

rate enhancements in aqueous micelles.<sup>1</sup> We are only at the beginning of our understanding of these factors, and as yet cannot rationalize all the specific rate effects, let alone predict them.

### Conclusion

The current status of investigations on reversed micelles as selective catalysts has been delineated in the present Account. Reversed micelles merit attention since in their polar regions they can bind substrates fairly strongly in specific orientations and configurations. In addition to providing a playground for doing fascinating chemistry, they bear resemblance to the active sites of enzymes as well as to biomembranes. Additionally there are many industrial

applications which are proprietary information. Reversed micellar systems are utilized for the selective concentration of corrosion-inducing acidic and basic substances, for the solubilization of polar dyes, for photographic processes, and for polymerizations. It is evident that only very few of the potential applications have been explored. If we have stimulated academic and industrial scientists to enter into this exciting area of research, our efforts in writing this summary have been amply rewarded.

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## Relaxation in Collisions of Vibrationally Excited Molecules with Potentially Reactive Atoms

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The details of the molecular collisions that bring about macroscopic chemical and physical change are now being closely examined by experimentalists and theoreticians. The outcome of these encounters is controlled by the electrostatic forces which are in operation while all the atoms are close together and by the positions and momenta of the nuclei at the "start" of each collision. Unfortunately, spectroscopic methods cannot be used to study these forces in the unstable regions that are important in molecular collisions, and consequently the form of the electronic potential must be inferred from less direct evidence. Measurements of thermal rate constants provide little information, apart from indicating the magnitude of any potential energy barrier to the process. More revealing are studies of (i) how *specifically* energy is distributed among the degrees of freedom of the collision products, and (ii) how *selective* excitation of the reactants can promote particular results—for example, chemical reaction.

To describe the results of kinetic experiments of this more detailed kind, and to relate them to the rate constants of "conventional kinetics", *cross sections* are frequently used. Thus, for collisions between X and Y in quantum states denoted by  $n$  at a relative velocity  $u_R$ ,  $\sigma_{n,n'}(u_R)$  corresponds to the

cross section for formation of species in final states  $n'$  ( $u_{R'}$  will be fixed by energy balance) and the rate at which these *selected* collisions yield these *specific* products is given by

$$d[\text{products}]_{n'}/dt = \sigma_{n,n'}(u_R)u_R\{[X][Y]\}_n \quad (1)$$

so that  $\sigma_{n,n'}(u_R)u_R$  clearly takes the form of a rate coefficient.

The results of bimolecular collisions fall into three general categories: X and Y may scatter elastically, i.e.,  $n = n'$  and  $u_R = u_{R'}$ ; inelastically, i.e.,  $n \neq n'$ ,  $u_R \neq u_{R'}$ ; or reaction may occur, in which case the atomic groupings as well as the quantum states change during the course of the collision. The simplest system where all three outcomes are possible is that where an atom (A) collides with a diatomic molecule (BC), and only collisions of this kind will be considered in this article. These may be considered *potentially reactive* when AB, AC, or ABC are known to exist as stable molecules.

Ideally one would like to determine cross sections for reactive, inelastic, and elastic events for various combinations of  $u_R$  and  $n$ , but in practice only partial, and partially averaged, information has been obtained up to the present time. The infrared chemiluminescence experiments of Polanyi's group<sup>1</sup> have provided perhaps the most detailed information of this kind. Analysis of the vibration-rotation spectrum emitted spontaneously by the products of simple exoergic reactions yields the relative rates at which these emitting states are populated. Where the

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(1) T. Carrington and J. C. Polanyi, *MTP Int. Rev. Sci.: Phys. Chem., Ser. One*, 9, 135.

reactants are thermally equilibrated—which is usually the case—these experiments yield a set of *detailed rate constants*, defined by

$$k_{n'}(T) = \sum_n \left[ \int_0^\infty \sigma_{n,n'}(u_R) u_R f(u_R) du_R \right] f'(n) \quad (2)$$

where  $f(u_R)$  and  $f'(n)$  are the Boltzmann distribution functions over relative velocity and internal states. A final summation of  $n'$  would yield the thermal rate constant for overall reaction.

These experiments, and others, have revealed that the energy released during chemical reactions is rarely distributed evenly among the degrees of freedom of the products. Where reaction is of the atom-transfer type, i.e.,  $A + BC \rightarrow AB^\dagger + C$ , energy is frequently channelled preferentially into the vibration<sup>2</sup> of AB, particularly if reaction occurs in direct collisions with a major portion of the energy being liberated as the reactants approach.<sup>3</sup> Because of microscopic reversibility, this specificity of energy disposal indicates that the reverse, endoergic, reactions should be preferentially promoted by selectively exciting the vibration associated with the bond that is to be broken in the reaction, but so far there have been few direct experimental tests of this hypothesis.

In experiments utilizing thermally equilibrated species, a high degree of reactant *selectivity* results naturally from the wide spacing of electronic and vibrational energy levels. This ensures that, except at very high temperatures, significant contributions to an overall rate are only made by collisions between species in their lowest vibronic states and hence the summation in eq 2 is essentially one over rotational levels. The behavior of molecules in excited vibronic states can be studied in photochemical experiments, and these have been performed on electronically excited species for many years. However, here the process of excitation alters the electronic structure and the results of collisional processes involving these species cannot therefore be related directly to those for ground-state species. *Vibrational photochemistry* has only really become possible much more recently with the development of powerful infrared lasers capable of exciting molecules in their relatively weak vibration-rotation bands, but this is a rapidly expanding field and one which this article is closely concerned with.

The commonest application of infrared photochemical techniques has been to vibrational energy transfer.<sup>4</sup> The relaxation of molecules that have been excited by absorption of pulsed laser radiation is followed by observing how the intensity of the vibrational fluorescence ( $I_{fl}$ ) decays with time. Where relaxation of the excited molecules is predominantly via collisions with a single component (Q) of the gas mixture

$$I_{fl}(t) = I_{fl}^0 \exp(-k_{1,0}^Q [Q]t) \quad (3)$$

where  $k_{1,0}^Q$  is the rate constant for



The method of laser-induced vibrational fluorescence is now being used in several laboratories to study the removal of vibrationally excited molecules in collisions with potentially reactive atoms. In their simplest (and, at the moment, most common) form—where only the overall loss of  $BC(v = 1)$  is observed—these experiments do not discriminate directly between reactive and inelastic scattering. Before confident predictions can be made about the enhancement of chemical reaction rates resulting from reactant vibrational excitation the relative importance of these two channels for removal of vibrationally excited molecules will have to be established for a number of systems. This difficulty is more fundamental than that encountered in infrared chemiluminescence experiments. There the spectroscopically observed distribution among product states may differ from that actually created in the reaction as a result of collisional relaxation, but this problem can be overcome by working at low total pressures and hence reaching the conditions of “arrested relaxation”.<sup>1</sup> In the case of *reactant* excitation, however, relaxation may be competitive with—rather than subsequent to—reaction, and then the rates of the two competing processes can only be determined by relating the amount of product formed to that of the excited reactant which is removed. Because rotational energy transfer usually occurs with high probability in collisions, it will be difficult to measure the effects of excess reactant *rotation* on chemical reaction rates except for very rapid reactions.<sup>5</sup>

This introductory section should not leave the impression that the current interest in collisions between vibrationally excited molecules and potentially reactive species arises solely because academics wish to scrutinize the dynamics of molecular encounters more closely. More practical considerations are also at work. One of these is the desire to predict the performance of chemical laser systems. When attempts are made to extract high powers from these devices, the concentrations of potentially reactive atoms become relatively large and, if they deactivate the laser-active molecules rapidly, these species may be a crucial factor in limiting the laser's performance. This appears to be the case in the laser pumped by the  $H_2-Cl_2$  chain reaction. Because the  $Cl + H_2 \rightarrow HCl + H$  step is not particularly fast, Cl atoms accumulate and rapidly relax the  $HCl^\dagger$  formed in the laser pumping reaction,  $H + Cl_2 \rightarrow HCl + Cl$ .

A second reason for practical concern arises from the possibilities of laser-induced chemistry.<sup>6</sup> This is of special interest because *isotopically* selective vibrational excitation is quite feasible with laser sources, and practical schemes for isotope separation may be built on this foundation.<sup>7</sup> These schemes require a secondary process, which may be chemical or photochemical, which acts selectively on excited species, and this must take place more rapidly than transfer of the excitation with loss of isotopic selectivity and also be fast enough to compete with relaxa-

(2) The superscript † is used throughout this article to denote vibrational excitation.

(3) J. C. Polanyi, *Acc. Chem. Res.*, **5**, 161 (1972).

(4) E. Weitz and G. Flynn, *Annu. Rev. Phys. Chem.*, **25**, 275 (1974).

(5) This comment excludes experiments where use is made of the different rotational state distributions associated with ortho- and para- $H_2$  such as those of R. D. Coombe and G. C. Pimentel, *J. Chem. Phys.*, **59**, 1535 (1973).

(6) J. T. Knudtson and E. M. Eyring, *Annu. Rev. Phys. Chem.*, **25**, 255 (1974).

(7) C. B. Moore, *Acc. Chem. Res.*, **6**, 323 (1973).

tion in other inelastic collisions. A chemical reaction—enhanced by vibrational excitation—could serve as this secondary process if the reaction of the excited species is faster than the nonselective thermal reaction during the whole time that the reactants are in contact. In order for such schemes to be assessed realistically there is a need for fundamental information regarding both the enhancement of different types of chemical reaction by reactant excitation and also the transfer of energy in collisions between vibrationally excited molecules and potentially reactive species.

### Theoretical Considerations

Although we are primarily concerned here with collisions where both chemical reaction and energy transfer are possible, it is useful to begin by discussing collisions between species such as  $A(^1S_0)$  and  $BC(^1\Sigma^+)$  which have closed electronic shells and where chemical change cannot take place, except at very high collision energies where BC may dissociate. Because only a single electronic state correlates with the separated species, the molecular dynamics will be controlled by this one potential so the collisions must be *electronically adiabatic*. The complete potential,  $V(r_{AB}r_{BC}r_{CA})$ , is properly referred to as a *hypersurface*, but if the number of independent variables is reduced,  $V$  can be represented as an energy surface in a contour line plot.

A surface typifying the collinear interaction of a bound diatomic molecule with a chemically inert atom is shown in Figure 1. Apart from the BC bond, the major forces are repulsive, and because A repels B, the atom nearer to it, more strongly than C, the equilibrium separation of BC will be reduced as A approaches in collinear, or near-collinear, collisions. The curvature in the path of minimum potential energy represents the degree to which A perturbs BC's vibrational motion, and the probability that energy is transferred between vibration and relative translation (V-T) depends on the extent to which trajectories penetrate the region where this curvature is appreciable.

In most of the numerous theoretical studies of V-T energy transfer in "nonchemical" collisions, a simplified intermolecular potential has been assumed; for example, angular anisotropy is generally ignored. In the Landau-Teller treatment, subsequently developed<sup>8</sup> by Schwartz, Slawsky, and Herzfeld into "SSH theory", only collinear collisions are treated explicitly. It is further assumed that A interacts only with B, giving rise to a potential-energy term

$$V(x, X) = C \exp(-\alpha|x - X|)$$

where  $x$  and  $X$  are the distances of A and B from the center of mass of BC, and  $\alpha$  is a parameter which describes the steepness of the repulsion between A and B. Following a first-order perturbation treatment, in which terms that depend on  $x$  and  $X$  are separated, the probability of BC being transferred during a collision between vibrational states  $i$  and  $f$  is found to be

$$P_{i,f} = \frac{16\mu^2}{h^4 k_i k_f} [H'_{i,f(\text{vib})}]^2 [H'_{i,f(\text{tr})}]^2 \quad (4)$$

(8) K. F. Herzfeld and T. A. Litovitz, "Absorption and Dispersion of Ultrasonic Waves", Academic Press, New York, N.Y., 1959.

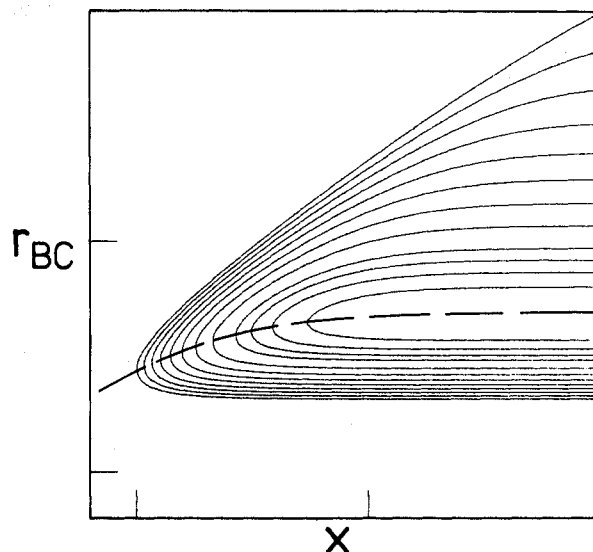


Figure 1. Potential energy surface representing the "nonchemical" interaction of an atom A with a diatomic molecule BC plotted as a function of  $r_{BC}$  and  $x$ , the distance of A from the center of mass of BC. The dotted line represents the path of minimum potential energy.

In this expression,  $H'_{i,f(\text{vib})}$  is an off-diagonal vibrational matrix element given by

$$H'_{i,f(\text{vib})} = \int_0^\infty \exp(\alpha X) \psi_f(X) \psi_i(X) dX \quad (5)$$

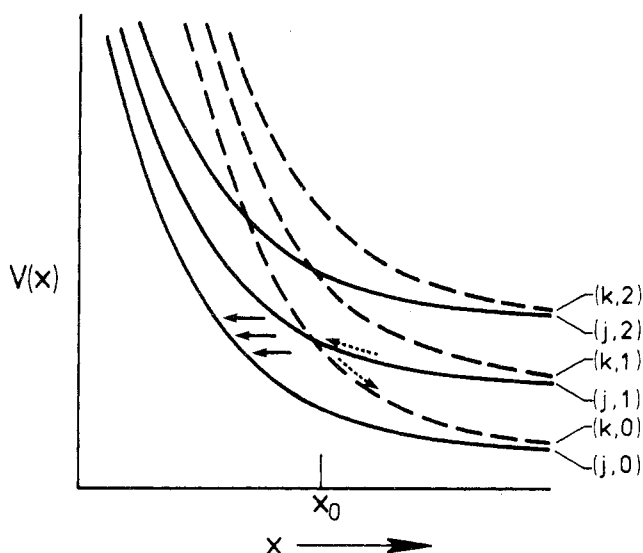
It is then usual to assume that  $\alpha^{-1}$  is appreciably greater than the vibrational amplitude so that  $H'_{i,f(\text{vib})}$  is approximately equal to  $\int_0^\infty (\alpha X) \psi_f(X) \psi_i(X) dX$ . This approximation is, however, a poor one for diatomic hydrides and, along with the neglect of rotation in the model, it is probably responsible for the poor agreement between experimental and predicted relaxation rates for such systems as  $\text{HCl}(v = 1) + \text{Ar}$ . The second matrix element

$$H'_{i,f(\text{tr})} = \int_{-\infty}^\infty C \exp(-\alpha x) F_f(x) F_i(x) dx \quad (6)$$

can be regarded<sup>9</sup> as the "overlap" of the initial and final translational state wave functions  $F_i(x)$  and  $F_f(x)$ —for which the momenta are  $p_i = h/\lambda_i = \hbar k_i$  and  $p_f = h/\lambda_f = \hbar k_f$ —on the interaction potential. Parallel curves representing  $C \exp(-\alpha x)$  for different vibrational levels within the same electronic state can then be drawn, as in Figure 2, and vibrational transitions require a horizontal "tunneling" process between these curves. Consequently,  $H'_{i,f(\text{tr})}$  is extremely small as the classical turning points on the two curves are well displaced from one another and also because  $p_i$  and  $p_f$ , and therefore  $\lambda_i$  and  $\lambda_f$ , are very different. Where other degrees of freedom, for example vibration of the collision partner or molecular rotation, can absorb some energy, these curves will be closer together and energy transfer can occur more readily.

Evaluation of eq 4 leads to the following general predictions for collision energies within the thermal range: (a)  $P_{i,f}$  will be very small, especially where the duration of the collision is much longer than the vibrational period; (b) the probabilities of molecules losing or gaining two or more quanta are very much smaller than those for  $\Delta v = 1$  processes; (c) for har-

(9) A. B. Callear, "Photochemistry and Reaction Kinetics", Cambridge University Press, London, 1967, Chapter 7.



**Figure 2.** Potential curves for the interaction of different vibronic states of BC with A where the close approach of A to BC causes a near degeneracy of the electronic states  $j$  and  $k$  to diverge. Vibrational relaxation in electronically *adiabatic* collisions requires "tunneling" transitions between parallel curves as represented by the horizontal arrows. Electronically *nonadiabatic* collisions can lead to vibrational relaxation via transitions at the crossing points, i.e.,  $x_0$  for  $(j,1) \rightarrow (k,0)$ , as represented by the dotted arrows (this figure is adapted from those in Nikitin's papers<sup>11</sup>).

monic oscillators, and to a good approximation for real molecules,  $P_{v,v-1} = vP_{1,0}$ .

For comparison with experimental data, it is necessary to allow for the distributions of orientation, impact parameter, and collision energy in a real system. The variation of the thermally averaged cross section<sup>10</sup> with temperature is then predicted to obey the relationship:  $-\log \bar{\sigma}_{1,0} \propto T^{-1/3}$ .

An additional mechanism for vibrational relaxation is present when either of the colliding species is in an electronic state with nonzero orbital angular momentum, i.e., A has  $L \geq 1$  or BC has  $\Lambda \geq 1$ . This category includes some systems which are not—in the sense defined earlier—potentially reactive, such as  $\text{NO}(X^2\Pi) + \text{Ar}(^1S_0)$ , as well as many that are, such as  $\text{X}(^2P) + \text{HX}(^1\Sigma^+)$ , where X represents a halogen atom. The interaction between A and BC now gives rise to nondegenerate electronic states, i.e., more than one potential hypersurface, with the energy between them increasing as the species approach one another. Vibrational state changes can then occur through electronically nonadiabatic transitions, which are most likely to arise where the splitting between electronic states corresponds to the vibrational transition energy.

An approximate treatment of this curve-crossing route for vibrational-energy transfer has been developed by Nikitin,<sup>11</sup> along lines similar to those outlined above for electronically adiabatic vibrational transitions. Once again the coupling between vibrational and relative translational motions is assumed to be small so that curves representing  $V(x)$  can be

(10) The "thermally averaged cross section" is defined by  $\bar{\sigma} = k(T)/\bar{c}$  where  $\bar{c}$  is average relative collision velocity. Frequently a probability is quoted which is the ratio of this cross section to that derived from transport properties assuming a hard-sphere potential.

(11) E. E. Nikitin and S. Ya. Umanski, *Faraday Discuss. Chem. Soc.*, **53**, 7 (1972); E. E. Nikitin in "Physical Chemistry, An Advanced Treatise", H. Eyring, D. Henderson, and W. Jost, Ed., Vol. 6A, Academic Press, New York, N.Y., 1974.

drawn for each vibronic state. Now, however, although the curves associated with each electronic level are parallel, those from the same vibrational level but different electronic states diverge, and this causes curves to cross where the spacings between vibrational levels and electronic states coincide.

Probabilities of vibrational energy transfer in these electronically nonadiabatic collisions are estimated making similar approximations to those in SSH theory. Where the intermolecular potentials are assumed to have exponential repulsive forms, the expression for  $P_{i,f}$  again includes a vibrational matrix element of the form given in eq 5. However,  $H'_{i,f(\text{tr})}$  is replaced by a term which expresses the probability that in an effective two-body collision initially controlled by curve  $(j,1)$  in Figure 2 the system will cross to the curve  $(k,0)$ . This is the problem originally treated by Landau and Zener. Although the wavelengths associated with relative translation on these two curves are quite different, the wave functions now overlap significantly close to  $x_0$  where they are appreciably distorted by the potentials. Consequently, if the coupling between the electronic states is reasonably strong, this calculation can yield a term greater than  $H'_{i,f(\text{tr})}$ , and then the transfer of energy will be dominated by electronically nonadiabatic collisions.

In two respects—the dependence of  $P_{i,f}$  on  $v$  and on  $\Delta v$ —Nikitin's theory for nonadiabatic collisions makes similar predictions to SSH theory for electronically adiabatic processes. In electronically nonadiabatic collisions multiquantum transitions are less likely than  $\Delta v = 1$  processes, first because  $H'_{i,f(\text{vib})}$  decreases rapidly as  $\Delta v$  increases and also because the crossing between vibronic curves associated with levels for which  $\Delta v > 1$  will occur at smaller  $x$ , so that there is generally a higher energy barrier than for  $\Delta v = 1$ . The dependence of  $P_{v,v-1}$  on  $v$  in both types of collision arises almost entirely from the vibrational matrix elements, so  $P_{v,v-1} \approx vP_{1,0}$ .

Thermally averaged cross sections have been estimated by Nikitin using both a simple collision treatment and a transition-state approach. They vary strongly with temperature if an appreciable collision energy is needed to reach the region where the vibronic states cross. If the dependence of the rate constant on temperature is marked, it is likely to be of a form expressed by the Arrhenius relationship

$$\ln k_{1,0} = \ln A - E_{\text{act}}/RT$$

Where this is the situation for a process which involves a hydride,  $E_{\text{act}}$  should be *less* for the deuteride because the crossing will occur at larger  $x$  and therefore at a lower collision energy.

The form of at least one of the hypersurfaces that characterize the interaction in collisions involving potentially reactive atoms should reflect the possibility that chemical reaction might occur. Surfaces I to IV in Figure 3 represent several possible types. On all of these, and in contrast to the behavior shown in Figure 1, the approach of A to BC tends to extend  $r_{\text{BC}}$ . One effect of this could be to promote energy transfer in nonreactive collisions—both electronically adiabatic and nonadiabatic—by increasing  $H'_{i,f(\text{vib})}$ . In addition, chemical reaction may take place. Where A and C are the same, this will yield chemically indis-

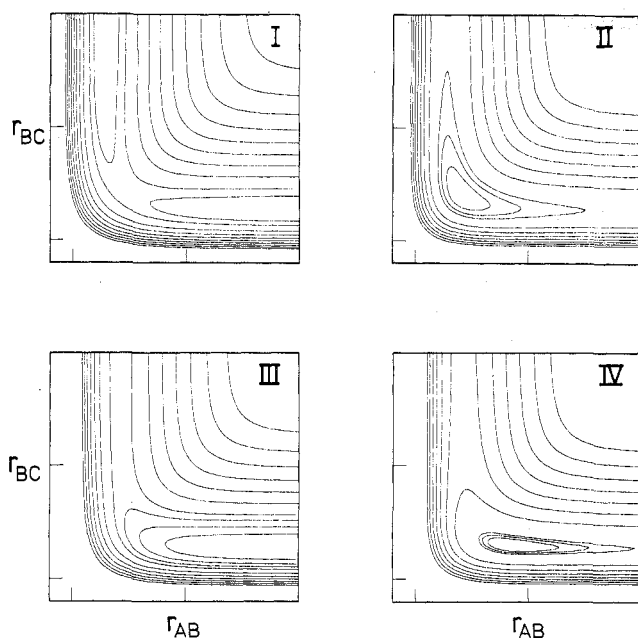


Figure 3. Potential surfaces representing different types of chemical interaction in  $A + BC$  collisions.

tinguishable products, but these collisions could bring about relaxation.

The dynamics of collisions on single potential hypersurfaces can be explored by computing classical trajectories,<sup>12</sup> and cross sections and rate constants can then be derived if Monte Carlo sampling procedures are used to select the parameters defining each collision. The use of the classical equations of motion and the necessity of slicing up the final, continuous distributions of vibrational and rotational energy into discrete distributions over product states are inherent approximations in this approach. Frequently, however, a larger source of error in calculations purporting to be on a particular system may arise through the use of an incorrect potential. Certainly the evidence for the form of the potential used in a calculation of this kind should be carefully examined, since frequently little or no firm information about the potential is available. Because of this difficulty we have tended to explore only the general features of collisions involving vibrationally excited molecules on reactive hypersurfaces, and it is these aspects that will be summarized here.

Smith and Wood<sup>13</sup> investigated symmetric (i.e.,  $A = C$ ) systems using potentials with barriers to exchange of the B atom equal to very nearly half the classical vibrational energy of  $BC(v = 1)$  for mass combinations corresponding to  $H + H_2$ ,  $Cl + HCl$ , and  $H + ClH$ . Although the rates of atom transfer were enhanced by exciting  $BC$ , the threshold and activation energies remained quite large, showing that dynamical constraints do limit the extent to which reactant vibrational energy can be utilized in surmounting the potential barrier. Large changes in vibrational energy occurred almost exclusively in either (a) reactive collisions, yielding  $AB + C$ , or (b) encounters in which the trajectory traversed the transition-state region defined by  $r_{AB} = r_{BC}$  an even number of times; these categories of collision made the

dominant contribution to the estimated rates of vibrational relaxation.

Collisions of types a and b were sufficiently frequent for the calculated rates of energy transfer to be much greater than usually found between closed-shell species. In other respects, these systems showed quite different behavior to that associated with electronically adiabatic nonchemical systems. Thus the probabilities of deactivating  $BC(v)$  to lower vibrational levels were not simply proportional to  $v$  but rose more steeply, nor, since the molecular motions were strongly coupled in the effective collisions, were transfers restricted to  $\Delta v = 1$ .

There also appear to be sufficient differences between the predicted behavior in these collisions and that in electronically nonadiabatic collisions for the predominant route causing energy transfer in any particular system to be distinguished once detailed experimental data become available. Thus, the dependence of  $P_{v,v-n}$  on both  $v$  and  $v - n$  is likely to be quite different.<sup>14</sup> In addition, deuterated molecules should relax by the curve-crossing mechanism more rapidly at low temperatures than hydrogenated species, whereas the reverse will be true for the reactive route since there is then a "normal" kinetic isotope effect.<sup>15</sup> In practice, this is the easiest difference to establish experimentally.

The dynamics of collisions between vibrationally excited molecules and atoms have also been studied on potentials of type II with symmetrically placed "wells".<sup>15,16</sup> Here, the formation of short-lived "collision complexes" is important. Where there is no barrier to the formation of these complexes (at least at certain orientations), they occur in a high proportion of trajectories, and since the motions then couple strongly, energy-transfer rates are large and not restricted to  $\Delta v = 1$  transfers. The absence of any energy barrier restricting formation of the complexes means that there is little dependence of the rates on temperature, initial vibrational excitation, or isotopic substitution. It seems likely that similar results will be found on surfaces of type IV with asymmetrically positioned minima.

Trajectories on surfaces of type III have been calculated for several mass combinations by Perry et al.<sup>17</sup> However, their primary concern was to investigate how the reactive cross sections depended on the selective excitation of different degrees of freedom of the reactants, and they did not report on the transfer of energy in trajectories where reaction did not take place. Preliminary calculations in this laboratory indicate that rapid relaxation may occur if  $AB$  is sufficiently excited for some of the trajectories to penetrate the region where the path of minimum energy is sharply curved.<sup>18</sup> In collisions of  $Br$  with  $HCl$  it appears that this may occur for  $v = 2$  but not for  $v = 1$ , so relaxation of these states may occur at very different rates.

In this section an attempt has been made to pro-

(14) The dominant mechanism for removal of vibrationally excited molecules will not, of course, necessarily be the same for different  $v$  and  $T$ .

(15) I. W. M. Smith, *J. Chem. Soc., Faraday Trans. 2*, 71, 1970 (1975).

(16) E. L. Breig, *J. Chem. Phys.*, 51, 4539 (1969).

(17) D. S. Perry, J. C. Polanyi, and C. W. Wilson, *Chem. Phys.*, 3, 317 (1974).

(18) A useful criterion for these collisions is that the trajectory crosses the surface defined by  $(r_{AB}/r_{e,AB}) = (r_{BC}/r_{e,BC})$ .

(12) R. N. Porter, *Annu. Rev. Phys. Chem.*, 25, 317 (1974).

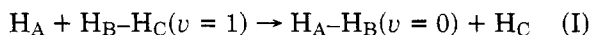
(13) I. W. M. Smith and P. M. Wood, *Mol. Phys.*, 25, 441 (1973).

vide a brief and simple description of two distinct routes that might cause vibrationally excited molecules to be removed rapidly when they collide with potentially reactive atoms, and to contrast the behavior that might be expected in each case, not only with each other, but also with that where chemical effects are absent. It appears that it will be possible to decide which mode of relaxation is predominant in any system once values of  $P_{v,v-n}$  have been obtained at different temperatures, for a range of  $v$  and  $n$ , and, where possible, for different isotopic variants. On the other hand, ignorance of the nature of the potential hypersurface and approximations in the treatment of the collision dynamics are likely to prevent *accurate* theoretical predictions of relaxation rates in collisions of this type.

### Collisions between $1\Sigma$ Molecules and S-State Atoms

The interaction of species with zero electronic orbital momentum (i.e.,  $L = \Lambda = 0$ ) but nonzero spin gives rise to a single, degenerate, electronic state of  $\Sigma$  type in  $C_{\infty v}$  symmetry and  $A'$  or  $A''$  character in  $C_s$  symmetry. Consequently, these collisions must be electronically adiabatic.

Collisions between  $H(2S)$  and  $H_2(1\Sigma_g^+)$  are an important example in this category. The rate constant for relaxation<sup>19</sup> of  $H_2(v = 1)$  by H atoms is  $3.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , corresponding to  $\bar{\sigma}_{1,0} = 0.01 \text{ \AA}^2$ , which is  $1.8 \times 10^3$  times greater than the cross section for V-T relaxation by  $H_2$  itself and  $1.5 \times 10^3$  times larger than the cross section for the atom-transfer reaction involving  $H_2(v = 0)$ . Heidner and Kasper<sup>20</sup> attributed their result to collisions in which a hydrogen atom was transferred, i.e.



The form of the potential for  $H_3$ —in particular the height of the barrier to atom transfer—is well known. In view of this, and of the fact that quantum effects might be particularly large in this system, it is encouraging that estimates of the rate of (I) based on classical trajectory calculations<sup>13</sup> are in good agreement with Heidner and Kasper's result and confirm their suggestion that energy transfer occurs in reactive collisions (along with collisions in which A + BC separate, the surface  $r_{AB} = r_{BC}$  having been crossed an even number of times).

Collisions of hydrogen halides with H atoms must also be electronically adiabatic. Arnoldi and Wolfrum<sup>21</sup> have studied the relaxation of  $HCl(v = 1)$  by H using laser-induced fluorescence. They determined  $\bar{\sigma}_{1,0} = 0.26 \text{ \AA}^2$  and found evidence that the (distinguishable) chemical reaction producing  $H_2 + Cl$  did not occur. Relaxation via  $H_A + Cl_B H_C(v = 1) \rightarrow H_A Cl_B(v = 0) + H_C$  seems likely, as the thermal isotope exchange reaction,  $H + DCl \rightarrow HCl + D$ , has a low activation energy.<sup>22</sup> Wolfrum's results may have a bearing on the relative probabilities of the two thermal reactions about which there is unresolved controversy.<sup>22</sup>

The situation with regard to relaxation of HF ( $v = 1$ ) by H atoms is confused. Measurement of this rate is not straightforward because of rapid V-V energy exchange between HF and  $H_2$ , the difficulty of producing H in the absence of  $H_2$  (and possibly also  $H_2^+$ ), and the relaxation of  $H_2^+$  as well as  $HF^+$  by H. Heidner and Bott<sup>23</sup> give  $\bar{\sigma}_{1,0} = 9 \times 10^{-3} \text{ \AA}^2$ , but this is considerably higher than the upper limit of  $6 \times 10^{-4} \text{ \AA}^2$  deduced by Quigley and Wolga.<sup>24</sup> Of the trajectory calculations that have been carried out, Thompson's<sup>25</sup> seem the most useful since the barrier height to F-atom transfer on his potential (28.6 kcal/mol) is closest to ab initio estimates<sup>26</sup> ( $\geq 40$  kcal/mol). Thompson calculated relaxation rates that were quite strongly temperature dependent, and his data extrapolate to a room-temperature value of  $k_{1,0}$  quite close to Bott and Heidner's measured value.

At the present time the balance of evidence appears to favor the conclusion that relaxation of HF ( $v = 1$ ) by H atoms is not *exceptionally* fast at room temperature, compared with some other relaxation processes induced by potentially reactive atoms, and that it probably occurs in adiabatic, nonreactive collisions. If this is so, the effective collisions may be those in which the "free" H atom impacts on the bound H atom, since this provides a favorable mass combination for energy transfer and because the H-H-F surface—which is of type III—may allow strong coupling between the vibrational and relative translational motions.

### Collisions between Hydrogen Halides and P-State Atoms

The interaction of hydrogen halides and P-state atoms, such as halogen and oxygen atoms in their ground states, gives rise to  $\Sigma$  and  $\Pi$  states in linear ( $C_{\infty v}$ ) configurations. In nonlinear ( $C_s$ ) geometries, the  $\Sigma$  state becomes  $A'$  or  $A''$  and the  $\Pi$  state splits, yielding  $A'$  and  $A''$  states; the multiplicity of all three states is the same as that of the isolated atom. Consequently, there are several potential hypersurfaces that correlate with the separated atoms, and during collisions electronically nonadiabatic transitions may occur. Relaxation of HF ( $v = 1$ ) and HCl ( $v = 1$ )—as well as of the deuterated molecules—by halogen and O( $^3P$ ) atoms has been studied by laser-induced fluorescence. The systems for which results are presented in Table I can be divided into two categories: (a) those where transfer of an H atom is thermoneutral,  $F + HF(DF)$  and  $Cl + HCl(DCl)$ , or nearly so,  $O + HCl(DCl)$ ; and (b) those where this reaction is endothermic even where the molecule is initially in  $v = 1$ , i.e.,  $Cl + HF(DF)$ ,  $O + HF(DF)$ , and  $Br + HCl(DCl)$ .

For the latter systems, energy might be transferred in collisions where the "attacking" atom approaches the H or D end of the molecule so the dynamics are controlled by a surface of type III. However, the ap-

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(19) Unless a temperature is stated, data quoted in this section are from room-temperature measurements.

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Table I  
Thermally Averaged Cross Sections ( $\text{\AA}^2$ ) for Deexcitation of Hydrogen and Deuterium Halides by Halogen and Oxygen Atoms at Room Temperature

	F	Cl	Br	O
HF( $v = 1$ )	0.035	0.11		0.37
DF( $v = 1$ )	0.082	0.29		0.93
HCl( $v = 1$ )		1.45	0.06	0.14
DCI( $v = 1$ )		1.11	0.14	0.17

precipally larger excitation energy of  $\text{HX}(v = 1)$  compared with  $\text{DX}(v = 1)$  should facilitate energy transfer since there would then be a greater likelihood of the trajectory reaching a point where the motions become strongly coupled. However, in all these cases,  $\text{DX}(v = 1)$  relaxes more rapidly than  $\text{HX}(v = 1)$ , which suggests strongly that these states relax predominantly in electronically nonadiabatic collisions—although electronically adiabatic collisions (possibly leading both to energy transfer and reaction) can clearly become important for higher vibrational levels.<sup>27</sup>

For the symmetric, thermoneutral systems interpretation is clouded by uncertainty about the barrier heights for H-atom transfer. For  $\text{F} + \text{HF}$ , ab initio calculations<sup>28</sup> predict a value of  $\geq 18$  kcal/mol, and some trajectory calculations<sup>29</sup> have been carried out on an appropriate potential hypersurface. The estimates of  $k_{1,0}$  are somewhat lower than those found experimentally, and the calculations also predict that  $\text{HF}(v = 1)$  should relax more rapidly than  $\text{DF}(v = 1)$ , contrary to what is observed. It therefore appears likely that—at least at low temperatures—the curve-crossing mechanism is mainly removing  $\text{HF}(v = 1)$  and  $\text{DF}(v = 1)$  in collisions with F atoms. The relatively marked increase of rate with temperature<sup>24,30</sup> probably reflects the essentially repulsive nature of the lowest  $\text{F} + \text{HF}$  potential.

As we have recently published papers on the relaxation of HCl and DCI by O and Cl atoms,<sup>15,31–33</sup> only brief comments about these systems will be made here. The extremely efficient deactivation by Cl atoms appears to be most readily explained by a reactive mechanism, although this requires a barrier to this process which is lower than can be consistent with measurements<sup>34</sup> on the thermal isotope exchange reaction:  ${}^i\text{Cl} + \text{HCl} \rightarrow {}^i\text{ClH} + \text{Cl}$ . Relaxation by atomic oxygen is slower, and DCI is relaxed twice as fast as HCl at 195 K; this again seems to suggest that a curve-crossing mechanism for energy transfer is predominant.

In summary, the results of studies on HF, DF, HCl, and DCI suggest that these molecules can be relaxed

quite readily in electronically nonadiabatic collisions with atoms for which  $L > 0$ . This conclusion supports the view put forward by Quigley and Wolga.<sup>24</sup> The electronically adiabatic reactive process may only become competitive where the cross section is  $\geq 0.01 \text{\AA}^2$ . Whether this is so will depend generally on the height of the energy barrier relative to the vibrational excitation energy of the reactant, but it does not seem as if all this energy can normally be employed in surmounting the energy barrier.

### Collisions of $\text{O}({}^3\text{P})$ with $\text{O}_2$ , CO, and $\text{N}_2$

In these three systems the triatomic species, i.e.,  $\text{O}_3$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$ , are known as stable molecules. However, their similarity is somewhat superficial since the electronic states and their interactions are quite different in each case.

Only for  $\text{O}({}^3\text{P}) + \text{O}_2({}^3\Sigma_g^-)$  is there a direct correlation between the separated species and the ground electronic state of the triatomic molecule—although this  ${}^1\text{A}_1$  state of  $\text{O}_3$  is apparently the only bound state of the 27 that are directly accessible to the colliding species. Useful empirical information regarding the frequency of strong-coupling collisions between  $\text{O}({}^3\text{P})$  and  $\text{O}_2({}^3\Sigma_g^-)$  is provided by “conventional” kinetics experiments of two kinds: (i) isotope exchange<sup>35</sup> occurs at  $298 \leq T \leq 402$  K with a rate constant  $k_{\text{ex}} = 6.5 \times 10^{-12} \exp(-1.1 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and (ii) the limiting high-pressure rate constant for association to  $\text{O}_3$  is  $k^\infty = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.<sup>36</sup> Based on the findings from trajectory calculations one would expect deactivation of  $\text{O}_2^\dagger$  by O atoms to occur at roughly the same rate as these two processes, even if no other mechanism was contributing to relaxation.

Shock tube measurements<sup>37</sup> yield a relaxation time for  $\text{O}_2$  by O atoms that is essentially independent of temperature for  $1000 \leq T \leq 3500$  K and corresponds to a rate constant of approximately  $8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ( $\bar{\sigma} = 0.4 \text{\AA}^2$ ) at 2000 K. In addition, results have been obtained<sup>38</sup> for  $\text{O}_2$  ( $14 \leq v \leq 19$ ) in room-temperature experiments. The interpretation of these latter experiments was not straightforward, but Webster and Bair were able to determine a rate constant for removal of  $\text{O}_2(v = 19)$  to all lower states of  $\sim 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ( $\bar{\sigma} = 4 \text{\AA}^2$ ).

Any conclusions regarding the mechanism of vibrational relaxation in  $\text{O} + \text{O}_2^\dagger$  collisions must, at the present time, be tentative. However, there seems little doubt that the association–dissociation process on the ( ${}^1\text{A}_1$ ) hypersurface will alone provide for efficient relaxation.<sup>39</sup> At higher temperatures or for higher vibrational levels of  $\text{O}_2$ , additional reactive, electronically adiabatic mechanisms may contribute. This would result from reactive encounters over hypersurfaces corresponding to electronically excited, non-

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bound states of  $O_3$  with only low barriers to the atom-exchange reaction. At the present time there does not seem to be compelling evidence for invoking curve-crossing collisions of the type treated by Nikitin.<sup>11</sup>

For both  $O(^3P) + CO(^1\Sigma^+)$  and  $O(^3P) + N_2(^1\Sigma_g^+)$ , formation of the  $^1\Sigma^+$  ground state of the triatomic molecule is "spin forbidden". The limiting high-pressure rate constant for association of O atoms with CO is given by<sup>36</sup>  $k^\infty = 2.7 \times 10^{-14} \exp(-2.93 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , the low value of the preexponential factor reflecting the necessity for a spin change. A quite different Arrhenius expression is obtained from studies on the isotope exchange reaction<sup>35</sup> at temperatures between 298 and 398 K:  $k_{ex} = 1.0_3 \times 10^{-10} \exp(-6.9 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and this suggests that there is a spin-allowed route for C-atom transfer with only a moderately low energy barrier on this reaction path. If this interpretation is correct, then there appears to be little doubt that the spin-allowed reactive mechanism will be the more important of these two in collisions involving  $CO^\dagger$ .

The only published results<sup>40</sup> on relaxation of  $CO^\dagger$  by O atoms are for  $1800 \leq T \leq 4000 \text{ K}$ . At 2000 K, the rate constant is  $6.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ( $\bar{\sigma} = 0.33 \text{ \AA}^2$ ) and shows a positive temperature dependence. It seems that at the high temperatures of these shock tube measurements the electronically adiabatic exchange reaction could proceed for  $CO^\dagger$  sufficiently fast to provide the dominant mechanism for relaxation.<sup>41</sup> Once again, however, rate determinations over a wider range of temperature and vibrational state are required before the relative importance of this mechanism and inelastic curve-crossing collisions can be established with certainty.

Association of  $O(^3P)$  atoms with  $N_2(^1\Sigma_g^+)$  has never been observed. Not only is the route to  $N_2O(^1\Sigma^+)$  spin forbidden, but Troe and Wagner<sup>36</sup> suggest that the triplet and singlet potential hypersurfaces cross at an energy  $\sim 25 \text{ kcal/mol}$  above the energy of the separated species. This appears to preclude formation of  $N_2O(^1\Sigma^+)$  as an efficient mecha-

nism for relaxation of  $N_2^\dagger$ , at least for the low-lying vibrational levels at moderate temperatures. An alternative is that energy transfer occurs as a result of electronically adiabatic collisions on the hypersurface (of type III) leading to  $N(^4S) + NO(X^2\Pi)$ . However, this reaction is so endoergic that it appears unlikely that any appreciable proportion of collisions will reach regions of the surface where the vibrational and translational motions couple strongly.

Measurements on the relaxation of  $N_2^\dagger$  by atomic oxygen cover the whole temperature range from 300 to 4400 K.<sup>42</sup> The rate constant, in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , increases from  $3.2 \times 10^{-15}$  at 300 K ( $\bar{\sigma} = 4.0 \times 10^{-4} \text{ \AA}^2$ ) to  $4.0 \times 10^{-14}$  at 723 K ( $\bar{\sigma} = 3.3 \times 10^{-3} \text{ \AA}^2$ ) to  $1 \times 10^{-12}$  at 4000 K ( $\bar{\sigma} = 3.5 \times 10^{-2} \text{ \AA}^2$ ). It certainly seems that for at least the lower end of this temperature range relaxation must be dominated by collisions in which the system crosses between the  $^3A' + 2^3A''$  hypersurfaces that correlate with the separated species.<sup>11</sup>

### Summary

The emphasis in this article has been placed on the factors which one should take into consideration when attempting to predict or interpret the results of collisions between vibrationally excited molecules and potentially reactive atoms. Particular systems were chosen for discussion to illustrate the different kinds of possible behavior with some actual examples, and to show how these possibilities depend critically on the number and nature of the electronic states that are accessible to the colliding species. The overall impression is probably of a field which is almost devoid of systems where the experimental results can be provided with a detailed and certain theoretical explanation. This is, however, a true reflection of the present state of knowledge in an area of molecular collision dynamics where much research remains to be done.

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