MASTER

CONF-790411--2

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Presented at the Faraday Discussion of the Chemical
Society No. 67 on Kinetics of State-Selected Species
Birmingham, England, April 9-11, 1979; also Submitted
to Faraday Discussions

VIBRATIONAL-ROTATIONAL EXCITATION - CHEMICAL REACTIONS
OF VIBRATIONALLY EXCITED MOLECULES

C. Bradley Moore and Ian W. M. Smith

March 1979

DISCLAIMER

MASTER

FARADAY DISCUSSION OF THE CHEMICAL SOCIETY no. 67

ON

KINETICS OF STATE-SELECTED SPECIES

Held in Birmingham, England; 9-11 April, 1979

INTRODUCTORY PAPER TO SECTION 2

ON

VIBRATIONAL-ROTATIONAL EXCITATION.

EF

VIBRATIONAL-ROTATIONAL EXCITATION

Chemical Reactions of Vibrationally Excited Molecules¹

BY

C. BRADLEY MOORE

Department of Chemistry, University of California, Berkeley,
California 94720, U.S.A.

AND

IAN W.M. SMITH

Department of Physical Chemistry, University Chemical
Laboratories, Lensfield Road, Cambridge CB2 1EP

Received

The obvious predecessors to our present meeting are the Faraday Discussion on Reaction Dynamics held in 1967 and that on Molecular Beam Scattering in 1973. Even in the six years which have elapsed since the second of these meetings, our knowledge of the chemical reactions of vibrationally excited molecules has expanded rapidly,¹⁻⁸ and new methods for exploring the dependence of reaction rate on vibrational state continue to appear with almost bewildering regularity. Despite this, our knowledge and understanding is, in many respects, still quite

primitive. Moreover, the field is an unusually inviting one, since it allows the microscopic models and fundamental assumptions of reaction rate theories to be tested, whilst simultaneously promising important practical applications.

If our review was to be of an acceptable length, we had to be selective. Furthermore, in preparing it, we had in mind a wider audience than the daunting assembly of experts attending the Discussion. Consequently, we have tried to make our paper easy to follow, and to consider only a limited number of systems which strike us as especially interesting, either on the grounds that the available results are capable of detailed dynamical interpretation or because they raise further interesting questions. Gas-phase processes lend themselves to the most detailed interpretation and, as elsewhere in this Discussion, they are emphasised in what follows. However, laser-induced chemistry in condensed phases and on surfaces can claim to be a 'new frontier', so we conclude with a resume of what has been - and might be - achieved in these areas.

Although the dynamics of reactions between atoms and diatomic molecules are now understood fairly well,^{3,4} this is not the result of direct measurements on the reactions of vibrationally excited species. These experiments sometimes raise as many problems as they answer. For example, the separate contributions of chemical reaction and non-reactive energy transfer to the overall removal of excited molecules are frequently not distinguished,⁹ although the relative rates for these separate channels have been determined in some experiments.^{8a,10,11} Our understanding is largely based on what the principle of microscopic reversibility tells us about the selectivity of the energy requirements

for endothermic reactions when we have information available about the specificity of energy disposal in the reverse process.¹² Such conclusions are supported and extended by the results of a multitude of quasiclassical trajectory calculations¹³ and a much smaller, but growing, number of theoretical studies using semiclassical or quantum dynamics.¹⁴ At least for this type of reaction, there is a generally accepted framework within which the enhancement of reaction via reagent excitation can be related to some qualitative features of the potential energy hypersurface.¹⁵

For polyatomic molecules, both bimolecular and unimolecular reactions are important and our understanding is less advanced. Serious questions concerning both the nature of the vibrationally excited states of polyatomics and their dynamics must be answered before we can feel comfortable with even qualitative notions. Since the discovery of molecular dissociation by intense ir laser pulses, it has been shown that excitation and dissociation do truly occur in the absence of collisions.^{7,16} Most observations to date are consistent with rapid redistribution of vibrational energy among the vibrational coordinates near the dissociation limit. Nevertheless, one must ask whether RRKM theory always works: whether mode-selective unimolecular vibrational photochemistry is possible? By comparison with the diatomic limit, it seems clear enough that the chemical reaction rates of the lowest excited states of polyatomic molecules will be detailed functions of the vibrational quantum numbers. For how large a molecule with how high an energy will reaction rates depend on the mode excited rather than ^{on} just the total excitation energy? For large molecules,¹⁷ is it useful to assume that the coupling between modes adjacent to a reaction site is stronger than that between these modes and the remaining modes, either in the rest of the molecule

or in the solvent? Direct excitation of high overtone levels using single visible photons,^{18,19} should both maximise the chances of mode-selective chemistry and answer some of these questions.

Vibrational photochemistry as a method for carrying out mode-selective chemical syntheses, isotope enrichments and chemical purifications has considerable practical promise, although the systems of most practical interest are often the most difficult to analyze fundamentally. Focusing a high power CO₂ laser into a gas can produce a hopelessly complicated set of interacting optical excitations, collisional energy transfers and chemical reactions. The very impressive isotopic enrichments (of elements from D to U!) which have been obtained via vibrational excitation encourage research in this area.^{6,20-26} Useful ir laser driven chemical processes do not necessarily rely on avoiding the statistical RRKM regime of excitations, or on maintaining a collision rate slower than the unimolecular reaction rate. Vibrational heating in which all the modes of all molecules are strongly coupled by collisions can still lead to nonthermal reactions.²⁷ In fact, even if the vibrations are equilibrated with rotations and translations, the chemistry induced by a powerful laser may differ greatly from that with a bunsen burner because the laser-heated zone can be well-separated from the walls.²⁸

A. EXCITED STATES AND THEIR PREPARATION

1. Discrete quantum states

Lasers make it possible to excite single vibration-rotation quantum states, or groups of states, in small molecules. These states are well-characterized by time-independent rovibronic wavefunctions. The population of each state as a function of

time can be observed spectroscopically, and rate constants for energy transfer and reaction can be deduced if the number of levels involved is sufficiently small and the number of independent data sufficiently large.

In practice, mapping the pathways for vibrational relaxation has proved difficult enough for triatomics and is only possible to a limited extent in molecules with five or more atoms.²⁹ For diatomic molecules, fundamental and overtone levels may be excited directly and, at least in principle, it is possible to measure reaction rates as a function of vibrational quantum number. Rates of energy transfer and/or chemical reaction have been measured for diatomics excited directly to levels as high as $v=4$.³⁰ The increasing availability of tunable infrared sources, such as the optical parametric oscillator and the F-centre laser, should allow many new systems to be studied.

Other optical techniques have been used to promote molecules to vibrationally excited levels, although they have, to date, been employed sparingly in studies of the reaction kinetics of vibrationally excited molecules. Electronically excited molecules may be prepared in a wide range of vibrational levels when the Franck-Condon factors permit. The reaction, $\text{ICl}(A, v) + \text{H}_2 \rightarrow \text{HCl} + \text{HI}$ has been studied for $v=8-24$.³² An alternative technique is to optically pump an electronic transition and rely on spontaneous^{33a} or stimulated^{33b} emission to return molecules to one or more vibrationally excited levels in the electronic ground state. It should be possible to extend these methods to many more systems as the development of excimer lasers throughout the uv region proceeds.³⁴ Coherent Raman excitation has been used to produce $\text{H}_2(v=1)$.³⁵ Use of a source frequency close to an allowed rovibronic transition can lead to excitation of high overtone levels through

resonant Raman transitions.³⁶ When such transitions are driven coherently with two lasers, efficient and selective excitation of a wide range of ground state levels should be possible.

Usable concentrations of vibrationally excited molecules can also be produced by passing a gas through an electrical discharge or by simply heating it. Some measure of control can be achieved by allowing time for translational and rotational, but not the vibrational, degrees of freedom to relax, or in beam or 'near-beam' experiments by comparing the effect of heating the atomic and molecular sources.³⁷ These techniques are particularly useful for molecules, such as H_2 ,³⁸⁻⁴¹ which cannot be excited directly by photon absorption, or for exciting low frequency vibrations, since laser techniques are exceptionally difficult for frequencies below 500 cm^{-1} .

Finally, excited molecules can be prepared by chemical activation, that is as the products of an exothermic reaction which precedes the reaction actually under investigation.^{8,42} Usually several vibrational levels are significantly populated, increasing the potential amount of information but complicating its analysis. Most experiments of this kind have been carried out in steady-state flow systems, but some of the inherent disadvantages can be removed in time-resolved experiments.⁴³

The net amount of chemical reaction following excitation of a specific vibrational state depends not only on the reaction rate from that state but also on the reaction rate from every state populated by vibrational energy transfer and on all of those rates of transfer. Direct time-resolved measurements following pulsed excitation can help sort out complicated systems. Since vibrational relaxation is often faster than reaction, it is

important to understand the distributions of vibrational populations which evolve as a molecular system relaxes. It is often true that energy is transferred among vibrations before it is coupled into rotation and translation. Equilibration by vibrational-vibrational (V-V) energy transfer λ in a mixture of two harmonic diatomic molecules yields a steady-state in which the lower frequency molecule has a much higher vibrational temperature than the higher frequency one when the translation-rotation temperature is much lower than both.⁴⁴ Inclusion of anharmonicity can lead to grossly non-Boltzmann distributions over sub-sets of vibrational levels in both molecules.⁴⁴ In polyatomic molecules, the most strongly excited mode following V-V equilibration might not be the one pumped by the laser. Detailed experimental studies on CH_3F ²⁷ are the first to explore this question thoroughly. For some molecules, high frequency vibrations are coupled less strongly to low frequency vibrations than the latter are coupled to translation. The asymmetric ν_3 stretch of CO_2 and the ν_1 and ν_3 stretching modes of H_2O are examples.^{29,45}

Any practical use of vibrationally induced chemical reactions clearly requires information about how the reaction rate varies with vibrational quantum number, about the rates and paths of vibrational relaxation, and about the competition between relaxation and reaction.⁴⁶ It will be particularly important to know the V-V equilibrated distributions and rate constants for levels populated in these distributions. Because of these complications, measurements of rate constants versus vibrational level for polyatomics should ideally be made using molecular beams. Unfortunately those systems in which reaction is slow compared with V-V energy transfer will be also the most difficult to study in beams. Nevertheless, advances in laser technology should make future experiments much less difficult than the

pioneering work on $K + HCl$.⁴⁷

2. Highly Excited States of Polyatomics

Two new forms of spectroscopy are beginning to produce new kinds of experimental information about highly vibrationally excited states of polyatomic molecules. As discussed later by Reddy and Berry,¹⁹ high overtones of H-stretching and other vibrations have been studied in the visible using intracavity photoacoustic dye laser spectroscopy. The transitions, which are five to ten orders of magnitude weaker than ir fundamental transitions, depend on anharmonicity for what little oscillator strength they have. Thus 'local' modes⁴⁸ are excited, concentrating the excitation initially in a single bond. Less anharmonic excitations, such as four quanta in one bond and a fifth in a different (but equivalent) bond, are much less intense. By contrast, in ir multiphoton excitation a single frequency nearly resonant with one fundamental normal mode excites a molecule through the most harmonic possible set of states. All equivalent bonds are approximately equally excited. Albrecht⁴⁹ illustrates this comparison with the case of benzene.

These new kinds of spectroscopy allow detailed investigation of vibrational states in the energy range too high for normal mode quantum number assignments and too low for the RRKM approximation.^{50,51} The high overtones of benzene exhibit linewidths larger than the rotational structure width,^{49,52} The CH stretching modes are strongly coupled to a bath of low frequency modes. This coupling has been treated theoretically and comparisons made between the calculated and observed spectra for benzene and deuterobenzenes.⁵³ Although the experiments do not prove that

all modes are involved in the bath it appears quite safe to apply the RRKM approximation for any process whose rate is $< 10^{12} \text{ s}^{-1}$. For a smaller molecule like C_2H_2 , the high overtone spectra show simple fully resolved rotational structure.^{54,55} Its chemical properties can be expected to depend on precisely which combination of vibrational modes is excited, as well as on the total energy of excitation.

Methane appears to be an intermediate case. The overall vibration-rotation band shape for the $\Delta v_{\text{CH}} = 6$ transition is similar to that for the fundamental band.^{55,56} However, the rotational structure does not resolve into lines neatly spaced by twice the rotational constant. At 1 cm^{-1} resolution the band appears almost continuous. Apparently the CH stretch is coupled to other modes covering a range of at least 20 cm^{-1} . At Doppler-limited resolution, however, the band is at least partially resolvable into a sharply structured spectrum with the order of 4 lines per cm^{-1} ,⁵⁶ whereas the total level density at this energy is about 10 per cm^{-1} .⁴⁹ Coupling of the modes in CH_4 is undoubtedly enhanced by the fact that the bending frequencies are roughly half those of the stretches. A laser exciting a single line in this methane spectrum produces a molecule in an eigenstate whose wavefunction must contain contributions from a large mixture of mode excitations. It seems unlikely that the chemical properties will depend strongly on the individual line excited. Thus RRKM theory should work unless the reaction coordinate is, for some reason, not part of the coupled manifold of levels. A clear opportunity of avoiding RRKM behaviour is presented only when the mode responsible for the oscillator strength corresponds to motion along the reaction coordinate, the excitation pulse

coherently excites all of the coupled levels, and the reaction is fast compared with the coupling width. Deviations from RRKM behaviour could therefore only be observed for subpicosecond processes under difficult and rather improbable conditions.

Intracavity acoustooptic spectroscopy allows the nature of the coupling among vibrational modes to be studied as a function of energy for a given molecule. The transition from discrete mode excitation, through coupled but resolvable lines, to contiguous bands can be studied as a function of molecular size and structure. As experiments at higher energies become practical and as theoretical treatments⁵⁰ move from two-oscillator systems into higher dimensions, realistic comparisons of experiment and theory will be possible.

Multiphoton ir absorption can excite a large fraction of a sample to a distribution over very high energy states and to dissociation. For SF_6 and C_2H_4 excited near $10\mu\text{m}$, the multiphoton dissociation (MPD) yield as a function of frequency exhibits a smooth peak shifted slightly to low frequency from the origin of the ordinary absorption spectrum.⁷ The mechanism of absorption through the discrete states is thought to involve a combination of power broadening, rotation^{al} and anharmonic compensation, and 2-, 3- and 4-photon transitions with nearly resonant intermediate states. After the first few absorptions the mode resonant with the laser is strongly coupled to other modes and broadened. Energy thus flows rapidly into other modes and prevents anharmonicity from shifting the absorption out of resonance with the laser. As careful studies of other molecules are carried out, it is becoming clear that a rich variety of multiphoton absorption spectra and dynamics occur in nature. In the following papers

by Ashfeld, Hancock and Ketley⁵⁷ on CH_3NH_2 and by Fuss, Kompa and Tablas⁵⁸ on $(\text{CF}_3)_2\text{CO}$, these subjects are discussed in detail.

Recently it has been shown that, for two very different molecules, the MPD yield spectrum reproduces detailed features in the ordinary ir absorption spectrum. For excitation of $\text{C}_2\text{H}_5\text{Cl}$ near $3.3\mu\text{m}$ a Q-branch 0.4 cm^{-1} wide is reproduced.⁵⁹ Broader resonances matching $v=2$ and $v=3$ levels are also observed, the large CH anharmonicity being compensated by the shift of higher frequency fundamentals into resonance with the laser. The width of the $v=3$ level in both the MPD spectrum and the normal second overtone spectrum is greater than the rotation-vibration structure width. Thus $v=3$ is the lowest quasicontinuous level.

↪ For the very large molecule $\text{UO}_2((\text{CF}_3)_2\text{HC}_3\text{O}_2)_2(\text{C}_4\text{H}_8\text{O})$, i.e., $\text{UO}_2(\text{hfacc})_2\text{THF}$, efficient isotopic^{ally} selective, MPD takes place.¹⁷ The asymmetric UO_2 stretch near $10\mu\text{m}$ exhibits a 4 cm^{-1} bandwidth, which is much greater than the rotational structure width for a molecule of this size. Since there are 126 vibrational modes, this molecule contains about $10,000\text{ cm}^{-1}$ of vibrational energy at room temperature. Thus the molecule very probably starts in the quasicontinuum and may absorb many CO_2 laser photons without any significant shift or broadening of the absorption features. It is further argued¹⁷ that dissociation of the THF ligand occurs before energy is distributed over all the ligands. Consequently, $\text{UO}_2(\text{hfacc})_2\text{THF}$ may be too large for RRKM theory to be applied to the entire molecule. It is certainly interesting and remarkable that, on the timescale of ir excitation (10^{-8} to 10^{-7}s), energy is not effectively distributed throughout the entire molecule.

B. DIRECT BIMOLECULAR REACTIONS

For bimolecular reactions, one seeks detailed rate constants-or detailed cross-sections - connecting defined rovibronic states of reagents and products. In practice, the task of selecting reagent states and simultaneously observing product state distributions is extremely difficult, and few systems have been examined this thoroughly. At the present time, more is known about energy disposal⁶⁰ than about the energy requirements for reaction. However, there are widespread attempts to remedy this deficiency, and it was surprising to find that none of the papers in this Section of the Discussion are concerned with collisional reactions proceeding via direct dynamics. Arguably, this is because a first generation of experiments has been almost completed, whereas examples of the second generation - using, *inter alia*, tunable lasers, molecular beams, and a combination of both - are just beginning to emerge.

1. Reactions of Atoms with Molecules

Reactions of the $A + BC \rightarrow AB + C$ type, where each letter denotes a single atom, have played a central role as our understanding of reaction dynamics has developed. In reviewing how vibrational excitation can promote reactions of this kind, answers should be sought to the following fundamental questions. How does the degree of vibrational enhancement depend on the position and height of the barrier on the potential energy hypersurface? How do the detailed rate constants for reaction from specified vibrational levels of BC vary with the excitation energy (or with v , BC's vibrational quantum number)? Finally, do the answers to these questions depend on factors such as the relative masses of A, B and C?

Despite the relative ease with which at least the $v = 1$ level of a diatomic molecule can be excited, little of the evidence on which answers to these questions are based comes from direct experiments. As was mentioned earlier, a major contribution has been made by deriving information about the detailed rate constants for an endoergic reaction from data on the reverse exoergic reaction and relationships based on the principle of microscopic reversibility.¹² There is especially extensive information, from infrared chemiluminescence experiments, on reactions involving hydrogen halides.⁸ As an example, we shall take the reaction:

The general form of the detailed balance equation is

$$\frac{k(n'|n;T)}{k(n|n';T)} = \left(\frac{Q'}{Q} \right) \left(\frac{g_{n'}}{g_n} \right) \exp(-\Delta E_{n',n}/kT)$$

where the detailed rate constant $k(n'|n;T)$ is for exoergic reaction from partly or fully selected states denoted by n to product states denoted by n' ; Q' and Q are partition functions associated with all those motions, including relative translation, which are not selected in the reagents (but have a thermal distribution at temperature T) and which are not identified in the products; $g_{n'}$ and g_n are the degeneracies of the specified levels; and $\Delta E_{n',n}$ is the difference in energy between levels n' and n . For reaction (1), the overall rate constant, $k(T)$,⁶¹ can be combined with the product state distributions found in infrared chemiluminescence experiments⁶² to yield absolute values of $k(v';T)$. These values can then be converted to those for the detailed rate constants, $k(|v';T)$, for reaction of $\text{I} + \text{HCl}(v')$, using the appropriate form of equation (2). For

$v' < 3$, the values of $k(|v'; T)$ will be very difficult to measure directly. To determine detailed rate constants for a highly endothermic reaction,⁶³ it is best to study the reverse exothermic process and apply detailed balance.

TABLE I

The rapid increase in $k(|v'; T)$ with v' is not itself surprising. To see whether a reaction is selectively promoted by vibrational excitation of HCl, the actual detailed rate constants should be compared with the prior values.¹² For reaction (-1), this is done in table 1. The vibrational surprisals increase as v' is raised from 1 to 4; the vibrational enhancement is selective.

The results for the $I + HCl$ reaction are typical. For strongly endoergic direct reactions, vibrational energy promotes reaction most effectively. Quasiclassical trajectory calculations^{15,3} show that this is because endoergic reactions typically have 'late' barriers. Consequently, vibrational motion in BC is almost parallel to motion along the reaction coordinate in the region of the potential barrier. On the other hand, if the barrier is displaced along the 'approach' coordinate, vibrational motion is roughly perpendicular to the reaction coordinate and translational motion is more effective. This is what is expected for exoergic reactions.

Approaches based on microscopic reversibility are apt to suffer from one serious defect. The experiments on the exoergic reaction usually employ thermal reagents, so the information obtained is restricted to that narrow band of total energies with which systems just surmount the energy barrier. Recognizing this, Polanyi and his colleagues⁶⁴ have used an approximate form of equation (2) which allows the separate effects of reagent

vibration, rotation and translation to be displayed on a single triangular diagram. To explore what happens at higher total energies, excited species must be prepared. This is more easily done in trajectory calculations than in experiments! What the calculations indicate⁶⁵ is that as a reaction becomes increasingly exothermic, that is the energy of ^{the} reagent state exceeds those of accessible product states by a larger amount,⁶² any selectivity diminishes. Thus, trajectory calculations on $I + HCl(v')$, which confirm the finding that $I(v')$ increases monotonically as v' is raised from $v'=0$ to 4, show that $I(v')$ starts to decrease slowly but steadily as v' is increased further.

Reactions of hydrogen halides (HX) also provide some of the best opportunities for direct experiments on vibrationally excited molecules, whether by optical excitation using a chemical laser or by observing the depletion of infrared chemiluminescence from molecules formed in a pre-reaction. The systems, $X + HX(v>0)$ have attracted special attention,^{3,9} but experiments using isotopic substitution⁶⁶ or theoretical calculations⁶⁷ are needed to discover the role of transfer of the 'odd' atom between the two like atoms. Table 2 summarises the results of some experiments where the reactive channel has been clearly identified by observations on the products. The results support the general thesis that vibrational enhancement is most pronounced for endoergic reactions.

Molecular beam experiments provide a particular powerful method of investigating reactions of vibrationally excited molecules. This was first demonstrated⁴⁷ for the $K + HCl$ reaction when it was found that the reaction cross-section for $K + HCl(v=1)$ was approximately 100 times that for $K + HCl(v=0)$ at the same mean collision energy. More recently, Zare and his coworkers⁶⁹ have studied reactions of $HF(v=1)$ in beam + scattering gas

experiments in which the metal fluoride product is observed by laser-induced fluorescence. Not only are any doubts caused by non-reactive relaxation avoided, but the product state distribution is also determined. For the endoergic reactions of HF with Ca and Sr, excitation to $v' = 1$ endows the HF reagent with 47.3 kJ mol^{-1} and the reaction cross-section is increased by at least 10^4 . On the other hand, DF($v=1$) possesses only 34.7 kJ mol^{-1} compared with reaction endoergicities of 43 kJ mol^{-1} for $\text{Ca} + \text{DF}$ and 33 kJ mol^{-1} for $\text{Sr} + \text{DF}$. In neither case could reaction of DF($v'=1$) be observed.

There have been several studies recently of reactions of vibrationally excited H_2 formed either electrically or thermally. The most interesting of these results - and possibly the most controversial - have been obtained for $\text{H} + \text{H}_2(v=1)$ and its isotopic analogues.³⁹ In these unusual experiments, the relaxation of H atoms from a selected hyperfine state ($F=1, m_F=0$) was observed in the storage bulb of an H-atom maser. At 300 K, addition of H_2 accelerated the relaxation only if it had first passed through an oven so that on entering the storage bulb about 0.35% of the molecules were in $v=1$. From their observations, Gordon et al³⁹ deduced a rate constant, for

of $5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, a value almost 10^4 times the thermal rate constant at room temperature.

These elegant experiments raise several interesting questions. The most obvious is why the rate for (3) should be ~ 17 times faster than the relaxation of $\text{H}_2(v=1)$ by H.³⁸ Gordon et al propose that the vibrationally adiabatic reaction is much more likely than either the non-adiabatic reaction yielding $\text{H}_A\text{H}_B(v'=0)$

or non-reactive vibrational energy transfer. This may be so, but classical trajectories on a realistic potential do not predict it,⁷¹ and the same calculations yield a value of k_3 which is (1/60)th of the observed value. Of course, for this reaction especially, one should be suspicious of predictions based on classical mechanics, but the quasiclassical and quantal rate constants for $H + H_2(v=0)$ only differ by a factor of 3.3 at 300 K.⁷² Although the results of three-dimensional quantum scattering calculations on $H + H_2(v=1)$ are tantalisingly out of reach at the present time, new theoretical results should soon emerge¹⁴ to improve our understanding of this celebrated prototype reaction.

A second attractive feature of reactions involving H_2 is that considerable selection of reagent rotation can be obtained by simply using $p\text{-}H_2$. The total $F + p\text{-}H_2$ reaction rate is only 2.5% faster than $F + n\text{-}H_2$ at 175 K, and there is no discernible difference in rate at higher temperatures.⁷³ There is, however a small but significant increase in the degree of HF vibrational excitation when $n\text{-}H_2$ is replaced by $p\text{-}H_2$.⁷⁴

2. More Complex Bimolecular Reactions

Rather little is known about how vibrational excitation in bonds other than the one broken in an atom-exchange reaction affects the rate of such a reaction. For excitation within an attacking radical, i.e., the species to which the atom is transferred, some pointers are provided via arguments based on detailed balance, similar to those described earlier. In direct exoergic reactions of atoms with polyatomic molecules, e.g., $F + RH \rightarrow HF + R$, little of the energy released is channelled into internal modes of the polyatomic fragment, R .⁶⁰ The corollary is that internal excitation of R will not effectively

promote the reverse endoergic reaction.

There are few direct measurements on the reaction rates of vibrationally excited radicals. The only substantial body of data is for $\text{OH}(v>0)$.⁷⁶⁻⁸⁰ The reactions of $\text{OH}(v=1)$ with H_2 and CH_4 are not measurably faster than the thermal reactions. However, $\text{OH}(v=1)$ is reported to react with HBr 9 times more rapidly than $\text{OH}(v=0)$.⁷⁶ This is an interesting result since the normal reaction is itself quite rapid ($k = 5.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and presumably has little or no activation energy. There are also indications that $\text{OH}(v>2)$ reacts with O_3 much faster than the $\text{OH}(v=0)$.⁷⁸⁻⁸⁰ In this case also the reaction has a small activation energy (4 kJ mol^{-1}).⁸¹ Both these results merit further experimental study and, if confirmed, some theoretical explanation.

There are essentially no results on how internal energy in a polyatomic molecule is distributed when such a molecule is formed in an exoergic atom-transfer reaction, such as $\text{AB} + \text{CD} \rightarrow \text{ABC} + \text{D}$. Consequently, arguments based on detailed balance can provide no guidance as to the relative rate enhancements which might be expected when energy is selectively fed into different modes of a polyatomic reagent. As with unimolecular reactions (see below, Section C), mode-selective effects are likely until a level of excitation is reached at which the vibrations couple strongly so that intramolecular energy transfer is rapid. The kinetic behaviour will then depend only on the magnitude of the internal energy and not on its initial location.

In the case of bimolecular reactions, an additional obstacle to mode-selective chemistry is that the excited species will probably undergo many, potentially relaxing, collisions before they react. These are likely to scramble the internal

energy by intramolecular V-V energy transfer as well as decreasing the excitation by transfer to translation and/or modes of the collision partner. It may actually be possible to use this competition to determine the rates of state-selected reactions, by employing a method similar to that used to determine the excitation functions of hot H atoms photochemically generated in an excess of inert 'moderator'.⁸² The possibilities of this method have been demonstrated by isotopically selective promotion of the $\text{Cl} + \text{CH}_3\text{Br} \rightarrow \text{CH}_2\text{Br} + \text{HCl}$ reaction by illumination with a relatively low power cw CO_2 laser.⁸³ Single photons from a CO_2 laser can also be used to excite O_3 to its (001) level. Extensive studies⁸⁴⁻⁸⁶ have been made of the effects of this excitation on the bimolecular reaction of NO with O_3 , which proceeds by two distinct routes:

for which the activation energies are 8.9 and 4.9 kJ mol^{-1} , respectively. The results of the experiments are not easy to interpret due to uncertainties about how the initial state-selective excitation is modified by energy transfer, especially in non-reactive collisions with NO. For reaction (4a), this source of uncertainty has been eliminated⁸⁶ by comparing the fractional increase in the chemiluminescence from NO_2^* with the directly measured fraction of O_3 excited in the CO_2 laser pulse. It was deduced that the rate of reaction (4a) when O_3 is excited to (001) at 298K is 7.6 times faster than the thermal rate, and that this acceleration is increased to a factor of 53 at 155K. An analysis⁸⁶ of these rate enhancements indicates excitation of O_3 to its (001) mode is more effective than is expected statistically, but is only about half as effective as the same

new
para

amount of translational excitation. This is consistent with reaction over a surface with a barrier slightly displaced into the 'approach' region.

Experiments have also been performed with $\text{NO}(v=1)$.⁸⁷ Both reactions occurred appreciably faster (by factors of ~ 4.2 for (4a) and ~ 18 for (4b)). These significant rate enhancements - although it should be remembered that $\text{NO}(v=1)$ contains roughly twice the energy of $\text{O}_3(001)$ - may be connected with the small increase in the NO bond length in these reactions.

C. REACTIONS OF HIGHLY EXCITED MOLECULES

Chemical activation studies of the unimolecular decomposition of highly excited polyatomic molecules suggest that energy randomization among all the vibrational modes of a molecule is usually fast compared with unimolecular reaction. In the exceptional cases where reaction occurs on timescales less than 10^{-12} s, there is good evidence for less than complete randomization. Traditional gas-phase studies of unimolecular reactions have been reviewed by Tardy and Rabinovitch.⁵ In the following paper, Lee and his collaborators⁸⁸ discuss the results of applying chemical activation methods in molecular beam experiments. These results are compared with those from multiphoton dissociation. It is argued that, in MPD, absorption of infrared photons proceeds only until the decomposition rate becomes comparable to the photon absorption rate (typically, $< 10^9 \text{ s}^{-1}$) and that intramolecular energy randomization is orders-of-magnitude faster than either. The molecular beam results obtained to date have all been consistent with this idea.⁸⁹ Modest shifts between reaction channels with similar thresholds as the laser power is altered are expected within the RRKM framework.⁹⁰ Reports of non-RRKM behaviour in gas cell MPD experiments are not fully convincing.⁸⁹

The best opportunities for selective photochemistry and the severest tests of RRKM theory may lie in direct single photon excitation of high vibrational overtone levels.¹⁹ The total energy of the molecule is defined and may be varied over a wide range. It may be possible to reach high energy reaction channels even if the energy is rapidly randomized. The absorption oscillator strength is contributed solely by excitation of a single bond. If the entire band is coherently excited, as by a pulse of duration $(2\pi\Delta\nu)^{-1}$, and if the reaction coordinate essentially corresponds to that of the bond excited, truly mode-selective chemistry should be observed. If only a portion of the band is excited, as with a narrow band cw laser, then a mixed state is prepared in which the energy is at least partially randomized from the beginning. In larger molecules, this coupling is likely to involve primarily vibrations which are close in space and frequency to the pumped mode. Thus, by analogy to the Rynbrandt and Rabinovitch experiments,⁹¹ sufficiently high excitation in one part of a molecule may cause reaction to occur there in preference to a ^{nearly} equivalent channel elsewhere in the molecule. The excitation of non-equivalent C-H modes, or of normal C-H and ¹³C-H stretches, can indicate the relative rates of energy migration and of various unimolecular reaction channels.

In some molecules, electronic excitation followed by rapid internal conversion provides a means of producing molecules in their electronic ground state with high narrowly defined amounts of internal energy. Rare gas halide lasers provide a variety of photon²⁸ energies for extending the experiments described below by Troe and his coworkers.⁹² However, the range of molecules which can be excited in this way is probably limited. Furthermore, although the excitation frequency controls

the energy supplied, the initial distribution of that energy is determined by the matrix elements for the internal conversion: these cannot be influenced, or probably known, by the experimenter.

Reddy and Berry¹⁹ report modest discrepancies between the rates for isomerisation of CH_3NC calculated using RRKM theory and those they deduce following single photon overtone ^{fairly} excitation. Since this is a small molecule and since energy transfer into the low frequency CNC bend is presumably required before isomerisation can occur, energy randomization might be expected to be complete. Reddy and Berry suggest several reasons for the discrepancy which they consider more probable than non-randomization of energy. Experiments on systems more likely to exhibit non-RRKM behaviour will surely be carried out in the near future. Interestingly, mode selectivity can be enhanced at high pressures⁹¹ or in condensed phases.⁹³ This occurs when chemical reaction of the initially prepared molecules is competitive with intramolecular energy randomization. Those molecules in which energy becomes randomized react more slowly and can therefore be relaxed by intermolecular energy transfer. Consequently, the selectivity for the product of the reaction occurring before energy randomization can be greatly enhanced although the quantum yield may be less than at low pressure.

The non-RRKM behaviour discussed in Section A for $\text{UO}_2(\text{hfacac})_2$ THF may perhaps be analyzed in terms of a model in which the bulk of the molecule provides a heat bath around the reaction site.¹⁷ Since high dissociation quantum yields are reported, this heat bath would have to be weakly coupled on the timescale of energy input. The hypothesis is intriguing even if difficult to accept. This work certainly suggests interesting

types of molecule for study, both with multiphoton excitation and with single photon excitation of high overtones.

Even if rapid energy randomization should prove to rule out truly mode-selective chemistry, vibrational photochemistry should still be a valuable synthetic method. Different product distributions can be selected by varying the excitation energy. Even where only the lowest energy reaction channel is important, there should often be advantages to optically, rather than thermally, driven syntheses. In vibrational photochemistry, the synthetic advantages of electronic photochemistry become available for reactions over the ground state potential surface.

D. REACTIONS IN CONDENSED PHASES

Studies of vibrational excitation, relaxation and photochemistry have only begun in the past few years. Relaxation times range from picoseconds to seconds.^{94,95} Energy transfer mechanisms in polyatomics are now being elucidated, but there have been very few reports of vibrationally driven chemical reactions.^{93,96-98}

The most detailed measurements on relaxation and chemistry have been carried out on molecules isolated in inert matrices at cryogenic temperatures. The vibrational lifetimes of well-isolated diatomic molecules are often equal to the radiative lifetimes.⁹⁵ The direct transfer of two or three thousand cm^{-1} of vibrational energy to lattice phonons is very slow. With diatomic hydrides, relaxation times range from microseconds to milliseconds, as transfer of vibrational energy to between 10 and 15 rotational quanta can be followed by rapid rotation-phonon coupling.^{95,99} Vibration-vibration transfer within the modes of a polyatomic or from one molecule to another which is nearby in the matrix frequently occurs in less than microseconds.⁹⁵

This could seriously limit the promotion of bimolecular reactions in which one reactant has low vibrational frequencies. Energy transfer involving simple changes in vibrational quantum number and a modest number of phonons occurs rapidly. For example, SF_6 ¹⁰⁰ apparently absorbs and relaxes sevca. 1 times during a 100 ns CO_2 laser pulse. Rapid relaxation will seriously limit multiphoton excitation and dissociation in condensed phases.

There are two firmly established examples of vibrational photochemistry in matrices. Some years ago, the cis-trans isomerization of HONO was shown to be induced when the OH vibration was excited using radiation at 3 μm from an ordinary Nernst glower.¹⁰¹ More recently, the interconversion of axial and equatorial CO's in partially ^{13}C labelled $\text{Fe}(\text{CO})_4$ has been induced by single photon excitation of the CO groups using lines from a cw CO laser.⁹⁶ There are preliminary reports of other reactions: $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ appears especially interesting,^{98,102} in view of the extensive work carried out on this reaction in the gas-phase. However, at this time, it is by no means clear how general vibrational photochemistry in matrices will be. Clearly, rapid intramolecular energy transfer and transfer of low frequency vibrational quanta to the matrix phonon bath will impose severe limits, but the range of possibilities might be increased by exciting overtone and combination bands with higher energy photons.

Cryogenic liquids possess many of the same advantages as matrices for vibrational photochemistry, although the range of solutes and solute concentrations is more limited. Absorption spectra are often sharp and vibrational relaxation can be slow. Reported relaxation times vary from 60 s for liquid N_2 ¹⁰³ to 27 ps

for SF_6 in liquid O_2 .¹⁰⁴ The extrapolation of gas-phase data to the densities and temperature of liquids or solution can provide useful estimates of relaxation times. As for the matrix isolated samples, MPD of SF_6 is defeated by rapid relaxation.¹⁰⁴ A very slow thermal reaction of O_3 dilute in liquid NO appears to be strongly accelerated by excitation of the O_3 with a cw CO_2 laser.¹⁰²

Vibrational relaxation times in liquids at room temperature are usually measured in picoseconds. By analogy with gas-phase observations, it is clear that relaxation will be particularly fast in aqueous solutions or other hydrogen bonded media. Nevertheless, the ionization of water, for which $\Delta H = 57 \text{ kJ mol}^{-1}$, can be induced by excitation of overtone and combination bands,^{18,95} the quantum yields rising from about 10^{-9} to 10^{-5} as the photon energy is increased from 90 to 170 kJ mol^{-1} . Despite these extremely small values, the transient increase in ionization is substantially greater than thermal. Because the excitation is very rapidly dissipated to the solvent, quantum yields for such processes must be very small. However, it is quite likely that intramolecular energy transfer is limited, so that any reaction which does occur could be highly mode- or site-selective. This suggests the possibility of interesting vibrational photochemistry in solutions. Both single photon absorption and Raman pumping could be practical. Selective chemical reactions of interest to inorganic and organic chemists - and perhaps even biochemists - might be possible. The ability to excite specific free base molecules vibrationally has already been demonstrated by picosecond infrared plus ultraviolet two-step dissociation.¹⁰⁵ It is difficult to imagine that vibrational excitation could be transferred to effect a chemical reaction

more than a few bond distances away from the site of absorption within a DNA molecule.

Several years ago, wavelength selective photochemical reactions between NH_3 and H_2O on silica gel were observed.¹⁰⁶ Apart from some preliminary results on the influence of CO_2 laser radiation on the decomposition of HCOOH on platinum,¹⁰⁷ there have been no other studies of vibrational photochemistry or relaxation of molecules adsorbed on surfaces. Only questions and speculation can be put forward. Can heterogeneous reactions be vibrationally assisted by laser radiation? Can catalyst poisons be efficiently and selectively desorbed or photoreacted using infrared lasers? Are chemisorbed species so strongly coupled to a surface that energy transfer to the lattice occurs before any chemistry is possible? In a recent study¹⁰⁸ of XeF_2 reacting with a silicon surface, vibrationally excited products were observed on the surface. Given the interesting fundamental problems and the potential practical applications, the kinetic behaviour of vibrationally excited molecules adsorbed on surfaces certainly merits further examination.

CONCLUSION

Assertions as to the future importance of laser-induced chemistry are widespread, but somewhat suspect, since they issue, in the main, from interested parties. However, it is worth pointing out to the skeptical that ^{13}C - and perhaps ^{235}U - is now prepared on a pilot plant scale by infrared multiphoton dissociation.¹⁰⁹ In 1973, this prospect would have appeared fantastic.

Nevertheless, many fundamental and practical questions must be answered before the full practical impact of vibrational

photochemistry can be properly assessed. Only a few parts of the subject have reached sufficient maturity for generalisations to be made with any degree of confidence. What can be positively asserted is that the tools now exist for tackling many of the other fundamental problems which we have referred to. In addition, those essential ingredients for scientific progress: intellectual curiosity, potential practical applications, and experimental challenge, all exist in full measure. The next five or six years will undoubtedly be a period of intense research activity. By the time the Faraday Division of the Chemical Society next call a General Discussion at which the reactions of vibrationally excited species are a central issue, it is certain that our review will appear more than a little dated.

We are indebted to a number of people who have discussed their work with us, in several cases prior to publication. They include: M.J. Berry, M.O. Bulanin, G. Flynn, D.M. Goodall, B.R. Henry, A. Kaldor, Y.T. Lee, J.C. Polanyi, J.J. Turner and J. Wolfrum. C.B.M. thanks the Division of Basic Energy Sciences U.S. Department of Energy, under contract No. W-7405-Eng-48, and the National Science Foundation for research support. I.W.M.S. thanks the U.S.A.F. Office of Scientific Research (grant no. 77-3240) and the Science Research Council for support.

TABLE 1. Detailed Rate Constants and Surprisals for $I + HCl(v') \rightarrow HI + Cl$

v'	$\frac{\Delta E_{v=0,v'}}{kJ\ mol^{-1}}$	$\frac{k(v';T)}{cm^3\ molecule^{-1}\ s^{-1}}$	$\frac{k^0(v';T)}{cm^3\ molecule^{-1}\ s^{-1}}$	$I(v') = -\frac{\ln k(v';T)}{\ln k^0(v';T)}$
4	1.3	2.2×10^{-11}	4.7×10^{-13}	3.8
3	32.2	1.2×10^{-16}	2.0×10^{-17}	1.8
2	64.3	1.1×10^{-22}	1.2×10^{-22}	-0.1
1	97.5	1.1×10^{-28}	3.1×10^{-28}	-1.0
0	132.1	2.0×10^{-35}	4.8×10^{-34}	-3.2

TABLE 2. - Examples of Vibrational Rate Enhancements for Atom-Transfer Reactions

Reaction	$\frac{\Delta E_0}{\text{kJ mol}^{-1}}$	$\frac{E_{\text{act}}}{\text{kJ mol}^{-1}}$	$\frac{k(v=1;T)}{k(v=0;T)}$ or $\frac{S(v=1)}{S(v=0)}^a$	Ref.
$\text{H} + \text{F}_2(\text{v}) \rightarrow \text{HF} + \text{F}$	-410	~ 9	~ 1	37
$\text{H} + \text{Cl}_2(\text{v}) \rightarrow \text{HCl} + \text{Cl}$	-188.5	4.9	≤ 1.8	37
$\text{F} + \text{HCl}(\text{v}) \rightarrow \text{HF} + \text{Cl}$	-136	~ 4	3.7	37
$\text{H} + \text{H}_2(\text{v}) \rightarrow \text{H}_2 + \text{H}$	0	41	$\sim 10^4$	39
$\text{O} + \text{HCl}(\text{v}) \rightarrow \text{OH} + \text{Cl}$	3.7	25	150-800	10,11,70
$\text{K} + \text{HCl}(\text{v}) \rightarrow \text{KCl} + \text{H}$	6	~ 9	130	47
$\text{Sr} + \text{HF}(\text{v}) \rightarrow \text{SrF} + \text{H}$	27	≥ 27	$> 10^4$	69
$\text{Ca} + \text{HF}(\text{v}) \rightarrow \text{CaF} + \text{H}$	36	≥ 36	$> 10^4$	69
$\text{Br} + \text{HCl}(\text{v}=2) \rightarrow \text{HBr} + \text{Cl}$	65.7	66	$\frac{k(v=2;T)}{k(v=0;T)} \sim 6 \times 10^{10}$	68

^a $S(|v)$ denotes the total reaction cross-section from the level v

REFERENCES

1. There have been very few kinetic studies of molecules in selected rotational levels, largely because the competing process of collisional relaxation is usually so efficient. Although the effects of reagent rotation are mentioned in Section B, our review is almost entirely concerned with the kinetics of vibrationally excited molecules.
2. M.J.Berry, Ann.Rev.Phys.Chem., 1975, 26 259
3. I.W.M.Smith, Physical Chemistry of Fast Reactions. II: Reaction Dynamics, ed. I.W.M.Smith (Plenum, New York, 1979), Chap. 1.
4. J. Wolfrum, Ber.Bunsenges.phys.Chem., 1977, 81, 114.
5. D.C.Tardy and B.S.Rabinovitch, Chem.Rev., 1977, 77, 369
6. V.S.Letokhov and C.B.Moore, Chemical and Biochemical Applications of Lasers, vol.3, ed. C.B.Moore (Academic, New York, 1978 chap. 1.
7. R.V.Ambartzumian and V.S.Letokhov, chap. 2 in ref. 6.
8. B.A.Blackwell, J.C.Polanyi and J.J.Sloan, Chem.Phys., 1977, 24, 25; Chem.Phys., 1978, 30, 299; and references therein.
9. I.W.M.Smith, Gas Kinetics and Energy Transfer, ed. P.G.Ashmore and R.J.Donovan (Specialist Periodical Reports, Chem.Soc., London, 1977) vol. 2, chap. 1.
10. R.G.Macdonald and C.B.Moore, J.Chem.Phys., 1978, 68, 513.
11. J.E.Butler, J.W.Hudgens, M.C.Lin and G.K.Smith, Chem.Phys.Letters, 1978, 58, 216.
12. H.Kaplan, R.D.Levine and J.Manz, Chem.Phys., 1976, 12, 447.
13. An up-to-date list of papers describing quasiclassical trajectory calculations on the dynamics of collision involving vibrationally excited molecules and potentially reactive atoms can be found in ref.3.
14. R.E.Wyatt, State-to-State Chemistry, ed. P.R.Brooks and E.F.Hayes (A.C.S.Symposium Series, no. 56, 1977) p. 185 and references therein.
15. J.C.Polanyi and J.L.Schreiber, Physical Chemistry - An Advanced Treatise, Vol.VIA, Kinetics of Gas Reactions, ed.H.Eyring, W.Jost and D.Henderson (Academic Press, New York, 1974) chap.6.
16. Aa.S.Sudbø, P.A.Schulz, E.R.Grant, Y.R.Shen and Y.T.Lee, J.Chem.Phys., 1979, 70, 912.
17. A.Kaldor, R.B.Hall, D.M.Cox, J.A.Horsley, P.Rabinowitz, and G.M.Kramer, J.Amer.Chem.Soc., in press
18. B.Knight, D.M.Goodall and R.C.Greenhow, J.C.S. Faraday II, in press
19. K.V.Reddy and M.J.Berry, following paper no. 10 in Faraday Discussi
67.

20. J.B.Marling and I.P.Herman, Appl.Phys.Letters, in press
21. M.Drouin, M.Gauthier, R.Pilon, P.A.Hackett and C.Willis, Chem.Phys.Letters. 1978, 60, 16.
22. J.J.Tier and C.Wittig, Appl.Phys.Letters, 1978, 32, 236.
23. S.M.Freund and J.L.Lyman, Chem.Phys.Letters, 1978, 32, 236.
24. R.V.Ambartzumian, Yu.A.Gurokhov, V.S.Letokhov and G.N.Makarov, J.E.T.P.Letters, 1976, 22, 43.
25. S.S.Miller, D.D. DeFord, T.J.Marks, and E.Weitz, J.Amer.Chem.Soc., 1979, 101, 1036.
26. A. Kaldor et al, Science, in press
27. I.Shamah and G.Flynn, J.Chem.Phys., 1978, 69, 2474.
28. E.R.Lory, S.H.Bauer and T.J.Manuccia, J.Phys.Chem., 1975, 79, 545.
29. E.Weitz and G.Flynn, Ann.Rev.Phys.Chem., 1974, 25, 275.
30. D.J.Douglas and C.B.Moore, Laser Induced Processes in Molecules, ed. K.L.Kompa and S.D.Smith (Springer-Verlag, Berlin, 1979) 000; Chem.Phys.Letters, 1978, 57, 485.
31. M.A.A.Clyne and I.S.McDermid, following paper no. 17 in Faraday Discussion 67.
32. S.J.Harris, J.Amer.Chem.Soc., 1977, 99, 5798.
33. (a) D.H.Jaffer and I.W.M.Smith, following paper no. 12 in Faraday Discussion 67; (b) J.Brooke Koffaul, R.W.Field, D.R.Coyer and S.K.Leone, Laser Spectroscopy, vol.3, (Springer-Verlag, Berlin, 1977) p.382.
34. J.J.Ewing, Chemical and Biochemical Applications of Lasers, vol. 2, ed. C.B.Moore (Academic, New York, 1977) chap. 6.
35. M.M.Audibert, R.Vilaseca, J.Lukasik and J.Ducuing, Chem.Phys.Letters, 1976, 37, 408.
36. W.Keifer and J.H.Bernstein, J.Mol.Spectr., 1972, 43, 366.
37. A.M.G.Ding, L.J.Kirsch, D.S.Perry, J.C.Polanyi and J.L.Schreiber, Faraday Discuss.Chem.Soc., 1973, 55, 252; J.C.Polanyi, J.J.Sloan. and J.Wanner, Chem.Phys., 1976, 13, 1.
38. R.F.Heidner and J.V.V.Kasper, Chem.Phys.Letters, 1972, 15, 179.
39. E.B.Gordon, B.I.Ivanov, A.B.Perminov, V.E.Balalaev, A.N.Ponomarev and V.V.Filatov, Chem.Phys.Letters, 1978, 58, 425.
40. G.C.Light, J.Chem.Phys., 1978, 68, 2831.
41. R.Zellner^t, J.Phys.Chem., 1979, 83, 18.

42. J.E.Spencer and G.P.Glass, Int.J.Chem.Kinetics, 1977, 9,97, and 111.
43. S.L. Baughcum, H. Hofmann, S.R. Leone and D.J. Nesbitt, following paper no. 15 in Faraday Discussion 67; D.J. Wrigley and I.W.M. Smith, unpublished results.
44. C.E.Tremor, J.W.Rich and R.G.Rehm, J.Chem.Phys., 1968, 48, 1798.
45. J.Finzi, F.E.Hovis, V.N.Panfilov, P.Hess and C.B.Moore, J.Chem.Phys., 1977, 67, 4053.
46. K.Bergmann, S.R.Leone, R.G.Macdonald and C.B.Moore, Israeli J.Chem., 1975, 14, 105.
47. T.J.Odiorne, P.R.Brooks and J.V.V.Kasper, J.Chem.Phys., 1971, 55, 1980.
48. B.R.Henry, Accounts Chem.Res., 1977, 10, 207.
49. A.C.Albrecht, Advances in Laser Chemistry, ed. A.H.Zewail. (Springer-Verlag, Berlin, 1978) p.235.
50. S.A.Rice in ref. 49, p.2.
51. R.A.Marcus, Faraday Discuss.Chem.Soc., 1973, 55, 9.
52. K.V.Reddy, R.G.Bray and M.J.Berry in ref. 49, p.48.
53. D.F.Heller and S. Mukamel, J. Chem. Phys., 1979, 70, 463.
54. M.J.Berry, R.G.Bray and K.V.Reddy, unpublished results.
55. J.S.Wong and C.B.Moore, unpublished results.
56. G.Stella, J.Gelfand and W.H.Smith, Chem.Phys.Letters, 1976, 39, 146.
57. M.N.R.Ashfold, G.Hancock and G.Ketley, following paper no.11 in Faraday Discussion 67.
58. W.Fuss, K.L.Kompa and F.M.G.Tablas, following paper no.9 in Faraday Discussion 67
59. H.-L.Dai, A.H.Kung and C.B.Moore, Phys.Rev.Letters, 1979, in press.
60. D.W.Setser in ref.2, chap.2.
61. K. Bergmann and C.B.Moore, J.Chem.Phys., 1975, 63, 643.
62. D.H.Maylotte, J.C.Polanyi and K.B.Woodall, J.Chem.Phys., 1972, 57, 1547.
63. Here the terms 'endothermicity' and 'exothermicity' refer not to the sign of the thermodynamic quantity ΔH^0 but to whether the state-specified reaction yields less or more translational energy in the products than was contained in the reagents.

References cont.

64. K.G. Anlauf, D.H. Maylotte, J.C. Polanyi and R.B. Bernstein, J.Chem.Phys., 1969, 51, 5716.
65. (a) E. Pollak and R.D. Levine, Chem.Phys.Letters, 1976, 39, 199; (b) E. Pollak, Chem.Phys., 1977, 22, 151.
66. (a) F.E. Bartoszek, D.M. Manos and J.C. Polanyi, J.Chem.Phys., 1978, 69, 933; (b) M. Kneba and J. Wolfrum, J.Phys.Chem., 1979, 83, 69.
67. C.F. Bender, B.J. Garrison and H.F. Schaefer III, J.Chem.Phys., 1975, 62, 1188.
68. (a) S.R. Leone, R.G. Macdonald and C.B. Moore, J.Chem.Phys., 1975, 63, 4735; (b) D. Arnoldi, K. Kaufman and J. Wolfrum, Phys.Rev.Letters, 1975, 34, 1597.
69. (a) J.G. Pruett and R.N. Zare, J.Chem.Phys., 1976, 64, 1774; (b) Z. Kurny and R.N. Zare, J.Chem.Phys., 1978, 68, 3360; (c) Z. Kurny, R.C. Estler and R.N. Zare, J.Chem.Phys., 1978, 69, 5199.
70. M. Kneba, U. Wellhausen and J. Wolfrum, Proc. 17th Symp. (Int.) Combust., Leeds, 1978.
71. I.W.M. Smith, Chem.Phys.Letters, 1977, 47, 219.
72. G.C. Schatz and A. Kuppermann, J.Chem.Phys., 1976, 65, 4668.
73. F.S. Klein and A. Persky, J.Chem.Phys., 1974, 61, 2472.
74. (a) R.D. Coombe and G.C. Pimentel, J.Chem.Phys., 1973, 59, 1525; (b) D.J. Douglas and J.C. Polanyi, Chem.Phys., 1976, 16, 1.
75. We consider only atom-transfer reactions here. Ref. 2 includes a discussion of four-centre reactions.
76. J.E. Spencer and G.P. Glass, Int.J.Chem.Kinetics, 1977, 9, 97 and 111.
77. J.E. Spencer, H. Endo and G.P. Glass, Proc. 16th Symp. (Int.) Combust. (The Combustion Institute, 1977).
78. A.E. Potter, Jr., R.N. Coltharp and S.D. Worley, J. Chem. Phys., 1971, 54, 992.
79. R.N. Coltharp, S.D. Worley and A.E. Potter, Jr., Appl. Optics, 1971, 10, 1786.
80. G.E. Streit and H.S. Johnston, J. Chem. Phys., 1976, 64, 95.
81. Reaction Rate and Photochemical Data for Atmospheric Chemistry - 1977 ed. R.F. Hampson and D. Garvin (N.B.S. Special Publication 513, 1977).
82. R.G. Gann, W.M. Ollison and J. Dubrin, J.Chem.Phys., 1971, 54, 2304.
83. T.J. Manuella and M.D. Clark, J.Chem.Phys., 1978, 68, 2271.
84. (a) R.J. Gordon and M.C. Lin, Chem.Phys.Letters, 1975, 22, 262; (b) R.J. Gordon and M.C. Lin, J.Chem.Phys., 1976, 64, 1058.

References cont.

85. (a) M.J.Kurylo, W.Braun, A.Kaldor, S.M.Freund and R.P.Wayne, J.Photochem., 1974, 3, 71; (b) W.Braun, M.J.Kurylo, A.Kaldor and R.P.Wayne, J.Chem.Phys., 1974, 61, 46; (c) M.J.Kurylo, W.Braun, C.M.Xuan and A.Kaldor, J.Chem.Phys., 1975, 62, 2065 and 63, 1042.
6. J.Mey, E.Bar-Ziv and R.J.Gordon, J.Chem.Phys., 1977, 66, 5439.
7. S.M.Freund and J.C.Stephenson, Chem.Phys.Letters, 1976, 41, 157.
8. R.J.Russ, M.J.Coggiola and Y.T.Lee, following paper no.6 in Faraday Discussion 67.
89. P.A.Schulz, Aa.S.Sudbø, D.J.Krajnovich, H.S.Kwok, Y.R.Shen and Y.T.Lee, Ann.Rev.Phys.Chem., 1979, 30, in press.
90. D.J.Krajnovich, A.Giardini-Guidoni, Aa.S.Sudbø, P.A.Schulz, Y.R.Shen and Y.T.Lee in Laser-Induced Processes in Molecules, ed. K.L.Kompa and S.D.Smith (Springer-Verlag, Berlin, 1979) p.176.
91. J.D.Rynbrandt and B.S.Rabinovitch, J.Chem.Phys., 1971, 54, 2275.
92. H.Hippler, K.Luther and J.Troc, following paper no.8 in Faraday Discussion 67.
93. D.M.Coodall and M.C.Greenhow, Chem.Phys.Letters, 1971, 9, 583.
94. W.Kaiser and A.Laubereau in Chemical and Biochemical Applications of Lasers, vol. 2, ed. C.B.Moore (Academic, New York, 1979) p.87.
95. F.Legay in ref. 94, p.43.
96. (a) B.Davies, A.McNeish, M.Poliakoff and J.J.Turner, J.Am.Chem.Soc., 1977, 99, 7573; (b) B.Davies, A.McNeish, M.Poliakoff, M.Tranquille and J.J.Turner, Chem.Phys.Letters, 1977, 52, 477.
97. E.Catalano and R.E.Barletta, J.Chem.Phys., 1977, 66, 4706.
98. H.Frei, L.Fredin and G.C.Pimentel, Abstracts of Am.Chem.Soc. Meeting, Honolulu, April, 1979
99. J.M.Wiesenfeld and C.B.Moore, J.Chem.Phys., 1979, 70, 930.
100. B.Davies, M.Poliakoff, K.P.Smith and J.J.Turner, Chem.Phys.Letters, 1978, 58, 28.
101. (a) J.D.Baldeschwieler and G.C.Pimentel, J.Chem.Phys., 1960, 33, 1009; (b) R.T.Hall and G.C.Pimentel, J.Chem.Phys., 1963, 38, 1889.
102. M.O.Bulanin, private communication.
103. S.R.J.Brueck and R.M.Osgood, Jr., J.Chem.Phys., 1978, 68, 4941.
104. S.R.J.Brueck, T.M.Deutsch and R.M.Osgood, Jr., Chem.Phys.Letters, 1979, 60, 242
105. P.G.Kryukov, V.S.Letokhov, D.N.Nikogosyan, A.V.Porodarkin, E.I.Budowsky and N.A.Simukova, Chem.Phys.Letters, 1979, 61, 375.

References cont.

106. M.S.Djidjev, R.V.Khokhlov, A.V.Kiselov, V.I.Lygin, V.A.Namoit, A.I.Osipov, V.I.Panchenko and B.I.Provotorov in Tunable Lasers and Applications, ed. A.Mooradian, T.Jaeger and P.Stokseih (Springer-Verlag, Berlin,1976).
107. A.Baronavski, J.E.Butler, J.W.Hudgens, M.C.Lin, J.R.McDonald and M.E.Umstead, in ref.49, p.62; M.E. Umstead and M.C. Lin, J. Phys. Chem., 1978, 82, 2047.
108. T.J.Chuang, Phys.Rev.Letters, 1979, 42, 815.
109. V.N.Bagrashvili, V.S.Doljikov, V.S.Letokhov and E.A.Ryabov, Proc. 2nd Intl.Symp. on Gas-Flow and Chemical Lasers, Brussels, September, 1978.