TILDEN LECTURE*
The Collision Dynamics of Vibrationally Excited Molecules

By Ian W. M. Smith
DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY CHEMICAL
LABORATORIES, LENSFIELD ROAD, CAMBRIDGE CB2 1EP

1 Introduction

Traditionally, chemical kinetics has been concerned with the rates of chemical change at defined temperatures. There is, however, at least one class of chemical reaction where the distribution of reagents over states can become markedly non-Boltzmann, even under quite ordinary conditions. At low total pressures, the states above and close to the threshold for unimolecular reaction become depleted as collisional redistribution of molecules into these levels fails to keep pace with their unimolecular rate of reaction. For bimolecular reactions, such effects are thought to be absent. At least for processes involving simple species at low and moderate temperatures, the reagents are predominantly in their lowest vibronic states. The variation of rate constant with temperature is generally believed to reflect the change of reaction cross-section with collision energy (and, possibly, rotational energy) and energy redistribution will occur more rapidly than reaction.[1]

Unfortunately, the dynamical details of reactive collisions are separated from the thermal rate constant by many 'layers of averaging'. One result of this is that it is essentially impossible to recover the form of the excitation function (*i.e.* how the reaction cross-section varies with collision energy) by measuring how the rate constant depends upon temperature. The situation in regard to collisional transfer of vibrational energy is rather similar. Early experimental methods, using ultrasonic absorption or dispersion, the photoacoustic effect, and shock tubes, probed bulk relaxation: that is, the overall transfer of energy between vibrational (V) and translational, rotational (T,R) degrees of freedom. It soon became apparent that bulk relaxation is virtually always controlled by the rate at which molecules are transferred between their two lowest levels.[2] At the other extreme, the rates of unimolecular dissociations (or the reverse association reactions) and their dependence on 'third-body' gas provide some measure of energy transfer rates at internal energies at the dissociation limit. Measurements on the transfer of molecules between levels of intermediate excitation are rare.

Undoubtedly optical excitation provides the best, most controlled technique for

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[1] I. W. M. Smith, 'Kinetics and Dynamics of Elementary Gas Reactions', Butterworths, London, 1980.
[2] J. D. Lambert, 'Vibrational and Rotational Relaxation in Gases', Clarendon, Oxford, 1977; J. T. Yardley, 'Introduction to Molecular Energy Transfer', Academic, New York, 1980.

perturbing a Boltzmann distribution over molecular states. We are not concerned here with photochemical dissociation but rather with the promotion of a molecular species to a specific rovibronic state as the result of irradiation of the species with a frequency corresponding to one of its discrete absorptions. Where electronic excitation is involved, laser sources are not essential—*electronic* photochemistry has a long history—although the power, tunability, monochromaticity, coherence, short duration, and polarization of lasers have enormously extended the range and potency of such experiments.[3]

Studies in *vibrational* photochemistry, however, rely on laser sources. The great power of some infrared sources—notably the CO_2 laser—has opened up an entirely new field of research: namely, that of the phenomenon of infrared multi-photon absorption and the isotopically selective dissociation that this process can bring about.[4] I shall not deal at all with this topic: partly because my group have not been involved in this work and partly because the multiphoton excitation process is not state-selective; after the laser pulse, molecules are left in a distribution over many highly energized states.

Absorption of single photons from a laser can lead to the immediate overpopulation of single rovibrational quantum states in small molecules. In principle, the evolution in time of the populations of the initially excited state and of neighbouring states can be observed spectroscopically, and state-specific rate constants for energy transfer and reaction can be deduced, if the number of levels involved is small and the number of independent observations sufficiently large.[5] In practice, mapping the pathways for relaxation and reactive loss at the state-to-state level proves very difficult, and indirect reasoning has frequently to be used to explain the limited number of observations that are possible. In particular, the role of molecular rotations in reactions and in vibrational energy-transfer processes is difficult to assess—at least, from bulk experiments like our own, where rotational relaxation is rapid. Experiments that combine molecular beam and laser excitation or detection techniques can provide information at this level of detail.

Two beautiful experiments that have been reported recently illustrate what can be done. Altkorn *et al.*[6] have used one laser (an optical parametric oscillator) to excite HF molecules to specific levels $v = 1$, J and a second laser to detect the $v'J'$ distribution of the CaF molecules that are formed in the reaction

$$Ca + HF(v = 1,J) \longrightarrow CaF(v',J) + H \qquad (1)$$
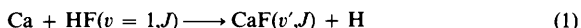
under single collision conditions. In a different experiment,[7] beams of He and I_2 collide with relatively high and variable collision energy and the final states of I_2 are

[3] M. A. A. Clyne and I. S. McDermid in 'Dynamics of the Excited State', ed. K. P. Lawley, *Adv. Chem. Phys.*, 1982, **50**, 1.
[4] D. S. King in 'Dynamics of the Excited State', ed. K. P. Lawley, *Adv. Chem. Phys.*, 1982, **50**, 105.
[5] C. B. Moore and I. W. M. Smith, *Faraday Discuss. Chem. Soc.*. 1979, **67**, 146.
[6] R. Altkorn, F. E. Bartoszek, J. Dehaven, G. Hancock, D. S. Perry, and R. N. Zare, *Chem. Phys. Lett.*, 1983, **98**, 212.
[7] G. Hall, K. Liu, M. J. McAuliffe, C. F. Giese, and W. R. Gentry, *J. Chem. Phys.*, 1983, **78**, 5260.

probed by laser-induced fluorescence. This allows one to extract cross-sections for transfer between specified v,J states at defined collision energies.

The observed result of any collection of molecular collisions is ultimately a reflection of the forces which act between the atoms during the collisions. Physical chemists prefer to think in terms of how the potential energy—the overall electronic binding energy—varies with the nuclear configuration.[1] In even the simplest system of interest—a total of three atoms labelled A, B, and C—the potential energy (V) depends on three spatial co-ordinates (frequently chosen as the internuclear separations r_{AB}, r_{BC}, and r_{CA}) and $V(r_{AB}, r_{BC}, r_{CA})$ is properly referred to as a *potential energy hypersurface*—though this rather unwieldy term is often shortened to potential energy surface.

It is useful, not just within the context of this lecture, to distinguish three broad types of potential energy surface. The first arises when the two colliding species both have closed electronic shells. (I shall call such species *molecules*, even when they are monatomic, to distinguish them from *radicals*, which have one or more unpaired electrons.) Collisions between Ar atoms and N_2 atoms in their singlet ground states serve as an example. The interaction gives rise to only one singlet potential energy surface. There is only weak, Van der Waals', attraction ($\varepsilon/k \simeq 106$ K), and the form of the potential reflects the strong bond between the N atoms, and the strong repulsion between N_2 and Ar as their electron clouds overlap. The potential energy surface in Figure 1 represents this case with the atoms collinear.
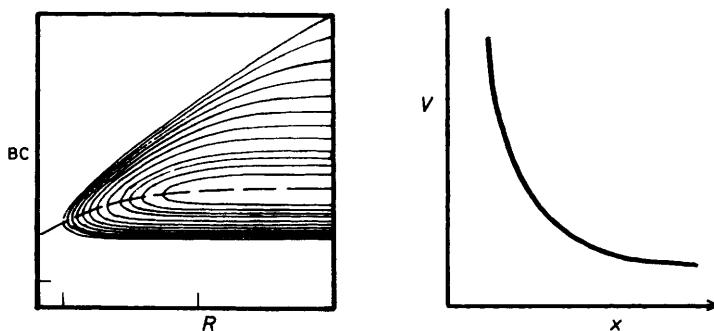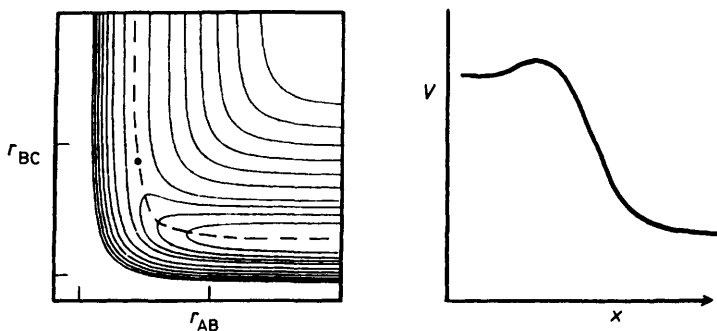

Figure 1 *Typical potential energy surface for the collinear collision of a diatomic molecule* BC *(e.g., N_2) with a noble gas atom* A. *Contours join points of equal potential energy;* R *is the distance from* A *to the centre-of-mass of* BC; *and the curve on the right indicates how* V *varies along the path of minimum energy, which is shown on the potential energy surface by the dashed line*

Clearly, no chemical reaction can occur in collisions of this kind at moderate energies. However, energy might be transferred. A simple (classical) argument can be used to explain qualitatively why the transfer of vibrational energy in N_2 + Ar collisions is extremely inefficient. Note that the approach of an Ar atom towards N_2 tends to compress the N_2 bond; but only very slightly until high energies are reached. Now imagine a collinear classical collision between a non-vibrating N_2 molecule and an Ar atom. At low and moderate collision energies, the incoming

and outgoing trajectory will scarcely deviate at all from the path of minimum energy, represented by the dashed line in Figure 1: there will be essentially no transfer of energy from relative translation to vibration. Only at very high collision energies, will inertia (or the 'bobsleigh' effect) cause much difference between the incoming and outgoing trajectories.

In practice, diatomic molecules are only transferred between neighbouring vibrational levels with low probability, especially when the states are relatively widely separated and the collision energy (or temperature, in a thermal experiment) is low. Transfer is more probable the more impulsive the collision: consequently, the probabilities of energy transfer decrease along the sequence He to Xe.


Figure 2 *Typical potential energy surface for the collinear collision of a diatomic molecule* BC *(e.g., HF) with an atomic radical* A *(e.g., Cl). As in Figure 1, the curve on the right shows the variation of V along the path of minimum energy, represented on the potential energy surface by the dashed line*

The second type of system whose collision dynamics I wish to consider has a potential energy surface like that shown in Figure 2. This form of surface arises when a radical and a molecule interact. Then if A is the radical, it is usually possible for an atom-transfer reaction, $A + BC \rightarrow AB + C$, to take place. Reaction occurs in an $A + BC$ collision if the system surmounts the *potential barrier* on the surface. For reaction in the exothermic direction, *e.g.*, $F + HCl \rightarrow HF + Cl$, this barrier is nearly always less than 10% of the energy of the bond being broken in the reaction—and is frequently very small. For systems where A and C are identical, reaction can only be experimentally observed by isotopic substitution, but vibrational relaxation may be enhanced substantially by the atom-transfer process.

A third case arises when two radicals interact.[8] Now it may be especially important to remember that more than one potential energy surface can correlate with the separated species, because of the existence of degenerate and near-degenerate states in species with open electronic shells. However, it is likely that at least one surface has a deep minimum or 'well', as electrons on the two radicals 'pair up' to form a chemical bond. Collisions on a potential energy surface like that shown in Figure 3 are likely to lead to the formation of *collision complexes* capable of surviving for at least several vibrations. The fate of these complexes can depend

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on conditions as well as on the detailed form of the surface. When there are different pathways for dissociation, the most exothermic channel is likely to predominate. For example, the reaction:

$$O + OH \longrightarrow O_2 + H; \Delta H_0 = -70 \text{ kJ mol}^{-1} \qquad (2)$$
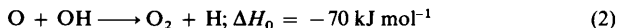
probably proceeds *via* an HO_2† complex which dissociates preferentially to O_2 + H rather than back to O + OH. On the other hand, the only simple dissociation channel for $HONO_2$ complexes from $OH + NO_2$ is redissociation; this process only competes against collisional stabilization of the adducts. However, when one of the radicals forming a collision complex is initially vibrationally excited, the association–dissociation process is very likely to be accompanied by relaxation, and consequently vibrational energy transfer is unusually rapid in radical–radical collision.[8,9]
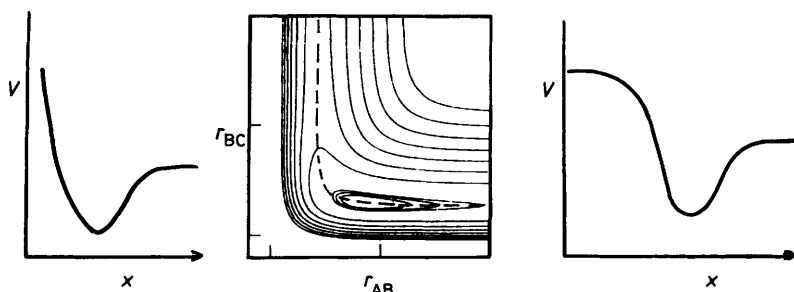
Figure 3 *Typical potential energy surface for the collinear collision of a diatomic radical* BC *(e.g., O_2) with an atomic radical* A *(e.g., H). The curve on the right shows how V varies along the path of minimum energy for a case where the* (ABC)† *complex can dissociate to* A + BC, *or to* AB + C; *the curve on the left shows the variation of V when only one such dissociation channel is accessible*

My main aims in this lecture are to describe how reactive and inelastic processes involving vibrationally excited molecules may be studied, and to see how the rates of such processes can be related to fundamental properties of the system in question—such as the form of the potential energy hypersurface. For each type represented by the potentials in Figure 1, 2, and 3, I shall consider systems studied recently by my own group, but the general conclusions will be based on a much wider range of data. An experimental technique used in several of our measurements is that of infrared fluorescence or laser-induced vibrational fluorescence (LIVF).[2,10]

In a LIVF experiment, a laser pulse is used to excite a fraction of molecules in a

[8] M. J. Howard and I. W. M. Smith, *Prog. Reac. Kinet.*, 1983, **12**, 55.
[9] M. Quack and J. Troe, *Ber. Bunsenges. Phys. Chem.*, 1975, **79**, 170; M. Quack and J. Troe, *Ber. Bunsenges. Phys. Chem.*, 1977, **81**, 160.
[10] I. W. M. Smith in 'Lasers as Reactants and Probes in Chemistry', ed. W. M. Jackson, Howard University, 1984, in press.

gas sample to a defined vibrational level. (Usually the laser output contains only one or a few frequencies that coincide with molecular absorption frequencies, but any rotational state specificity is rapidly destroyed.) The lifetime of the vibrationally excited molecules is determined by observing the intensity of infrared fluorescence as a function of time: *i.e.*, $I_F(t)$. In the simplest case, an exponential decay of the fluorescence from the initially excited level is observed:

$$I_F(t) = I_F(t = 0) \exp(-k_{1st}t)$$

where $k_{1st} = k_F + \Sigma k_Q[Q]$ with k_F being the effective first-order constant for removal by radiative decay and the $k_Q[Q]$ are pseudo-first-order constants for removal of the molecules from the initial excited level in collision with Q, a component of the gas sample; *e.g.*

$$AB(v) + Q \longrightarrow AB(v' < v) + Q \tag{3}$$
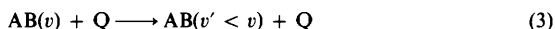
Second-order constants can be found by studying how k_{1st} varies as the composition of the gas sample containing AB is systematically changed. In general, k_F is *ca.* 10^2 s^{-1} and makes only a small contribution to k_{1st}.

To exploit the LIVF method fully, one needs a powerful pulsed laser source which is tunable so that a variety of molecular levels can be accessed. Even with such a source it is difficult to promote adequate concentrations of molecules to other than low-lying levels. Most molecules in equilibrium samples are in the zeroth vibrational level and overtone and combination bands are weak. Even when higher excitations are possible it may be difficult to differentiate between fluorescence from the initially excited level and that from lower, but still excited, levels which are populated as the molecules relax down the manifold of levels. Finally, it has to be recognized that the method measures *total* loss from a particular level: it does not discriminate between reaction and relaxation in those cases where Q and the excited molecules can react, nor does the method usually provide direct evidence about the mechanism for relaxation, that is the states to which the excited molecules are transferred.

2 Collisions Between Molecules

Collisions between diatomic molecules and rare gas atoms are relatively simple to treat theoretically. Unfortunately, virtually all the experiments on vibrational relaxation in such systems probe transfer between the lowest levels of the diatomic, $v = 0$ and $v = 1$. As well as overcoming the difficulty of exciting molecules to levels above $v = 1$ conditions have to be reached so that relaxation is predominantly by V—T,R energy transfer in collision with the rare gas, rather than by the intrinsically much faster V—V processes like

$$AB(v) + AB(v = 0) \longrightarrow AB(v - 1) + AB(v = 1). \tag{4}$$
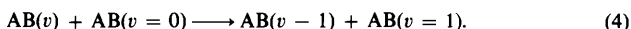
In this section, I shall give a brief review of experiments that we have carried out on the vibrational relaxation of HCN, which has interesting similarities to, and

differences from, the hydrogen halides. Furthermore, it is sufficiently simple that *ab initio* theory or theoretical analysis of the rovibrational spectra of HCN and its isotopic variants may provide a good intramolecular potential, and wavefunctions that accurately describe the nature of its vibrational eigenstates.

From LIVF experiments we have determined rate constants for relaxation of HCN from four different vibrational levels: (001),[11] (002),[12] (011),[13] and (101).[14] This has been made possible by a high energy *optical parametric oscillator* (OPO). This device, pumped by 100 mJ pulses from a Nd:YAG laser system (J. K. Lasers Ltd.) generates pulses of 1—5 mJ energy, 10—20 ns in duration, with a linewidth of *ca.* 0.2 cm^{-1}. The tuning range of our OPO is shown in Figure 4, where it is displayed alongside the vibrational energy levels of HCN. The solid lines on the energy diagram show which absorptions have been successfully used in our LIVF measurements.
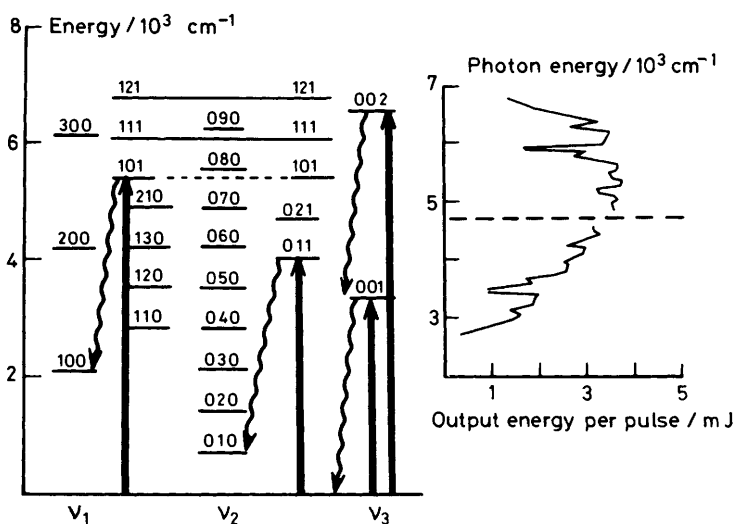
Figure 4 *Output of the optical parametric oscillator compared with the vibrational energy levels of HCN. The vertical arrows show the absorption bands that have been directly excited in our LIVF experiments;[11-14] the diagonal arrows show the emission bands that have been observed*

A common feature of the four HCN levels that have been excited is that they all contain at least one quantum of energy in the v_3 mode, which is essentially the C–H stretch. The v_3 fluorescence lies at *ca.* 3 μm, the best region for observing time-resolved infrared fluorescence. However, when an overtone (002) or combination (011 or 101) level is excited, the fluorescence at 3 μm may include contributions from molecules in levels other than that initially excited. Fortunately, judicious use

[11] G. S. Arnold and I. W. M. Smith, *J. Chem. Soc.. Faraday Trans. 2*, 1981, **77**, 861; G. S. Arnold, R. P. Fernando, and I. W. M. Smith, *J. Chem. Phys.*, 1980, **73**, 2773.
[12] P. W. Hastings, M. K. Osborn, C. M. Sadowski, and I. W. M. Smith, *J. Chem. Phys.*, 1983, **78**, 3893.
[13] B. D. Cannon and I. W. M. Smith, *Chem. Phys.*, 1984, **83**, 429.
[14] B. D. Cannon, J. S. Francisco, and I. W. M. Smith, *Chem. Phys.*, 1984, **89**, 141.

of a 'cold gas filter' (CGF)[13] differentiates between v_3 emissions arising from different states. The CGF consists simply of a small gas cell containing HCN. It is placed between the fluorescence cell and the detector. The pressure of HCN in the filter can be adjusted either to absorb emissions from all levels with $v_3 = 1$[12] or to remove just the (001, 000) fluorescence.[13] Comparison of the infrared fluorescence signals with and without the CGF allows one to determine rates of relaxation both from the initially excited state and from (001). Moreover, in some cases, the route for relaxation can be deduced.

Rate constants have been determined for the removal of energy from vibrationally excited HCN by a variety of collision partners.[10-14] Table 1 summarizes only the data for collisions with noble gases. The numbers listed are the *probability* (*P*) of transfer of HCN from the specified level per collision. Two features of these results stand out:

(*i*) the probabilities are, in all cases, small but show considerable variation depending on the HCN level;

(*ii*) the dependence of *P* on rare gas (M) is different for different HCN levels. For example, for HCN(001) the values of *P* are almost independent of M, but for HCN(011) *P* falls quite steeply from M = He to M = Xe.

This is not the place to reproduce in detail our interpretation of the interesting data summarized in Table 1. However, the results merit some discussion, especially as they seem to represent the only case in which relaxation rates have been determined for all modes of a simple polyatomic molecule.

Table 1 *Probabilities[a] of vibrational energy transfer between* HCN(*mn*1) *and the noble gases at* 298 K

	He	Ne	Ar	Kr	Xe
HCN(001)	1.9 (−5)	2.9 (−5)	2.9 (−5)	3.2 (−5)	2.8 (−5)
HCN(002)	1.6 (−5)	1.9 (−5)	1.4 (−5)	1.6 (−5)	—
HCN(101)	0.95(−4)	1.32(−4)	1.27(−5)	1.24(−5)	1.43(−5)
HCN(011)	2.3 (−3)	7.8 (−4)	5.7 (−4)	3.4 (−4)	—

[a] 1.9 (−5) = 1.9 × 10⁻⁵; thermally averaged probabilities are calculated from the 'hard-sphere' formula: $P = k/(\pi\sigma^2)c$ where k is the observed rate constant and $(\pi\sigma^2)$ and c are the collision cross-section and mean relative velocity, respectively. The following cross-sections were used: HCN + He, Ne, Ar, Kr, and Xe: 2.84, 2.94, 3.26, 3.36, and 3.58 Å

It is appropriate to begin by considering relaxation of the v_3 mode, which is a rather localized CH stretching vibration resembling the sole vibration of a hydrogen halide. Despite this parallel, it is clear that, in relaxation of its v_3 mode by noble gases, HCN acts as a polyatomic.[11] The evidence for this is that the probabilities listed in the first row of Table 1 are much larger than those for deactivation of HCl($v = 1$)[15] and HF($v = 1$)[16] by rare gases, and they show

[15] R. V. Steele, Jr. and C. B. Moore, *J. Chem. Phys.*, 1974, **60**, 2794.

[16] (*a*) J. F. Bott and N. Cohen, *J. Chem. Phys.*, 1971, **55**, 3698; (*b*) J. K. Hancock and W. H. Green, *J. Chem. Phys.*, 1972, **57**, 4515.

virtually no dependence on the nature of the rare gas. This is a clear indication that HCN(001) is not relaxed by direct transfer back to the (000) vibrational ground state, but by transfer to levels associated with the other, lower frequency, vibrations. In terms of the 'breathing sphere' modification[17,18] of SSH theory,[19] the insensitivity of P to the reduced mass of the colliding species means that the rate-determining step in the relaxation from the level being monitored is a *resonant* one in which the internal energy of the excited molecules changes by $\lesssim k_B T$: that is, transfer is induced to a level with a similar energy but in other vibrational modes. For transfer from HCN(001), only the levels (120) and (050) appear close enough to fit the bill. Arnold and Smith[11] argued that the dominant process is probably

$$\text{HCN(001)} + \text{M} \longrightarrow \text{HCN}(12^0 0) + \text{M}; \Delta E = +191 \text{ cm}^{-1} \qquad (5)$$
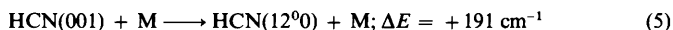
on the basis that the (001) and $(12^0 0)$ levels are both Σ^+ vibrational states and that there was some evidence for mixing of these zeroth-order states in isolated HCN.[20]

The reverse process would occur with a somewhat larger rate constant than that for the process as written. However, HCN$(12^0 0)$ will relax rapidly to lower levels, so the transfer back to (001) can be ignored.

The proposed mechanism for relaxation of HCN(001) was supported when measurements were made on HCN(002). At first sight, it is surprising that (002) should relax more slowly than (001): calculations based on harmonic oscillator behaviour[21] would predict an *increase* in relaxation rate by a factor of *ca.* 2. However, the equivalent process to equation 5, *i.e.*

$$\text{HCN(002)} + \text{M} \longrightarrow \text{HCN}(12^0 1) + \text{M}; \Delta E = +247 \text{ cm}^{-1} \qquad (6)$$
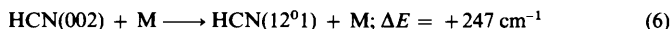
is now less resonant. This will reduce the term in the matrix element for collision-induced transfer which depends on the 'overlap' of translational wave-functions. In addition, the vibrational part of the matrix element will not increase as much as it might in the harmonic oscillator limit, because the increase in energy discrepancy reduces the mixing of the zeroth-order wavefunctions. The extent of the second factor is difficult to estimate. However, the way in which the ratios of the probabilities, P_{002}/P_{001}, vary with rare gas is reproduced extremely well by calculations based on the 'breathing sphere' model.[12]

These results highlight a major difficulty in trying to predict the rates and pathways for vibrational energy relaxation in polyatomic molecules: namely, our ignorance of the true form of the vibrational eigenfunctions. Even for quite low-lying levels, the labels that we attach to vibrational states give a misleading impression of their 'purity'. The eigenfunctions can be expressed as linear combinations of those for harmonic oscillators,—for example, for a triatomic

[17] F. I. Tanczos, *J. Chem. Phys.*, 1956, **25**, 439.

[18] J. L. Stretton, *Trans. Faraday Soc.*, 1965, **61**, 1053.

[19] R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, *J. Chem. Phys.*, 1952, **20**, 1591; R. N. Schwartz and K. F. Herzfeld, *J. Chem. Phys.*, 1954, **22**, 767.

[20] V. K. Wang and J. Overend, *Spectrochim. Acta, Part A*, 1976, **32**, 1043.

[21] D. Rapp and T. E. Sharp, *J. Chem. Phys.*, 1963, **38**, 2641.

molecule, as $\Sigma a_i|\varphi_m\varphi_n\varphi_l\rangle$, but it is formidably difficult to calculate the mixing coefficients a_i accurately, either by *ab initio* methods or semi-empirically from an experimental knowledge of the energies of the vibrational levels. This is an area in which one might hope for progress, with measurements of radiatively and collisionally induced transition probabilities playing a role in establishing the true nature of vibrational states in polyatomic molecules.

The experiments on relaxation of HCN from its (101) and (011) levels demonstrate that excitations in the v_1 and v_2 modes are lost more rapidly than excitation in v_3. For HCN(101),[14] the values of P are all 4—5 times greater than those for HCN(001). Again the lack of dependence on M is strongly suggestive of a near-resonant intramolecular $V—V$ transfer mechanism. The most likely process is

$$HCN(101) + M \longrightarrow HCN(03^11) + M; \Delta E = -27\,cm^{-1} \qquad (7)$$

which would be assisted either by direct mixing of the initial and final states *via* a Coriolis interaction, or by mixing between the zeroth-order (101) and (02^01) Σ^+ states.

HCN(011) is relaxed very much faster than either HCN(101) or HCN(001) and the probabilities now depend rather strongly on M, the noble gas. Since the experimental observations demonstrate that the v_3 excitation is retained in the first step of relaxation from (011), then that process must be

$$HCN(011) + M \longrightarrow HCN(001) + M; \Delta E = -692\,cm^{-1} \qquad (8)$$
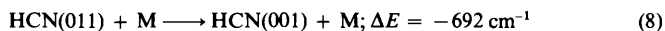
Now, ΔE, the energy which has to be transferred to the relative translational and rotational motions of HCN and M, is much greater than k_BT, and a more marked dependence on the reduced mass of the collision pair is to be expected. However, the simple breathing sphere theory[17,18] would actually predict a much more marked variation of P along the sequence M = He to M = Kr.

We have obtained[13] much better agreement with experiment by adapting a theoretical model which includes the effects of molecular rotation in an approximate, classical manner.[22,23] The physical basis for these calculations is illustrated in Figure 5. HCN is treated as three 'embedded hard-spheres' and it is reasonably assumed that the most effective collisions in promoting energy transfer to and from the v_2 bending mode are those in which M collides with the H atom perpendicular, or nearly perpendicular, to the HCN axis. As implied in the Introduction, the probability of energy transfer will be greatest for the most impulsive collisions. However, rotational motion of the HCN, as well as the translational motion, is assumed to contribute to the *effective* velocity at which the H and M atoms approach. The magnitude and direction of the relative velocity and the rotational momentum of the HCN are chosen by Monte Carlo methods. For each choice, a transition probability is calculated *via* first-order perturbation theory—subject to the constraints of energy and angular momentum

[22] A. Micklavc and S. F. Fischer, *Chem. Phys. Lett.*, 1976, **44**, 209.
[23] A. Micklavc, *J. Chem. Phys.*, 1978, **69**, 281; A. Micklavc and S. F. Fischer, *J. Chem. Phys.*, 1980, **72**, 3805.
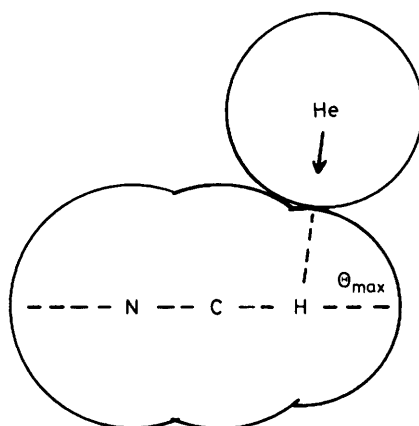
Figure 5 *'Embedded hard-sphere' model used in calculations on the V–R,T energy transfer from* HCN(011) *to noble gas atoms. The approach shown defines* Θ_{max}, *the maximum angle between the molecular axis and the atom's direction of approach for which the noble gas atom can impact on the* H *atom*

conservation.[23] Calculations are carried out for a large sample to yield a thermally averaged collisional probability.

For M = He, the value of P calculated by this method is less than that from the simple breathing-sphere calculations, largely because steric and mode-matching effects [22] are accounted for more correctly. For the heavier rare gases, the rotational contribution to the effective velocity of approach becomes dominant and raises the values of P by factors of 3.8 (Ne), 4.7 (Ar), and 6.5 (Kr) above the breathing-sphere values. Overall, the calculations parallel the variation of P with M extremely well. The absolute values calculated are approximately four times those observed experimentally, possibly reflecting the shortcomings of an approach based on first-order perturbation theory.

In an excellent review on vibrational energy flow in polyatomic molecules, Weitz and Flynn[24] postulate three 'propensity rules'. The first is that molecules can be transferred rapidly between levels associated with the same single mode by near-resonant, intermolecular $V—V$ exchange as represented in equation 4. Secondly, they proposed that energy transfer between modes is fast when their fundamental frequencies lie within *ca.* $k_B T$ of one another, which is not the case in HCN. Finally, they suggested that transfer between levels associated with different modes is enhanced by mechanical Fermi mixing, or by large mechanical or electrical anharmonicity of the lowest frequency mode. Our results on relaxation in HCN lend support to this third propensity rule. In addition, our data indicate that molecular rotation can help to induce relaxation of energy in bending modes.

[24] E. Weitz and G. Flynn in 'Photoselective Chemistry', ed. J. Jortner, R. D. Levine, and S. A. Rice, *Adv. Chem. Phys.*, 1981, **47**(2), 185.
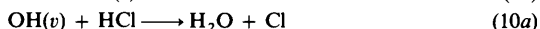
Such V—R,T energy transfer will be especially important for hydrides and deuterides.

3 Collisions Between Radicals and Molecules

In this part of my review, I want to consider explicitly two examples of simple radical–molecule reactions:
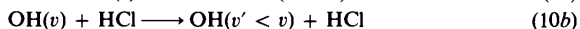
$$O + HCl(v) \longrightarrow OH + Cl \qquad (9a)$$

and
$$OH(v) + HCl \longrightarrow H_2O + Cl \qquad (10a)$$
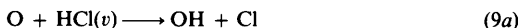
In the first of these two cases, the vibration which is excited is one along the bond that is broken in the reaction; in the second, it is along a bond that retains its integrity through the reaction. In both reactions, vibrational relaxation, *i.e.*

$$O + HCl(v) \longrightarrow O + HCl(v' < v) \qquad (9b)$$

and
$$OH(v) + HCl \longrightarrow OH(v' < v) + HCl \qquad (10b)$$
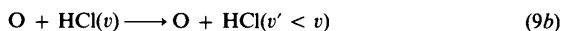
can compete with reaction. Many experiments, including our own, measure the *total* rate of loss of the vibrationally excited species, but I hope to demonstrate that one can assess the relative importance of reaction and relaxation by comparing the rates for isotopically related processes. Moreover, it should be possible to relate the effects of vibrational excitation and isotopic substitution on reaction rates since both changes leave the underlying potential energy surface unaltered.

Reaction (9a) is very nearly thermoneutral ($\Delta H_0^0 = +3.4$ kJ mol^{-1}) and has an
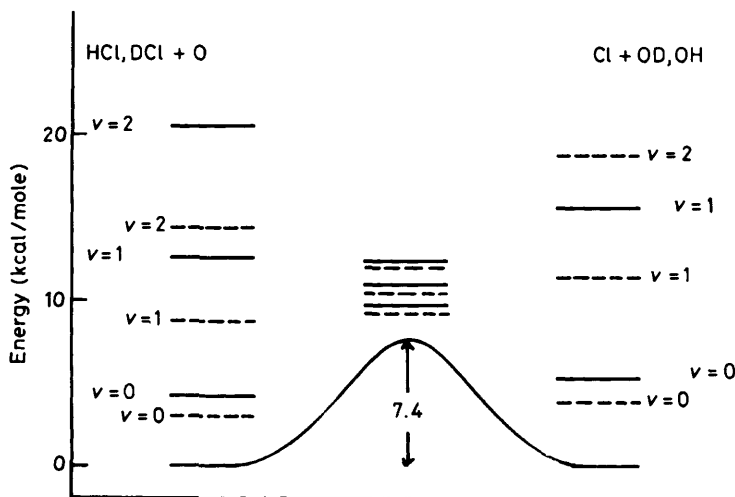
Figure 6   *Energy level diagram for the reactions:* $O + HCl(v), DCl(v) \rightarrow OH(v'), OD(v') + Cl$. *The full lines represent vibrational levels of the hydrogenated species, the dashed lines those of the deuterated species*

activation energy of *ca.* 25 kJ mol^{-1}.[25,26] Using these data and spectroscopic information, the approximate energy level diagram in Figure 6 can be constructed. The thermal rate constants exhibit a normal primary kinetic isotope effect ($k_{HCl} > k_{DCl}$) which is consistent with $\Delta E_0^{\ddagger}$ (the difference between zero-point levels in the transition state and in the reagents) being greater in the deuterated system.[1]

Our experiments[27] on the kinetics of HCl($v = 1$) and DCl($v = 1$) in the presence of O-atoms used the LIVF method, steady-state concentrations of O-atoms being created in a discharge-flow system. The rate constants which these experiments gave are compared in Table 2 with those for reaction of the ($v = 0$) molecules. Although DCl($v = 1$) molecules have only just as much energy as the transition-state species, whereas HCl($v = 1$) molecules have much more energy, the DCl($v = 1$) molecules are removed more rapidly. This observation led us to conclude that the predominant channel for removal of the ($v = 1$) molecules is not reaction but vibrational relaxation—probably by an electronically non-adiabatic mechanism of the kind first proposed by Nikitin[28] to explain the anomalously rapid self-relaxation of NO($v = 1$).

Table 2 *Rate constants^a for reaction and relaxation of* HCl(v) *and* DCL(v) *with* O-*atoms at* 298 K

		k/cm^3 molecule^{-1} s^{-1}	*Ref.*
HCl ($v = 0$)	reaction	1.2 (-16)	25*a*
	reaction	1.4 (-16)	26
DCl ($v = 0$)	reaction	2.7 (-17)	25*b*
HCl ($v = 1$)	reaction + relaxation	1.0 (-12)	27
DCl ($v = 1$)	reaction + relaxation	1.3 (-12)	27
HCl ($v = 1$)	reaction + relaxation	8.9 (-13)	29
HCl ($v = 2$)	reaction + relaxation	5.2 (-12)	29
	reaction	1.5 (-12)	29
HCl ($v = 1$)	reaction	2 (-14)	30
HCl ($v = 2$)	reaction	3 (-12)	30
HCl ($v = 1$)	reaction + relaxation	1.0 (-12)	31
	reaction	6.4 (-14)	31
HCl ($v = 2$)	reaction + relaxation	6.3 (-12)	31

^{a} 1.2 (-16) = 1.2 × 10^{-16}

[25] (*a*) R. D. H. Brown and I. W. M. Smith, *Int. J. Chem. Kinet.*, 1975, **7**, 301; (*b*) R. D. H. Brown and I. W. M. Smith, *Int. J. Chem. Kinet.*, 1978, **10**, 1.

[26] D. L. Baulch, R. A. Cox, P. J. Crutzen, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, *J. Phys. Chem. Ref. Data*, 1982, **11**, 327.

[27] R. D. H. Brown, G. P. Glass, and I. W. M. Smith, *Chem. Phys. Lett.*, 1975, **32**, 517.

[28] E. E. Nikitin, *Opt. Spectrosk.*, 1960, **9**, 8 and 1961, **11**, 452; E. E. Nikitin and S. Ya Umanski, *Faraday Discuss. Chem. Soc.*, 1972, **53**, 1.

This conclusion does not, of course, exclude the possibility that the O + HCl,DCl reactions are efficiently promoted by vibrational excitation. After all, the rate constant for removal of HCl($v = 1$) is 10^4-times that for reaction of HCl($v = 0$) so even though reaction makes only a small contribution to the overall removal it could represent a very significant rate increase. In fact, more detailed and elegant experiments[29-31] than our own—in which the production of OH was observed—indicate that this is the situation. Table 2 gives rate constants that have been measured for *reaction* of HCl($v = 1,2$) with O-atoms. The observation that excitation of the vibration along the bond broken in an atom-transfer reaction enhances the reaction rate very appreciably has been confirmed in studies of some other nearly thermoneutral reactions.[32-33] Before considering how such observations might be interpreted, I shall summarize briefly our results[34,35] for reaction (10*a*) and its deuterated analogues.

The rate of the thermal reaction between OH and HCl has now been measured directly in about eight independent studies. (The results are summarized most recently in *ref.* 36.) The activation energy is variously reported as between 2.4 and 4.4 kJ mol^{-1}, though the spread in rate constant values at 298 K is only about 15%. Our objective is to see whether vibrational excitation in the radical reagent in simple radical–molecule reactions can enhance their rates. A lot of the data in the literature have been derived from rather indirect experiments and provide no consistent answer. The OH + HCl reaction seems a specially suitable case for study since isotopic substitutions can be made in both reagents, and the possibility also exists of observing the effect of vibrational excitation of the molecular (HCl) reagent.

In the present experiments, OH or OD radicals are generated by pulsed photolysis of H_2O, HNO_3, or D_2O, DNO_3. At variable delays after the photolysis pulse, radiation from a tunable, pulsed, dye laser is used to induce $A^2\Sigma^+$—$X^2\Pi$ fluorescence from the radicals. This LIF detection method is extremely sensitive and highly specific. (The laser excites a single line in either the (0,0) or (1,1) band of the A—X system of OH or OD, but rotational equilibration is extremely rapid, so no rotationally specific information is obtained.) The photodissociation processes give only low yields of vibrationally excited radicals, but this is a positive advantage since any effects of stepwise vibrational relaxation can be ignored.

As with our LIVF experiments, these measurements yield rate constants for the sum of relaxation and reaction. In systems comprising two diatomics, a likely mechanism for rapid relaxation is intermolecular V—V transfer.[2] However, the rates of V—V exchange will depend strongly on ΔE_{V-V}, the discrepancy between

[29] R. G. Macdonald and C. B. Moore, *J. Chem. Phys.*, 1978, **68**, 513.

[30] J. E. Butler, J. W. Hudgens, M. C. Lin, and G. K. Smith, *Chem. Phys. Lett.*, 1978, **58**, 216.

[31] M. Kneba and J. Wolfrum, Proc. 17th Int. Combust. Symp., The Combustion Institute, Pittsburgh, 1979, p. 497.

[32] R. Zellner and W. Steinert, *Chem. Phys. Lett.*, 1981, **81**, 568.

[33] V. B. Rozenshtein, Yu. M. Gershenzon, A. V. Ivanov, and S. I. Kucheryavii, *Chem. Phys. Lett.*, 1984, **105**, 423.

[34] B. D. Cannon, J. S. Robertshaw, I. W. M. Smith, and M. D. Williams, *Chem. Phys. Lett.*, 1984, **105**, 380.

[35] I. W. M. Smith and M. D. Williams, to be published.

[36] L. F. Keyser, *J. Phys. Chem.*, 1984, **88**, 4750.

$BC = AB + C$, from this viewpoint. As Figure 2 shows, a path of minimum energy can be traced across the potential energy surface, and the variation of potential energy reduced to a one-dimensional representation, $V(x)$. To apply the vibrationally adiabatic form of transition-state theory,[1,41] it is also necessary to examine how V varies with small displacements orthogonal to x. One then computes rate constants at various points along x and finds the minimum value, that being the best transition-state theory estimate. Each calculation depends importantly, but not only, on $\Delta E_0^{\ddagger}$ which corresponds to the maximum energy on the $v = 0$ vibronic state curve. In general, this curve does not run parallel to $V(x)$, since the zero-point energy changes as the interatomic forces alter. According to transition-state theory, it is the change in $\Delta E_0^{\ddagger}$, because of different zero-point effects, that is largely responsible for kinetic isotope effects.[1]

In vibrationally adiabatic transition-state theory, these ideas are simply extended, the system being assumed to stay in the same vibrational state (but not retain the same vibrational energy) as it progresses from separated reagents to the transition state. The rate of reaction now crucially depends on $\Delta E_v^{\ddagger}$, the height of the barrier on the vibrationally adiabatic curve for state v. The extent to which vibrational excitation promotes reaction depends on how ΔE_v is reduced as v is increased.

It is clearly vital to ask how vibrationally adiabatic the collisions are likely to be, up to the point where trajectories reach the transition state. The answer to this depends crucially on the location of the transition state. The earlier the position along the reaction path which the transition stage occupies, the less is the coupling between relative translational and vibrational motions up to that point, and vibrational adiabaticity is likely to be a good approximation.[42] However, because the $V—T$ coupling is weak the vibrationally adiabatic or vibronic curves are likely to run almost parallel, the values of $\Delta E_v^{\ddagger}$ only change slowly with v, and effects of vibrational excitation are slight. This case is illustrated in Figure 7a.

The opposite limit is reached when the barrier is 'late'; *i.e.*, as the products separate.[1,43] This is typical for a strongly endothermic reaction. Now there is very strong curvature in the reaction path and strong $V—T$ coupling before the barrier is reached on the potential: at least the simplest versions of vibrationally adiabatic theory cannot be applied.

In intermediate cases, vibrationally adiabatic transition-state theory is more appropriate than one might immediately suppose—especially for those reactions, which have been comparatively widely studied, in which an H-atom is transferred between two heavier species. Now, as v is increased, $\Delta E_v^{\ddagger}$ falls appreciably and, in addition, the position of the barriers on the vibrationally adiabatic curves move to progressively earlier positions along the reaction path, thereby improving the approximation of vibrational adiabaticity. Figure 7b illustrates this effect for a supposedly thermoneutral reaction, such as (9a).
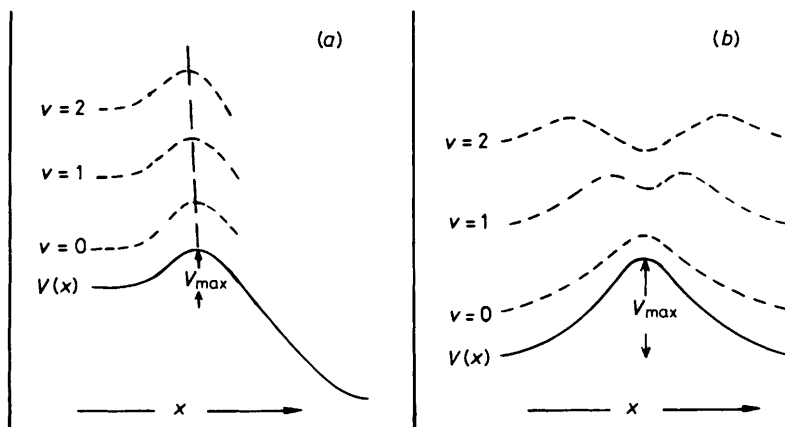
So far I have implicitly considered systems in which vibrational excitation is in

[41] P. Pechukas, *Ann. Rev. Phys. Chem.*, 1981, **32**, 159.
[42] I. W. M. Smith, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 747.
[43] J. C. Polanyi, *Acc. Chem. Res.*, 1972, **5**, 161.

Figure 7 *Variations of potential energy (V) and vibronic energies for: (a) an exothermic atom-transfer reaction with a low and early potential energy barrier, so that the barriers on the vibrationally adiabatic curves vary only slightly with v; and (b) a thermoneutral reaction with a high and symmetrically located barrier where the heights and positions of the vibrationally adiabatic barriers depend strongly on v*

the bond which 'disappears' in the reaction. However, the ideas of vibrationally adiabatic transition-state theory are even more appropriate to excitation of other reagent modes. For example, Isaacson and Truhlar[40] have considered the effects of both OH and H_2 excitations on the reaction

$$OH(v_1) + H_2(v_2) \longrightarrow H_2O + H \tag{11}$$
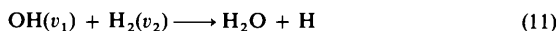
which is, of course, closely related to reaction 10a. They calculated normal mode frequencies at all points along the reaction path. For excitation of the H_2 molecule, the vibronic curves are not parallel to one another or to $V(x)$; consequently, $\Delta E_{v_2}^{\ddagger}$ decreases appreciably as v_2 is raised. On the other hand, the OH vibration which correlates through to the v_1 stretching mode in H_2O is almost unchanged along x. Hence the v_2 vibronic curves are almost parallel to $V(x)$, the values of $\Delta E_v^{\ddagger}$ are almost independent of v_1, and there is very little change of the rate constant with OH excitation. This is entirely consistent with experiments on reaction (11)[32] and with our own results on the OH,OD($v_1 = 1$) + HCl,DCl systems.

4 Collisions Between Free Radicals
As was pointed out in the Introduction, the result of collisions between two radicals will usually be dominated by the motion of the system on a potential energy surface (or surfaces) which has a deep 'well' or minimum.[8] Collision complexes are formed easily and it is their rate of formation which is rate-determining for many radical–radical processes. In trying to estimate what this rate might be, several factors must be borne in mind. One is that $V(x)$, the potential energy along the path of minimum energy, will probably show no maximum. The transition state can be chosen by variational[41] or maximum free-energy criteria[9]—or the concept of a defined

transition-state for canonical reaction can be abandoned altogether.[44] Whichever approach is taken, it is clear that the critical configurations are 'loose' or 'early'. So the vibrationally adiabatic curves for different states will be very nearly parallel up to this region and the rates of formation of collision complexes should be virtually independent of initial vibrational state.

A second factor to be remembered is that interactions of two radicals lead to more than one potential energy surface with statistics determining what fraction of collisions occur on any particular surface. It may be necessary to take account of the fact that more than one such surface leads to bound states[45] and hence to recombination, reaction, or vibrational relaxation.

Here, I shall concentrate on the dynamics of radical–radical collisions when one of the radicals is vibrationally excited. In the two studies which I shall specifically refer to, the experimental difficulties were reduced by making one radical NO or NO_2. In the first set of experiments,[46] which we did a few years ago, NO was vibrationally excited in 'indirect' LIVF experiments. It is not easy to find a pulsed i.r. laser to excite NO directly. However, it can be excited by V—V energy transfer from HCl:

$$HCl(v = 1) + NO(v = 0) \longrightarrow HCl(v = 0) + NO(v = 1); \Delta E = -1009\ cm^{-1} \quad (12)$$
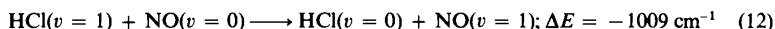
when the HCl is excited by radiation from a pulsed HCl chemical laser. These experiments gave the results for $NO(v = 1)$ listed in Table 4. The data for $OH(v = 1)$ and $OD(v = 1)$ were found[47] by the same experimental method that was used for studying the kinetics of these radicals with HCl and DCl.

The rate constants shown in Table 4 are all within an order-of-magnitude of rate constants for the total number of 'hard-sphere' collisions. In contrast, relaxation at

Table 4 *Rate constants* $(10^{-11}\ cm^3\ molecule^{-1}\ s^{-1})$ *at* 298 K *for relaxation of* NO $(v = 1)$ *by* O, Cl *and* Br *atoms and of* OH, OD $(v = 1)$ *by* NO *and* NO_2[a]

	k_{relax}	k_{rec}^{∞}	k_{est}
NO $(v = 1)$ + O	6.5 ± 0.7	~ 2.8	5.0
NO $(v = 1)$ + Cl	3.5 ± 0.5	~ 5.8	6.9
NO $(v = 1)$ + Br	2.0 ± 0.3	~ 3.3	5.4
OH $(v = 1)$ + NO	3.8 ± 0.6	~ 2	1.4
OD $(v = 1)$ + NO	2.7 ± 0.3	—	1.4
OH $(v = 1)$ + NO_2	4.8 ± 0.8	$\gtrsim 3$	2.0
OD $(v = 1)$ + NO_2	4.3 ± 0.3	—	2.1

[a] Experimental data from *ref.* 46 and 47, values of k_{rec} and k_{est} are taken from Howard and Smith's review,[8] which lists the original references

[44] M. Quack and J. Troe, *Ber. Bunsenges. Phys. Chem.*, 1974, **78**, 240.
[45] I. W. M. Smith, *Int. J. Chem. Kinet.*, 1984, **16**, 423.
[46] R. F. Fernando and I. W. M. Smith, *Chem. Phys. Lett.*, 1979, **66**, 218; R. P. Fernando and I. W. M. Smith, *J. Chem. Soc.. Faraday Trans. 2*, 1981, **77**, 459.
[47] I. W. M. Smith and M. D. Williams, to be published.

room temperature of $NO(v = 1)$ and $OH(v = 1)$ by argon requires more than 2×10^{7}[48] and more than 10^{5}[47] collisions, respectively. In addition, it should be remembered that, in all these systems, more than 50% of collisions between radicals occur on potential energy surfaces without significant minima on them.

The most reasonable explanation for the unusually facile vibrational relaxation found in these radical–radical collisions, is that the initial specific vibrational excitation is randomized during the lifetime of the collision complexes that form. At the same total energy, a much greater volume of phase space is associated with separated radicals when they are not vibrationally excited, than when they are. As a result, when the complexes redissociate there is only a very low probability that they do so to yield the radicals in excited vibrational states. If this explanation is correct, and if the rate of formation of collision complexes is independent of whether or not the colliding radicals are vibrationally excited, the relaxation rate constants (k_{relax}) should correspond quite closely to the rate constants for recombination of the same pair of radicals in thermal collisions and the limit of high pressure (k_{rec}^{∞}). Unfortunately, for these small systems, the latter rate constants can be determined only after a long, and rather uncertain, extrapolation. Within the errors of estimating k_{rec}^{∞}, the values are in reasonable agreement with those of k_{relax}.

The experimental values of both rate constants can be compared with estimated values based on Quack and Troe's maximum free-energy interpolative method.[9] Again, fair agreement is found, given that the theoretical model is quite sensitive to the form assumed for the long-range potential. However, uncertainties about the real form of potential energy surfaces in the regions where chemical bonds just start to influence the potential energy is a real stumbling block to making accurate calculations on radical–radical processes.

5 Conclusions

In this review, an attempt has been made to sketch out the connection between the results of elementary bimolecular processes involving vibrationally excited species, as revealed by measured rate constants, and the form of the potential energy hypersurface which controls the dynamics of collisions between any particular pair of species. Our knowledge and understanding is steadily improving, not least because of the stimulating interplay between experiment and theory. However, I am afraid that my simple and short account may leave the reader with the impression that, in this field, few problems remain. This is certainly not so. The state of our present understanding is fragile, based as it is on the results of rather few definitive studies and these often limited; for example, to the behaviour of molecules in low-lying states of vibrational excitation.

Some very interesting problems relate to systems which cannot easily be placed into the categories that I have identified and considered. For example, we remain largely ignorant about the dynamics of isolated molecules at intermediate levels of excitation: that is, between the regime of discrete levels associated with normal mode motions and investigated by infrared absorption spectroscopy, and the ergodic

[48] J. C. Stephenson, *J. Chem. Phys.*, 1973, **59**, 1523.

region near dissociation limits where rapid intramolecular vibrational relaxation and statistically based unimolecular rate theories are the order of the day. In bimolecular processes, there is a similar region of uncertain behaviour. Thus, it is not yet clear when transitions occur between direct dynamics and collisions involving complexes, as either the collision energy or the strength of intermolecular attraction is increased. One would like to know how deep the attraction between colliding species must be for complexes to form in bimolecular collisions, and whether other factors have any influence on complex formation.[49,50] In summary, this field of research endeavour is vital and challenging, and it promises to remain so for many years yet.

[49] Ch. Schlier in 'Energy Storage and Redistribution in Molecules', ed. J. Hinze, Plenum Press, New York, 1983, p. 585.

[50] M. K. Osborn and I. W. M. Smith, *Chem. Phys.*, 1984, **91**, 13.