rangle^-$ states of the H_2O were excited by overtone pumping and specific vibrational states of OH products were detected by laser induced fluorescence. The influence of the initial state on the OH product vibration is enormous. The reaction of the $|0,4\rangle^-$ state produces no detectable vibrationally excited OH even though the OH($v=1$) is energetically accessible, while in contrast, the reaction of the $|1,3\rangle^-$ state produces about eight times more OH($v=1$) than OH($v=0$). Similar phenomena were also observed for the $Cl + H_2O$ reaction. The reaction of water molecules excited to the $|0,4\rangle^-$ vibrational state mostly produces OH($v=0$) while the reaction of the $|1,3\rangle^-$ water molecules forms predominantly OH($v=1$) products. These results support a spectator model for reaction in which the vibrational excitation of the products directly reflects the nodal pattern of the vibrational wavefunction in the energized reactant.
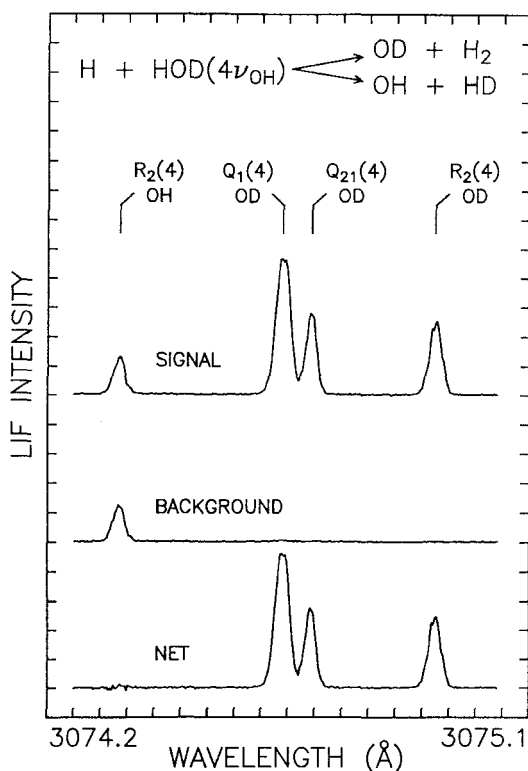
Figure 3.   Laser induced fluorescence excitation signals for OD and OH from reaction
HOD($4\nu_{OH}$) + H. The upper part shows the excitation signals from OH and OD when
722·6 nm light from the vibrational overtone laser is present. The middle part shows the
signals acquired without the overtone excitation laser light. The OH signal comes from the
minor contaminants in the microwave discharge. The lower trace shows the difference in
the total signal and background. The net signal shows that the reaction produces only OD.
This figure is reproduced by the courtesy of the American Physical Society.

3.3. *Intramolecular vibrational redistribution*

In light of the results on H_2O, a fundamentally important question to ask is whether
the same type of selectivity exists in much larger molecules or if this result is a special
feature of H_2O. Intramolecular vibrational relaxation (IVR) can be a significant
obstacle to this achievement and has been the subject of much experimental
investigation. Early work in this area established that the vibrational density of states is
of crucial importance in understanding the rate of IVR. However more recently, it has
become ever more clear that the picture is much more interesting and complex than
this.

Hydrogen peroxide is a prototypical example of a small molecule that exhibits IVR.
This molecule is particularly well suited to OP studies since, due to its weak O–O bond,
the absorption can be probed via laser induced fluorescence of the OH photo-product.
Some of the most beautiful experiments were carried out in order to investigate the IVR
and unimolecular dissociation of single quantum states of highly vibrationally excited
H_2O_2 molecules using infrared, optical double resonance (Luo and Rizzo 1990, 1991,
Luo *et al.* 1990). The double resonance technique ensures that single quantum states are

prepared at or near the dissociation limit. Hydrogen peroxide was excited to the OH stretching fundamental band or a combination band using a Nd:YAG laser pumped optical parametric oscillator (OPO). Then a Nd:YAG laser pumped dye laser was used to excite an overtone transition to put the molecule into a state that was above the O–O dissociation threshold. $6v_{OH}$ (Luo and Rizzo 1990), $5v_{OH} + v_{OO}$, $5v_{OH} + v_{OOH}$ (Luo and Rizzo 1991) and $4v_{OH} + v_{OH'}$ (Luo *et al.* 1992) were studied in this way. These spectra exhibited 'clump' like structure at levels of excitation where the vibrational state density was 5–8 cm^{-1}. The clump structure is due to intensity borrowing from the bright overtone state by the dark bath states, and reflects the anharmonic mixing between the vibrational states which in turn is indicative of the rate of IVR. Due to the double resonance approach it was quite a simple matter to investigate the rotational quantum number influence on this clump structure. One of the most important results from this work is the clear experimental observation that both J and K rotational quantum numbers have an influence on the rate of IVR in hydrogen peroxide. The clumps of lines change into a smooth Lorentzian envelope as J increases from 1 to 21. The overall clump width decreases with J, reaching an asymptotic value of 0·67 cm^{-1}. Luo and Rizzo explained this using a model with a J dependent density of bath states that couple to the zero-order bright state. It was also found from the relative magnitudes of the overall clump widths and the widths of the individual lines within a clump that subsequent to coherent excitation, the K quantum number is conserved for a time comparable to the lifetime of the dissociating H_2O_2. Interestingly, for the $6v_{OH}$ band, the linewidths of the individual features range from 1 to 3 cm^{-1}, but show no systematic dependence upon the rotational quantum numbers.

Another very interesting experiment showed that the IVR rate out of the fundamental and the first overtone acetylenic hydride stretches could be measured, and that placing a heavy 'blocking' atom in the molecule dramatically lowered the rate of IVR (Lehmann *et al.* 1990, Kerstel *et al.* 1991). Emission spectroscopy on p-difluorobenzene and p-fluorotoluene also suggest that the rate of IVR can be dramatically influenced by the presence of a methyl rotor (Parmenter and Stone 1986). SEP has also been applied to problems of IVR. Specifically, the beautiful work on HFCO has given clear evidence that even at vibrational state densities as high as 12 cm^{-1}, selective excitation is possible (Choi *et al.* 1990, Choi and Moore 1991). In this work it was found that increasing the energy of the molecule did not increase the complexity of the SEP spectrum. In fact, when larger and larger numbers of out of plane bending quanta were deposited in the molecule, the SEP spectra became simpler, implying a decreased rate of IVR for molecules with extreme amounts of out of plane bend.

Very recent results on the SEP spectroscopy of propynal (Rogaski *et al.* 1992) also suggest that localized excitation is possible in medium sized molecules. Because of the unique Franck–Condon factors of this molecule, SEP is effectively the same as doing direct overtone absorption spectroscopy, but on the v_4, CO, stretch. Molecular beam SEP spectroscopy of $v_4 = 1$ through 4 were recorded, yielding simple spectra even under conditions where the vibrational state density was as high as 100 cm^{-1}. For $v_4 = 3$ with 20 state cm^{-1}, only a single vibrational state was observed. Rotational constants could be measured and were consistent with CO stretching states of propynal. For $v_4 = 4$, it was quite easy to determine molecular rotation constants for the *two* vibrational states observed, which appear to be in Fermi resonance with one another. This is quite a surprising result when one considers that the vibrational density of states is at least 100 cm^{-1}. It appears that Fermi resonance interaction between only a very small

fraction of the total number of vibrational states is a better description of this molecule than rapid vibrational randomization. The bandwidth of the DUMP laser was $0.08 \, \text{cm}^{-1}$ and limited the observed linewidth. This indicates the lower limit to IVR must be at least 60 ps, even at this high state density. Indeed it may be much longer. When simple OP spectra are observed at high vibrational state density one normally argues that the high frequency hydride stretch is out of resonance with the other vibrational motions of the molecule. Such an argument is clearly not applicable in the case of propynal. This is the first observed example of a heavy atom vibration 'hanging on' to a large fraction of the vibrational excitation even when the vibrational state density is as high as 100 states cm^{-1}.

All of these experiments suggest that state density is not the only factor involved in determining the rate of IVR; the structure is also important. If one can understand the structural dependence of IVR, the possibility of extending Crim's bond selective ideas to other molecules is a truly viable possibility.

4. Collisional energy transfer

We have already seen many of the interesting chemical properties that highly vibrationally excited molecules can exhibit, and the remarkable control afforded by modern laser technology. Naturally, it is of considerable importance to begin to characterize the collisional energy transfer properties of such molecules.† If collisional energy transfer were much faster than chemical transformations, it might have serious implications to the 'big picture' that we are trying to paint. Up to now only a small number of detailed state-to-state experiments have been performed on highly vibrationally excited molecules, and there is undoubtedly still a great deal to learn. For example, we need to determine to what extent theories of 'low-vibrational-energy' structure and energy transfer can be applied in the chemical energy regime and whether collisions easily scramble 'vibrational information' which has been stored in a molecule with sophisticated laser methods. Many other interesting questions come to mind, the answers to which we presently have no clue. Nevertheless, we are beginning to peel back the 'cocoon' created by a lack of applicable methods and discover the colourful 'pupa' of natural phenomena existing inside.

This Section is divided into several parts.‡ First, we will present work on highly vibrationally excited NO relaxation, which has given one of the most complete pictures of the vibrational quantum number dependence of vibrational relaxation. We will then discuss the role of vibrational relaxation of highly vibrationally excited O_2, which is directly relevant to the ozone depletion problem. Some very interesting experiments on highly vibrationally excited OH vibrational energy transfer have also been performed. Finally, we will discuss the *rotational* energy transfer of highly vibrationally excited molecules.

4.1. *Nitric oxide self relaxation*

NO/NO vibrational energy transfer is a very peculiar example of vibrational relaxation even at low vibrational energy. The vibrational relaxation is much faster than nominally 'similar' species such as CO and O_2. NO is a weakly polar molecule,

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† Some of the earlier work on hydrogen halides can be found in other reviews (Truhlar 1990).
‡ There are some other studies on energy transfer of highly vibrationally excited molecules. For example, for $I_2(v)$–He relaxation studies, a detailed review can be found in an article by Krajnovich *et al.* (1989).

with a dipole moment of $0 \cdot 153$ Debye. Its vibrational frequency, $1878 \, \mathrm{cm}^{-1}$, lies between CO and O_2. But unlike O_2 and CO, NO is an open shell molecule and forms a weakly bound dimer with a binding energy of $560 \, \mathrm{cm}^{-1}$ and an oriented structure.

NO is a particularly favourable molecule for SEP (Yang and Wodtke 1990). It has a ground state equilibrium bond length of $1 \cdot 16$ Å and an excited electronic state (the $B^2\pi$ state) with an equilibrium bond length of $1 \cdot 44$ Å. So the B–X emission system has a long vibrational progression indicating a large number of sizable Franck–Condon factors which makes it ideal for SEP. In fact the largest Franck–Condon factors correspond to preparation of NO in $v = 20$ or so and the possibility of producing an optically pumped infrared laser has been discussed (Yang and Wodtke 1990). Studies of vibrational (Yang *et al.* 1990a, b, c, Yang *et al.* 1992) as well as rotational energy transfer (Yang and Wodtke 1992) of highly vibrationally excited NO have been carried out.

In these investigations, a tunable ArF laser, operating at $193 \cdot 3 \, \mathrm{nm}$, was used as the pump laser, exciting the NO B(7)–X(0) band, and a pulsed tunable dye laser induced emission to any vibrational state below $v = 25$ of the ground electronic state. A third tunable (dye) laser is used as a probe to detect the results of bimolecular encounters. Vibrationally state specific energy transfer properties of $NO(^{14}N^{16}O$ and $^{15}N^{18}O)$ from $v = 8$ to 25 were determined, giving an uncommonly complete picture of the vibrational dependence of the energy transfer. The vibrational relaxation rates are listed in table 1, and the vibrational dependence of the energy transfer rates are shown in figure 4. The $v = 2$ vibrational relaxation was measured by Stephenson (1973). In the same set of experiments vibrational relaxation of $NO(v = 22)$ with H_2 was also studied.

The vibrational-state-specific, vibrational relaxation rate constants were linearly proportional to the vibrational quantum number up to about $v = 13$. Above this level of vibrational excitation the dependence on vibrational excitation was much stronger and the vibrational relaxation rate of NO at $v = 24$ of NO was found to be almost 200 times faster than that for $v = 1$. These results were interpreted as evidence for two qualitatively

Table 1.   NO(v) vibrational energy transfer probabilities with NO(0).

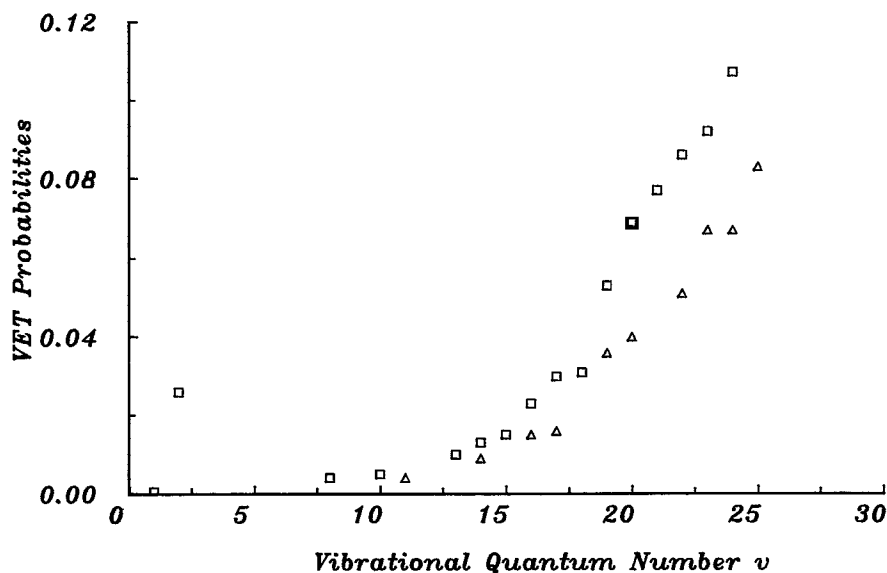| v	$P(^{14}N^{16}O)$	$P(^{15}N^{18}O)$
1	0·0005	—
2	0·026	—
8	0·004	—
10	0·005	—
11	—	0·004
13	0·010	—
14	0·013	0·009
15	0·015	—
16	0·023	0·015
17	0·030	0·016
18	0·031	—
19	0·053	0·036
20	0·069	0·040
21	0·077	—
22	0·086	0·051
23	0·092	0·067
24	0·107	0·067
25	—	0·083

Figure 4.   Vibrational dependence of the relaxation probabilities for NO(v)–NO(0) relative to the hard sphere gas kinetic rate for NO at room temperature. $\square$: $^{14}N^{16}O$, $\triangle$: $^{15}N^{18}O$.

distinct energy regimes for vibrational energy transfer. In the low-energy regime below $v = 14$ single quantum vibrational relaxation apparently dominates, giving rise to the linear dependence on vibrational quantum number. This linear dependence is a fundamental prediction of the SSH theory of vibrational energy transfer, which has achieved some success for diatomics at low vibrational energy. At least in this simple system it appears that low energy transfer theories can perhaps be applied even up to 50 kcal (mol)$^{-1}$ of vibrational excitation!!

Despite this success of SSH theory, it is well known that the magnitude of the vibrational relaxation rate for NO($v = 1$) is about five orders of magnitude faster than would be expected from SSH theory applied to 'similar' species such as CO and O_2. Of course this casts doubt on the interpretations of the last paragraph. This prompted a re-interpretation of SSH theory for molecules that have significant attractive forces such as the NO/NO system. It was shown that molecules that have attractive wells at relatively short bonding distances, such as in the NO dimer, will by necessity have a much steeper repulsive wall than molecules that collide through very long-range and weak, electrostatically bound complexes. Since the steepness of the repulsive wall is the single most important molecular property required to determine the vibrational relaxation rate in SSH theory, Yang was able to show that a physically reasonable re-interpretation of the SSH theory could account for the 'anomalously' high vibrational relaxation rate for NO/NO (Yang and Wodtke 1992).

The other competing model for vibrational self relaxation of NO suggests that the multiple potential energy surfaces present for collisions between two $^2\pi$ molecules in some way accelerates vibrational energy transfer through electronically non-adiabatic curve crossings. This may, however, not be as important as was previously supposed. As evidence of the lack of necessity to invoke non-adiabatic 'curve-crossing' effects in order to understand NO/NO vibrational energy transfer, consider table 2 (see also figure 5) which shows the strong correlation between dimer binding energies and

Table 2. Correlation between the vibrational relaxation rates and the intermolecular potential well depths.

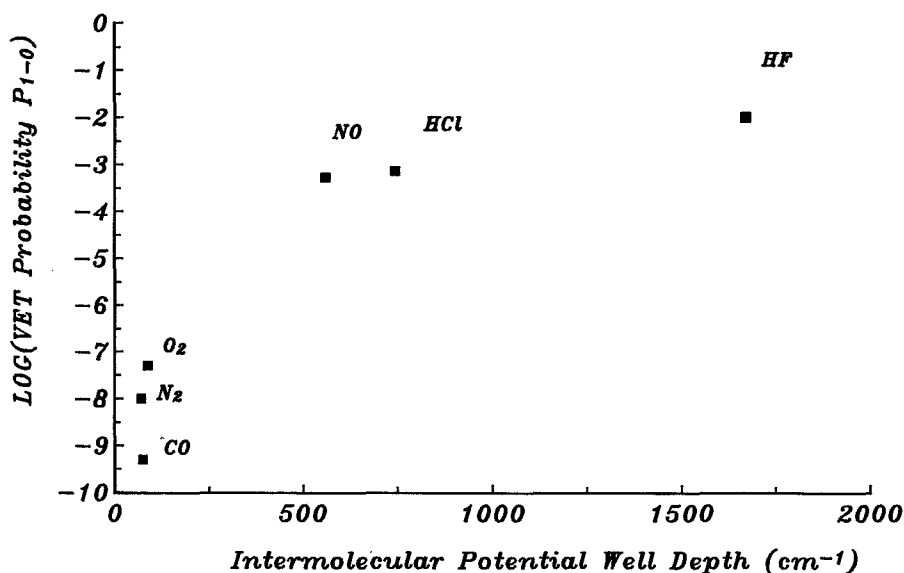| Systems	Probabilities	Potential well depths (cm^{-1})
HF	1.0×10^{-2}	1672
HCl	7.3×10^{-4}	744
NO	5.3×10^{-4}	560
O_2	5.0×10^{-8}	90
N_2	1.0×10^{-8}	72
CO	5.0×10^{-10}	75

Figure 5. Correlation between the vibrational relaxation rates and the intermolecular potential well-depths.

vibrational energy transfer rates. For a few examples see Truhlar (1990), Yardley (1980). The vibrational relaxation rates of NO are comparable to that of the hydrogen halides, even though the nature of the dimerization of NO is completely different from that of hydrogen halides. It appears that NO/NO falls nicely into the hydrogen halide family when it comes to vibrational relaxation.

As was mentioned previously, above $v = 14$ the vibrational relaxation is much more strongly than linearly dependent on vibrational quantum number. This motivated investigation of the role of multiquantum vibrational relaxation. Experimental results on $v = 19$ of NO indicate that double-quantum relaxation is approximately as important as single quantum relaxation in the high-energy region. It is quite difficult to imagine how a low-energy transfer theory, which assumes relatively weak interactions between the collision pairs, could be used to explain the fact that the molecule

exchanges $2800\,\mathrm{cm}^{-1}$ of vibrational energy as easily as it exchanges $1350\,\mathrm{cm}^{-1}$. Especially when one considers that the collision energy is characterized by $kT = 208\,\mathrm{cm}^{-1}$.

These interesting results were interpreted as evidence of 'transient chemical bond formation' in the transition state leading to vibrational energy transfer. Several concrete pictures are possible. First, it is possible that the transition state for vibrational energy transfer lies near the transition state for the chemical reaction $NO + NO \Rightarrow N_2O + O$. One would expect much larger anharmonic coupling between the vibrational motions of the energy-transfer transition-state than for trajectories which sample a shallow well. Another possibility was suggested by *ab initio* calculations which indicate many high-energy complexes exist at these levels of vibrational excitation (Gordon 1991). If the energy transfer transition state sampled or came close to these complexes, energy transfer could be dramatically enhanced.

As can be seen we are just beginning to understand how highly vibrationally excited molecules behave in bimolecular collisions, but it is already clear that many new ways of thinking will be required in order to theoretically describe these phenomena.

4.2. O_2 Vibrational relaxation in the stratospheric ozone layer and the role of highly vibrationally excited molecules in the atmosphere

Model predictions of ozone concentrations differ by a factor of 1·5 to 2 from observations in the upper atmosphere between 50 and 80 km (Froidevaux *et al.* 1985, Clancy *et al.* 1987). Frederick *et al.* (1984) have argued that the underestimation of ozone production is the possible source of the error in the models, while others have pointed out that increased ozone production can only occur through increased O_2 dissociation (Slanger *et al.* 1988). Traditionally, atmospheric models have neglected all quantum state specific effects. This point of view is based on the often correct assumption that relaxation back to equilibrium distributions is much faster than any other atmospheric process. This is the so-called 'local thermodynamical equilibrium' (LTE) assumption. In recent years it has become increasingly clear that the LTE assumption does not hold for vibrational quantum numbers in molecules found above about 30 km of altitude. Slanger has proposed that this is the source of the error in many of the ozone models (Slanger *et al.* 1988).

Ozone photodissociation proceeds through two main channels, one channelling the u.v. photon energy into product electronic excitation, and one channelling it into product vibration (Fairchild *et al.* 1978, Sparks 1980)

$$O_3 + h\nu \Rightarrow O_2(^1\Delta) + O(^1D)\ 85\%,$$

$$\Rightarrow O_2(^3\Sigma,\ \mathrm{vib}) + O(^3P)\ 15\%.$$
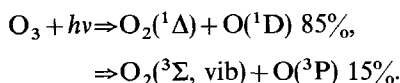
Recent experiments have shown the efficient production of ground electronic state O_2 in vibrational states as high as $v = 22$ (Slanger *et al.* 1992). It appears that these molecules must be present in the stratosphere, and if so, it may be possible that solar visible or near u.v. radiation can dissociate the $O_2(\mathrm{vib})$ by exciting them to the B electronic state through the Schumann–Runge region. This would allow O_2 to become a photochemical precursor of ozone, which is normally not possible since O_2 absorbs first at wavelengths that are too short to penetrate to the stratosphere. The photodissociation rate of $O_2(4 < v < 21)$ was estimated using known solar flux data for altitudes above 50 km. The results show that O_2 in a high vibrational level is a much

more potent source of ozone via photodissociation followed by three body recombination

$$O_2 + h\nu(\text{vis}) \Rightarrow O + O,$$

$$O + O_2 + M \Rightarrow O_3 + M,$$
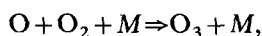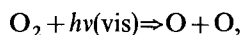
than is O_2 in $v=0$, especially if the vibrational relaxation is a relatively slow process.

Slanger also estimated the vibrational quantum number dependence of the $V-V$ energy transfer for O_2 self relaxation using a semiclassical theory by Rapp and Englander-Golden (1964, 1965). This theory gives reasonable agreement for the $V-V$ energy transfer in CO, which has been extensively studied (Deleon and Rich 1986). This analysis predicts a dramatic *decrease* in the vibrational relaxation rate of O_2(vib) as vibrational energy is increased. Most importantly, these estimates suggest that the collisional lifetime of highly vibrationally excited O_2 could well be long enough to allow it to be photodissociated in the stratosphere. Experimental confirmation of the vibrational relaxation rates of highly vibrationally excited O_2 is very much needed, especially in light of the NO self relaxation results which showed a dramatic *increase* in the rate of vibrational relaxation with vibrational quantum number (see above). Such data would allow the confirmation of a possibly very important new ozone formation channel, that has not been previously included in the atmospheric modelling.

In addition, it is important to understand the role of other quenching partners. The fastest atmospheric quencher of O_2(vib) is $O(^3P)$, but the ratio $[O(^3P)/(O_2)]$ is only 10^{-5} at 70 km and 10^{-6} at 50 km (Brasseur and Soloman 1984). The estimation by Slanger *et al.* (1988) shows that the quenching of O_2 by $O(^3P)$ should become significant only when the $V-V$ energy transfer probability for $O_2(v) + O_2(0)$ falls into the 10^{-7} to 10^{-8} range. This could become important for the highest vibrational levels of O_2.

Another highly vibrationally excited molecule of relevance to the atmosphere is the hydroxyl radical, which has been observed in the mesosphere in vibrational states as high as $v=9$, and is presumably produced by the exothermic chemical reaction of hydrogen atoms with ozone (Meinel 1950, Meriwether 1989). The excited molecules can either be deactivated by collisions with other molecules or radiate to lower vibrational states, interestingly through extremely strong $\Delta v > 1$ near i.r. overtone transitions. In the mesopause, where the emission is the strongest, these processes proceed competitively. Therefore in order to model the upper atmosphere's near i.r. emission, one has to account for the vibrational relaxation of the vibrationally excited OH as well as the radiative Einstein coefficients.

In a recent study by Sappey and Copeland (1990), OH molecules were prepared by the reaction of

$$H + O_3 \rightarrow OH(X\,^2\pi,\ v \leqslant 9) + O_2.$$
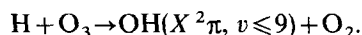
A tunable dye laser was used to pump OH molecules from $v=8$ to $v=12$ and a probe laser was used to probe the population in $v=12$ via laser induced fluorescence through the B–X system. These experiments have obtained the largest quantity of data on the influence of different collision partners. The collisional relaxation of OH($v=12$) was measured with six different quenchers: CO_2, O_2, He, H_2, Ar, and N_2. The O_2 measurement was found to be the most important for the upper atmosphere. O_2 and CO_2 are the most efficient among the six collision partners. The relaxation of OH in $v=12$ with O_2 is 100 times faster than that at $v=1$. Experimental results (Finlayson-Pitts and Kleindienst 1981, Dodd *et al.* 1989, Rensberger *et al.* 1989, Raiche *et al.* 1990)

show that the vibrational energy transfer rate of OH at $v = 1, 2, 9$ with O_2 is 20 times faster than that with N_2, while Sappey and Copeland's results show that the relaxation of OH at $v = 12$ with O_2 is only six times faster than that with N_2. The relative efficiency of the vibrational relaxation of OH with O_2 over N_2 appears to decrease with increasing vibrational excitation. In the case of O_2, the process $OH(v = 12) + O_2(v = 0) \rightarrow OH(v = 11) + O_2(v = 1)$ is only $75 \, cm^{-1}$ exothermic, suggesting the possible near resonant V–V energy transfer. But the decreasing relative efficiency of the OH relaxation with O_2 over that with N_2 implies that the V–V energy transfer of OH at high vibrational excitation is negligible as in the case of NO and HF. This could be a general case for many molecular systems.

4.3. Rotational energy transfer of vibrationally excited molecules

Another area of interest is the rotational energy transfer of highly vibrationally excited molecules. So far, almost all evidence suggests that rotational energy transfer proceeds in high vibrational states in a very similar fashion to that of low vibrational states.

Rotational and spin–orbital state-to-state energy transfer rates were measured for NO $v = 19$ and 8 (Yang and Wodtke 1992). Comparing with the $v = 2$ results, there is virtually no difference. Collisional energy transfer in $H_2CO(X^1A_1)$ at an internal energy of $E_{vib} = 11\,400 \, cm^{-1}$ was studied (Temps et al. 1987). This study applied the experimental method stimulated emission pumping-transient absorption spectroscopy (SEP-TAS). A specific rovibrational level of the X state is populated using SEP with two pulsed dye laser. The time dependent population in the parent level and adjacent collisionally populated levels is detected by direct absorption using a continuous wave (c.w.) dye laser. Energy transfer from the parent level was detected into the levels $3_{1,2}$, $4_{1,3}$, $5_{1,4}$, $7_{1,6}$ and $8_{1,7}$ of the $2_4 4_4$ vibrational state. No relaxation could be observed into other nearby vibrational states even though the energy gap could be much smaller than the observed collisional transitions. The total decay rate constants corresponds to a velocity averaged cross-section of $\sigma = 483 \, Å^2$. This result is in good agreement with the value measured using SEP-transient polarization (Vaccarro et al. 1983, Vaccarro 1986). The large cross-section indicates that the relaxation is controlled by long-range interactions. This study shows that molecules at one rotational state of a very highly vibrationally excited state favourably transfers its energy to rotational states within the same vibrational manifold. This indicates that the memory of the vibrational identity is very strong. Further studies will be required to see if this is a general phenomenon.

4.4. Li$_2$ and Na$_2$ scattering in crossed molecular beams

Because of their accessibility with continuous wave dye lasers, Li_2 and Na_2 have received far more experimental attention than many other diatomics. Moreover, c.w. excitation allows elimination of the well known 'duty cycle problem' associated with low repetition rate pulsed lasers and it is for this reason that some of the only examples of crossed-molecular beam experiments on highly vibrationally excited molecules exist for these two molecules. Consequently, we devote one Section to this area of research, which overlaps with some of the other topics discussed in this article.

Vibrationally enhanced atom–molecule scattering has been the topic of many experimental studies (Rubahn and Bergmann 1990). The first systematic study of the influence of vibrational excitation of electronic ground-state molecules on the total collision cross-section was performed by Fuchs and Toennies (1986). They used a Li_2 molecular beam and generated vibrationally excited molecules using Franck–Condon

pumping with a c.w. single mode dye laser. Following the pump step, the primary beam was attenuated in a collision cell by the rare gases He and Kr. The change in intensity of the laser-induced fluorescence was measured for individual vibrational states using a second c.w. single-mode dye laser. The percentage change of the integral cross-section with vibrational state was derived by applying Beer's law. Similar experiments on total collision cross-section as a function of vibrational state for the reactive system Li_2–Na were also carried out (Rubahn *et al.* 1987).

Of these three systems, only Li_2–Na exhibited monotonically increasing collision cross-sections as a function of vibrational excitation. For Li_2–rare gas, the cross-section first decreases with increasing vibrational excitation to a minimum and then increases. The remarkably different results for the Li_2–He, Kr and Li_2–Na has been attributed to the fact that in the former case the collision energy (78 and 413 meV) is considerably larger than the potential well depths (0·17 and 2·63 meV), while in the second case, the collision energy and well depth are comparable (about 500 meV) (Rubahn and Toennies 1988). Therefore, for Li_2–Na the well region and the long-range part of the potential are governing the scattering process, whereas for Li_2–rare gas the very large collision energy leads to the totally different results that the change in integral cross-section with vibrational state is sensitive both to the long-range forces as well as the short-range forces.

It has also been demonstrated that it is possible to derive information on the change of the potential anisotropy with changing vibrational state by measuring integral cross-sections (Rubahn and Toennies 1988). Recently, scattering experiments with *m*-state-selected molecules have been performed (Hefter *et al.* 1986, Mattheus *et al.* 1986). It was found that for Li_2–Kr the long-range anisotropy increases by a factor of 3 from $v = 0$ to 20.

Details of short-range potential anisotropy might be investigated with high precision by measuring rotational rainbows in inelastic scattering. This study has been performed for $Na_2(v = 1)$–Ne (Gottwald *et al.* 1987) and $Na_2(v = 31)$–Ne (Keller *et al.* 1991, Ziegler *et al.* 1991). In both cases, Na_2 in a molecular beam was pumped initially by FCP, then a second laser was introduced to measure the population in the final level at a particular scattering angle. It was found that the rational rainbows for $Na_2(v = 1)$–Ne show essentially the same anisotropy as for $Na_2(v = 0)$–Ne. While for $Na_2(v = 31)$–Ne, significantly increased anisotropy was found.

Inelastic transitions in vibrationally excited Na_2 by electron impact were also studied by Kumar *et al.* (1991). Differential cross-sections for rotational transitions from vibrationally excited $Na_2(v = 2$ and 31) by electron impact at 150 eV were measured. Experimental results show that the rotational inelasticity and the cross-sections for vibrational transitions increases with the initial vibrational quantum number. Kumar *et al.* also show that the experimental results can be explained by a two-centre model.

5. Concluding remarks

In the last decade we have witnessed exciting developments in the understanding and control of highly vibrationally excited molecules, in many cases with the assistance of rapidly expanding laser technology. Above all we have seen the development of several important new methods for depositing an enormous amount of vibrational energy into a particular part of a molecule with high efficiency. In fact, it is now a well established notion that one can control the outcome of chemical processes through such selective laser preparation of reactants, at least for small molecules. Even for larger

molecules it has become clear that there will be many examples of restricted IVR, where large amounts of vibrational energy will remain localized for long periods of time. In the isomerization studies we have seen how one can even go so far as to influence the chemical *identity* of a molecule through laser preparation. The success of these new approaches have caused many scientists to believe that the era of *'molecular engineering'* is closer than ever.

We are also beginning to understand how vibrational energy is transferred out of highly vibrationally excited molecules in bimolecular collisions and that new ideas, such as 'transient chemical bond formation' may be required to understand such phenomena. The new onslaught of data has provided us first-hand experimental information, which pushes our theoretical understanding to (and perhaps beyond) its breaking point. *Highly vibrationally excited molecules are also very important in the upper atmosphere where the two conditions:* high u.v. photon density and reduced total pressures give rise to non-LTE vibrational distributions which may have very important implications to the production of highly vibrationally excited molecules.

Through this review we hope to have provided the readers with a complete picture of the current status of research in the field of high vibrationally excited chemistry. Unfortunately, no review is ever complete and becomes obsolete nearly as quickly as it is published. Nevertheless, we hope that this article will be helpful for both beginners and veterans in the field.

Acknowledgments

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