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REACTIONS OF VIBRATIONALLY EXCITED MOLECULES

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Reactions of Vibrationally Excited Molecules

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I. Introduction

The energy dependence of the chemical reaction rate is traditionally studied under conditions in which the rate of reaction is slow compared to that of collisional energy transfer. Under these conditions the energy of the reactants can be characterized by a temperature; the temperature variation of the reaction rate constant can be expressed often with sufficient accuracy by the Arrhenius equation. Deviations of experimental data for bimolecular reactions from the simple Arrhenius equation are discussed in detail in the contribution by Fontijn and Zellner (Chapter 1). Arrhenius parameters contain, however, no direct information on how the various degrees of freedom in the reacting molecules and in the "activated complex" contribute to overcoming the potential energy barrier of the reaction. Information on chemical reactivity as a function of specific excitation of the reactants can

give important insights into the microscopic dynamics of a chemical reaction, i.e. into the process of bond breaking under the influence of new bond formation. This knowledge is also of basic interest for potential practical applications in which external energy is used to drive chemical reactions more selectively than by using thermal heating. Despite the progress made in recent years in calculating wave functions for polyatomic systems, we are still far from obtaining such information quantitatively by *ab initio* theoretical calculations for many systems. Experimental investigations of reactions of state selected molecules are especially interesting for degrees of freedom for which a nonequilibrium population of excited states can be maintained for some time, so that the enhanced chemical reactivity can compete with energy transfer processes. Excitation of relative translation and rotation of the reactants will relax to equilibrium within a few collisions. Longer lifetimes can be expected for vibrational and electronic excitation. The chemistry of electronically excited species is described in the following chapters by Breckenridge (Chapter 4) and Slinger (Chapter 5).

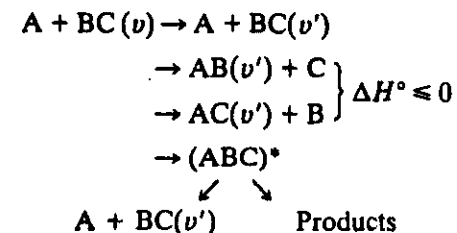
A relation between chemical reactivity and the effectivity of vibrational energy transfer was suggested fifty years ago by Franck and Eucken (1933). Indirect experimental evidence for the dependence of the rates of bimolecular atom exchange reactions on vibrational excitation rather than on total energy was reported by Bauer and Resler (1964). More systematic studies have become possible only recently, especially with the development of powerful laser light sources. The coherence, collimation, monochromaticity, high quantum flux, polarization, short pulse duration and tunability of laser light sources now available in the infrared, visible and ultraviolet allow the preparation and detection of vibrationally excited molecules with an unprecedented degree of selectivity. After the first report on the isotropic selective dissociation of a highly vibrationally excited polyatomic molecule in the electronic ground state by high power infrared lasers (see e.g. Letokhow, 1975), a large number of experimental and theoretical investigations were focussed on unimolecular reactions induced by monochromatic infrared radiation. However, as discussed in Chapter 2 by Luther and Troe, near the dissociation threshold the density of states becomes very high and intramolecular energy migration very fast. For a more detailed understanding in terms of elementary processes, bimolecular reactions with lower potential energy barriers involving low vibrational energy levels of the reacting molecules are more suitable. In the present chapter examples for bimolecular reactions of vibrationally excited neutral molecules in the electronic ground state and in the gas phase will be considered. The examples are selected according to the total number of atoms in the reacting system. Typical experimental arrangements are dis-

cussed and experimental results will be compared with the predictions of various theoretical models.

In this chapter $\dot{A} = 0.1$ nm is used to identify interatomic distances.

II. Reactions of Atoms with Vibrationally Excited Diatomic Molecules

The simplest system in which the effect of selective vibrational excitation can be studied is that of reactions of free atoms with vibrationally excited diatomic molecules. The various channels for removal of the vibrationally excited molecules $BC(\nu)$ may be written as



As discussed in Chapter 1, most of the different reaction types mentioned above show similar behaviour in the variation of the total reactive cross section as a function of the relative translational energy of the reactants. After reaching a maximum beyond a certain threshold energy the reactive cross section decreases for high translational energies due to the shortening of the interaction time of the reactants at high relative velocities. A much more varied picture is obtained for vibrational excitation. Thus, no simple functional form or correlation could be found for experimental data on reactions of vibrationally excited molecules.

A. Reactions of Vibrationally Excited Hydrogen Molecules

The exchange reaction between a hydrogen atom and a hydrogen molecule provides the simplest case where for neutral species the kinetic process of bond breaking under the influence of new bond formation can be studied experimentally and theoretically. In the development of microscopic models for the theoretical description of chemical reactions, the H_3 -system plays a central role as the simplest bimolecular reaction of neutral species. The theoretical determination of macroscopic rate parameters in the H_3 (and any other systems) can be divided into three major steps:

1. Construction of the Born–Oppenheimer potential energy hypersurface of the reaction complex, i.e. the determination of the potential energy

as a function of the coordinates of the particles involved. Within the framework of the Born–Oppenheimer approximation isotopic substitution has no effect on the surface.

2. Description of the dynamics of the chemical reaction on the potential energy hypersurface, i.e. the dependence of the temporal development of the system from the given initial states and the calculation of transmission amplitudes between initial and final states in the form of specific cross sections.
3. Evaluation of macroscopic reaction rate constants assuming partial or total Maxwell–Boltzmann distribution in the energy of external and internal energy states of the reacting particles. In the case of reactions with vibrationally excited species specific rate constants of selected vibrational states can be compared with experimental results.

As shown in Fig. 1 it is often necessary to refer to different approximations during the steps of the calculations. The recently reached standard in the theoretical treatment of the H_3 system is supposed to be very near to quantum mechanical reality. The different steps will now be discussed in detail.

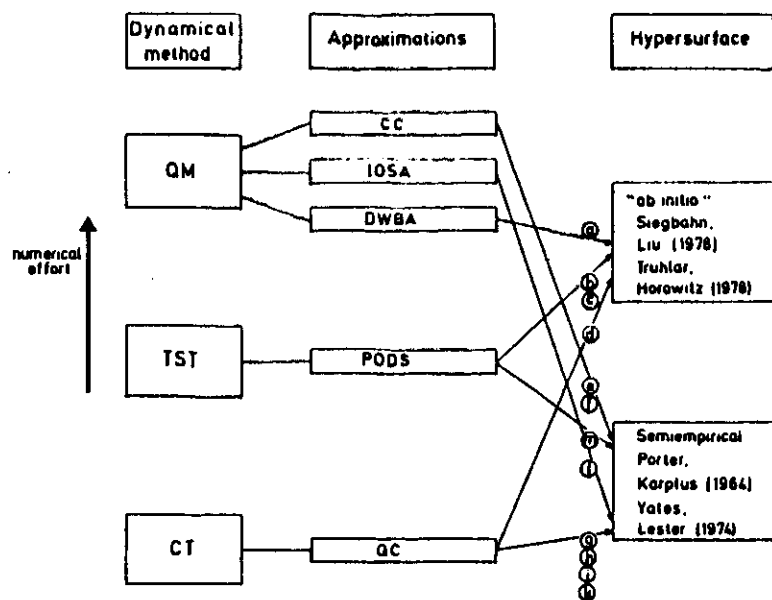


Fig. 1. Survey of various methods for the theoretical determination of rate parameters in the H_3 -system (for symbols see text). (For references (a)–(m) see Table I).

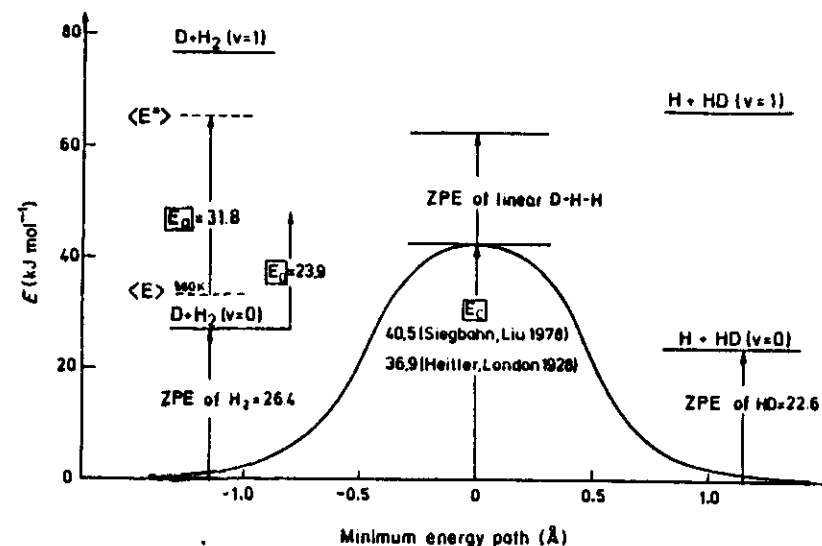


Fig. 2. Characteristic energies for the $D + H_2(v)$ reaction.

1. Potential energy hypersurface of the H_3 system

More than half a century ago London (1928) first pointed out that the $H + H_2$ reaction can be understood in terms of a quantum mechanically calculated potential energy surface. London regarded the H_3 complex as a superposition of three H_2 molecules. The potential energy of the H_3 system was expressed in terms of three coulombic interaction integrals and three exchange integrals. As shown in Fig. 2 this simple valence bond calculation leads to a potential energy barrier $E_c = 36.9 \text{ kJ mol}^{-1}$, not far from the result obtained with modern high speed electronic computing devices. However, a more precise treatment of the London method including contributions resulting from overlap and three centre terms destroys the good, accidental agreement with modern results. The unsatisfactory results of the early *ab initio* approaches led to the development of semi-empirical treatments. In the London–Eyring–Polanyi (LEP) procedure the coulombic interaction integrals were approximated by a Morse function multiplied by a constant factor. Sato (1955) later replaced this adjustable factor by the square of the Heitler–London overlap integral. The best modern semi-empirical H_3 surface was generated by Porter and Karplus (1964). They used the complete formulae for the non-ionic valence bond treatment for the three-orbital three-electron system given by Slater (1931).

The integrals were evaluated by a combination of theoretical and semi-empirical treatments. More recently it was possible to construct a modern *ab initio* surface for the H₃ system. *Ab initio* means in this case, that for important and well chosen constellations of the hydrogen nuclei the exact determination of the corresponding potential energy is achieved by starting with the Born–Oppenheimer approximation and the Coulomb law without using any thermodynamic or spectroscopic data. In the order of 150 thoroughly selected *ab initio* points were calculated by Siegbahn and Liu (1978) and fitted to an analytical function which represents the potential energy hypersurface mathematically in a smooth and easily handleable way by Truhlar and Horowitz (1978). Although this surface is an enormous advance in modelling chemical reactions, it should be kept in mind, that the accuracy of the fit in the different regions of the surface depends strongly on the choice of the *ab initio* points.

2. Reaction dynamics of the H₃ system

The central point of chemical dynamics is the determination of the probability of ending with a defined final state of products from a well defined initial state of reactants. In the context of quantum mechanics this means: what is the probability that a given initial state, which can be described by a linear combination of eigenfunctions of a system in the reactant region couples with different product channels, which can be described by a linear combination of eigenfunctions in the product region. In general one has to consider a change in the coordinate system in the collision process, since the eigenfunctions of the reactants and products are usually not orthogonal. The probability P_{if} for a transition of one initial state i to the final state can be described by a transition matrix S_{if} ; so that

$$P_{if} = |S_{if}|^2. \quad (1)$$

The numerical effort of a dynamical calculation increases rapidly with the size of the S -matrix, i.e. the number of coupled states that have to be considered in the dynamical model. Therefore a number of quantum mechanical approximation methods were developed in order to keep the number of matrix elements as small as possible.

The most accurate approximation is the j_z -conserving or centrifugal-sudden approximation, where certain off-diagonal terms in the kinetic energy expression, which couple the body fixed projection states, are neglected (Elkowitz and Wyatt, 1976; Kuppermann *et al.*, 1977). However, this approximation still involves a considerable numerical effort.

Searching for further simplifications one comes to the rotational sudden approximation (IOSA), which neglects the coupling between the different rotational states (Bowman and Lee, 1980; Baer *et al.*, 1980). Although these approximations introduce considerable interventions into the system (the j_z conserving method interferes with the law of conservation of angular momentum, and the rotational sudden approximation even affects the law of conservation of energy) all the qualitative features of the reaction dynamics are preserved and the introduction of these approximations into the system is the foundation for calculating more complex systems.

Another quantum treatment of reactive scattering is the so-called Distorted-Wave-Born-Approximation (DWBA; Sun *et al.*, 1980; Clary and Connor, 1980). The method involves the solution of a nonreactive elastic scattering problem for reactants on the one side, and the analogous problem on the product side. After that, the transition amplitude is calculated, using the full potential surface. The DWBA approach can relatively easily be generalized to other reactions in three dimensions and gives good results in predicting the distribution of the states in the different product channels (Shan *et al.*, 1978; Clary and Connor, 1979).

Besides the various quantum mechanical approximations, the dynamics of the chemical reaction can also be described as the motion of a "billiard-ball passing through the mountains and valleys" of the potential energy surface (CT). Contrary to the classical case, where initial conditions like vibration, rotation and translation are continuously adjustable, quantum mechanics in general allows only discrete values for the energy of the system. The quantisation of the initial and final conditions of a system on one side, and the maintaining of the picture of the classical trajectory on the other side is characteristic of the quasiclassical theory (QC). With the quasiclassical complex trajectory method tunnelling probabilities can also be determined quite accurately. Nevertheless, the method is rather difficult to apply, particularly in three dimensions (Doll *et al.*, 1973).

Another approach is transition state theory (TST) as discussed in detail in the previous chapter. Rate constants derived from TST calculations always provide an upper bond of the exact rate constant. To minimize the TST rate some variational methods have been developed.

Recently the method of periodic orbit dividing surfaces (PODS) has been introduced to treat a collinear atomic–diatomic system (Pechukas and Pollak, 1979). By combining TST-methods with methods for determining tunnelling probabilities, rate constants for the H + H₂ reaction in three dimensions have been obtained, which are in excellent agreement with quantum close coupling calculations (CC) on the Porter–Karplus surface (Garrett and Truhlar, 1979, 1980a).

3. Comparison of calculated and measured rates for vibrationally excited H₂ molecules

As shown in Fig. 2 single quantum vibrational excitation of the H₂ molecule exceeds the Arrhenius activation energy (E_a), the threshold energy (E_0) as well as the classical barrier height (E_c) of the reaction D + H₂. This reaction including the isotopic equivalents is therefore very suitable for a detailed comparison of theoretical and experimental results on the effect of vibrational excitation on the dynamics of a chemical reaction. Table I gives an overview of the results obtained so far. Experiments however, are hampered by the difficulties in preparing known concentrations of vibrationally excited hydrogen molecules which are not infrared active. One experiment (Gordon *et al.*, 1978) employed a hydrogen maser technique to measure the rate constant of hydrogen atom exchange with thermally generated H₂, HD and D₂ in the ($v = 1$) state at 300 and 356 K. In another experiment (Kneba *et al.*, 1979) the excitation of H₂ ($v = 1$) was achieved by an indirect excitation technique using energy transfer from laser-excited HF ($v = 1$). The H atoms formed during the reaction D + H₂ ($v = 1$) were followed by Lyman- α resonance absorption. The most recent experiment by Glass and Chaturvedi (1982) used a microwave discharge for generation of H₂ ($v = 1$) and ESR spectroscopy for H and D atom detection. As shown in Table I there is still a wide scatter among the experimental data and between experimental and theoretical results. The rate constant measured for the vibrational nonadiabatic reaction plus inelastic deactivation channels is significantly lower than the total rate measured for the exchange reaction. The dominance of the adiabatic route and the magnitude of the experimental vibrational rate enhancement both depart considerably from theoretical predictions. A central point in this comparison of calculated and measured rates is the question of whether the observed discrepancies are caused by insufficient accuracy of the potential energy hypersurface in the region, which is important for the reaction of H₂ ($v = 1$). In calculations using quantised periodic orbits a barrier has been found on the $v = 1$ adiabatic surface in the entrance channel far from the saddle point (Pollak, 1981). Extension of this calculation to three dimensions (Pollak and Wyatt, 1983) gives a barrier of 18.3 kJ mol⁻¹ in good agreement with exact quantum calculations (Walker *et al.*, 1978). Since the barrier is found far away from the saddle point where only a few *ab initio* points are calculated, more points must be generated in this region for comparison with experiment. Clearly, the disagreement between theory and experiment for this reaction, which should be the best-understood of all chemical processes, surely provides a continuing theoretical and experimental challenge. Better agreement between experiment and theory is obtained for the

Table I. Comparison of experimental and calculated rate constants for the H₂-system

H + H ₂ Reactive $k_{0 \rightarrow \text{all}}$	Rate constant (300 K) (cm ³ molecule ⁻¹ s ⁻¹)				Surface and dyn. method	Reactive $k_{1 \rightarrow \text{all}}$	Surface and dyn. method	Surface and dyn. method
	Surface and dyn. method	Reactive $k_{1 \rightarrow 0}$	Surface and dyn. method	Total $k_{1 \rightarrow 0}$				
3.1×10^{-16}	PK, QC ^g	1.3×10^{-13}	PK, QC ^h	1.8×10^{-13}	PK, QC ^h	4.0×10^{-13}	PK, QC ^h	PK, QC ^h
9.9×10^{-16}	PK, CC ⁱ	1.6×10^{-13}	PK, IOSA ⁱ	6.0×10^{-14}	YL, QC ^h	8.3×10^{-13}	PK, QC ^h	PK, QC ^h
2.2×10^{-16}	YL, CC ⁱ	4.3×10^{-12}	YL, CC ⁱ	1.7×10^{-11}	YL, QC ^h	5.6×10^{-13}	PK, IOSA ⁱ	PK, IOSA ⁱ
1.2×10^{-16}	SLTH, QC ^h	5.5×10^{-14}	SLTH, QC ^h	7.3×10^{-14}	SLTH, QC ^h	8.5×10^{-14}	YL, QC ^h	YL, QC ^h
9.3×10^{-17}	SLTH, DWBA ^a	5.4×10^{-14}	SLTH, DWBA ^a	3.0×10^{-13}	Exp. ^p	5.0×10^{-12}	YL, CC ⁱ	YL, CC ⁱ
1.95×10^{-16}	SLTH, TST ^b					1.3×10^{-13}	SLTH, QC ^h	SLTH, QC ^h
2.6×10^{-16}	Exp. ^q					5.0×10^{-13}	SLTH, DWBA ^a	SLTH, DWBA ^a
						5.2×10^{-12}	Exp. ^r	Exp. ^r
D + H ₂								
Rate constant (300 K) (cm ³ molecule ⁻¹ s ⁻¹)								
Reactive $k_{0 \rightarrow \text{all}}$	Surface and dyn. method	Reactive $k_{1 \rightarrow \text{all}}$	Surface and dyn. method					
2.2×10^{-16}	SLTH, TST ^c	1.67×10^{-13}	SLTH, QC ^h					
3.1×10^{-16}	Exp. ⁿ	0.98×10^{-12}	Exp. ⁱ					
		1.2×10^{-11}	Exp. ^j					

^a Sun *et al.* (1980); ^b Garrett and Truhlar (1979); ^c Garrett and Truhlar (1980); ^d Mayne and Toennies (1979); ^e Redmon (1979); ^f Schatz and Kuppermann (1976); ^g Karplus *et al.* (1965); ^h Mayne (1979); ⁱ Osherov *et al.* (1978); ^j Smith (1977); ^k Bowman and Lee (1979); ^l Pollak (1981); ^m Mitchell and LeRoy (1973); ⁿ Schultz and LeRoy (1965); ^o Heidner and Kasper (1972); ^p Gordon *et al.* (1978); ^q Kneba *et al.* (1979); ^r Mayne and Toennies (1981); ^s Glass and Chaturvedi (1982).

$O(^3P) + H_2 (\nu = 1)$ reaction. Light (1978) has measured the rate of production of OH ($\nu = 0, 1$) using laser-induced fluorescence.

A total reaction rate constant of $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained at 302 K with a branching ratio OH ($\nu = 0$)/OH ($\nu = 1$) of 0.5. The reported rate for $H_2 (\nu = 1)$ is about 2×10^3 times higher than that measured for thermal H_2 at room temperature and confirms a previously (Birely *et al.*, 1975) reported upper bound. The large vibrational rate enhancement led to the suggestion that differences in the reported rate constant values for thermal H_2 at low temperatures might be explained by the presence of vibrationally excited H_2 in these studies. Theoretical calculation on the $O + H_2$ reaction (Schinke and Lester, 1979; Clary *et al.*, 1979) are consistent with the experimental findings. They not only predict the observed large vibrational reaction rate enhancement but also predict the branching ratio OH ($\nu = 0$)/OH ($\nu = 1$).

Large vibrational rate enhancements have also been found for the Cl, Br and I atom reactions with $H_2 (\nu)$ in theoretical (Raff *et al.*, 1970; Porter *et al.*, 1973; Gray *et al.*, 1978) and experimental (Stedman *et al.*, 1970; Sims *et al.*, 1975) studies. As expected, the most endothermic reaction, $I + H_2$, gives the highest acceleration and the thermal reaction occurs almost exclusively through excited vibrational states of H_2 . However, it should be emphasized that a quantitative interpretation of the experimental studies is difficult as they cannot separate the possibly large contributions from the higher H_2 vibrational states and they do not measure the fraction of excited H_2 . A dramatic reaction rate enhancement was reported for $Br + H_2$ in a direct study using simultaneous spin orbit and vibrational excitation (Nesbitt and Leone, 1980).

B. Reactions of Vibrationally Excited Hydrogen Halides

Vibrationally excited hydrogen halides HX ($X = F, Cl, Br, I$) are well suited for direct investigations of the effect of vibrational energy on the reactivity. Hydrogen halides undergo a great number of atom reactions with energy barriers that can be overcome by one or a few HX vibrational quanta. It is relatively simple to prepare them in excited vibrational states by exothermic pre-reactions or by direct optical pumping with hydrogen halide chemical lasers and to study their behaviour in the presence of atoms by observing the depletion of infrared chemiluminescence or the infrared fluorescence decay. To distinguish between reactive and inelastic pathways it is necessary to measure the absolute consumption of reactants and/or formation of products. This is a general problem in direct studies of

reactions of vibrationally excited molecules that have been overcome so far only in a rather limited number of experiments.

An indirect method for deriving information about the detailed rate constants and the energy consumption for endothermic reactions involving hydrogen halides applies relationships based on the principle of microscopic reversibility (Anlauf *et al.*, 1969; Kaplan *et al.*, 1976). The method is especially useful in providing information on the vibrational state specific rate constants of highly endothermic chemical reactions (Polanyi, 1972). An information theoretic analysis of detailed rate constants may be used to extrapolate to vibrational levels where direct measurements are not available. This approach also gives some general rules for the utilization of vibrational energy. Initially, the reaction rate will increase exponentially with increasing reactant excitation. Once the reactant excitation equals the

Table II. a. Rate constants for the reaction of HCl ($\nu = 1$) molecules with Cl atoms

HCl ($\nu = 1$) + Cl → Products	$k(T)$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	T range (K)	Remarks	Reference
HCl ($\nu = 0$) + Cl	10.5×10^{-12}	300	Exp.	<i>a</i>
	10.0×10^{-13}	298	Exp.	<i>b</i>
	$(7.6 \pm 2.3) \times 10^{-12}$	295	Exp.	<i>c</i>
	$(5.8 \pm 0.8) \times 10^{-12}$	295	Exp.	<i>d</i>
	51.5×10^{-12}	300	Theor.	<i>e</i>
	$(27 \pm 8) \times 10^{-12}$	295	Theor.	<i>f</i>
	32×10^{-12}	300	Theor.	<i>g</i>
	$(6.1 \pm 1.3) \times 10^{-12}$	298	Exp.	<i>h</i>

^a Craig and Moore (1971); ^b Ridley and Smith (1971); ^c Bott and Heidner (1976); ^d Arnoldi and Wolfrum (1976); ^e Wilkins (1975); ^f Valencich *et al.* (1977); ^g Smith and Wood (1973); ^h Kneba and Wolfrum (1979).

b. Rate constants for the reaction of HCl ($\nu = 2$) molecules with Cl atoms

HCl ($\nu = 2$) + Cl → Products	$k(T)$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	T range (K)	Remarks	Reference
HCl ($\nu = 1$) + Cl	$(3.2 \pm 0.8) \times 10^{-11}$	294	Exp.	<i>a</i>
	$(3.4 \pm 0.7) \times 10^{-11}$	381	Exp.	<i>a</i>
	$(3.7 \pm 1.0) \times 10^{-11}$	411	Exp.	<i>a</i>
HCl ($\nu = 0$) + Cl	$(1.0 \pm 0.3) \times 10^{-12}$	294	Exp.	<i>a</i>
	$(4.0 \pm 4.0) \times 10^{-12}$	381	Exp.	<i>a</i>
	$(0 \pm 3) \times 10^{-12}$	411	Exp.	<i>a</i>

^a Macdonald and Moore (1978).

endoergicity, the situation changes. The rate constant will then increase very slowly with further increase in the vibrational energy (Levine, 1978).

In this section experimental methods and results for reactions of different atoms with vibrationally excited hydrogen chloride molecules are described in some detail. A summary of results given in Tables II–V.

Table III. Reactions of HCl (ν) and DCl (ν) molecules with H and D atoms

Reactants → Products	$k(T)$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	T range (K)	Remarks	Reference
HCl ($\nu = 1$) + D →	$(11 \pm 3.3) \times 10^{-12}$	295	Exp.	<i>a</i>
HCl ($\nu = 0$) + D } DCI + H	$(8.3 \pm 2.5) \times 10^{-12}$	295	Exp.	<i>b</i>
	$(30 \pm 6.6) \times 10^{-12}$	295	Theor.	<i>c</i>
DCI ($\nu = 1$) + H →	$(2.5 \pm 0.5) \times 10^{-12}$	295	Exp.	<i>a</i>
DCI ($\nu = 0$) + H } HCl ($\nu = 0$) + D	$(14.3 \pm 6.2) \times 10^{-12}$	295	Theor.	<i>c</i>
DCI ($\nu = 1$) + D →	$(2 \pm 0.7) \times 10^{-12}$	295	Exp.	<i>a</i>
DCI ($\nu = 0$) + D	$(10 \pm 2.5) \times 10^{-12}$	295	Exp.	<i>c</i>

^aBott and Heidner (1976); ^bArnoldi and Wolfrum (1976); ^cValencich *et al.* (1977).

1. Thermoneutral exchange reactions of the type $X + \text{HX}(\nu)$ and $\text{H} + \text{HX}(\nu)$

Simple thermoneutral halogen and hydrogen atom exchange reactions have attracted special attention as model systems for testing theoretical calculations on the competition between energy transfer processes and chemical reactions under nonequilibrium conditions. However, it is still difficult to calculate accurate *ab initio* potential energy surfaces for such open shell systems with many electrons.

(a) *The reaction $\text{Cl} + \text{HCl}(\nu)$.* In 1964 Klein *et al.* measured the thermal rate of the reaction $\text{Cl} + \text{HCl}$ by using the radioactive ^{36}Cl isotope and the $\text{Cl} + \text{D}_2$ system as a reference reaction in a competitive method. With more direct measurements for the reference reaction one derives from their data an Arrhenius activation energy of 25 kJ mol^{-1} . However, quite contradictory evidence on the potential energy surface was obtained from the results of BEBO calculations by Truhlar *et al.* (1972) on the properties of $\text{X}-\text{H}-\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{on I}$) species. In the case of $\text{Cl}-\text{H}-\text{Cl}$ a well depth of 6.5 kJ mol^{-1} and a bond strength of 12.6 kJ mol^{-1} were predicted. On the other hand, calculations by Polanyi (1963) using the LEPS methods

Table IV. a. Rate constants for the reaction of HCl ($\nu = 1$) molecules with $\text{O}(^3P)$ atoms

HCl ($\nu = 1$) + $\text{O}(^3P) \rightarrow$ Products	$k(T)$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	T range (K)	Remarks	Reference
OH + Cl HCl ($\nu = 0$) + O	$(1 \pm 0.2) \times 10^{-12}$	295	Exp.	<i>a</i>
	$1.3 \times 10^{-11} \times \exp[1(528 \pm 100) \text{ K}/T]$ $(0 \pm 1.3) \times 10^{-13}$	196–400	Exp.	<i>a</i>
OH ($\nu = 0$) + $\text{Cl}(^2P_{3/2})$ OH ($\nu = 0$) + $\text{Cl}(^2P_{1/2})$ HCl ($\nu = 0$) + $\text{O}(^3P)$	$(6.2 \pm 2.5) \times 10^{-14}$	296	Exp.	<i>b</i>
	$(2.7 \pm 1.5) \times 10^{-15}$	298	Exp.	<i>c</i>
	$(9.3 \pm 0.5) \times 10^{-13}$	298	Exp.	<i>c</i>

^aBrown *et al.* (1975); ^bMacdonald and Moore (1978); ^cKneba and Wolfrum (1978).

b. Rate constants for the reaction of HCl ($\nu = 2$) molecules with $\text{O}(^3P)$ atoms

HCl ($\nu = 2$) + $\text{O}(^3P) \rightarrow$ Products	$k(T)$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	T range (K)	Remarks	Reference
OH ($\nu = 0, 1$) + Cl HCl ($\nu = 1$) + O OH ($\nu = 0, 1$) + Cl HCl ($\nu = 1$) + $\text{O}(^3P)$	$(5.2 \pm 0.4) \times 10^{-12}$	296	Exp.	<i>a</i>
	$(1.5 \pm 1.2) \times 10^{-12}$	296	Exp.	<i>a</i>
	$(3.8 \pm 1.2) \times 10^{-12}$	296	Exp.	<i>a</i>

^aMacdonald and Moore (1978).

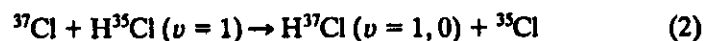
Table V. Rate Constants for the reaction of HCl(ν) molecules with Br($^2P_{3/2}$) atoms

HCl($\nu = 1$) + Br($^2P_{3/2}$) Products	$k(T)$ ($\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$)	T range (K)	Remarks	Reference
HCl($\nu = 0$) + Br($^2P_{3/2}$)	$(4.2 \pm 1) \times 10^{-13}$	300	Exp.	<i>a</i>
HCl($\nu = 0$) + Br($^2P_{1/2}$)	$(2.8 \pm 0.7) \times 10^{-13}$	300	Exp.	<i>a</i>
HCl($\nu = 2$) + Br($^2P_{3/2}$) Products	$k(T)$ ($\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$)	T range (K)	Remarks	Reference
HBr($\nu = 0$) + Cl	$(15 \pm 10) \times 10^{-13}$	300	Exp.	<i>a, b</i>
	$(3 \pm 3) \times 10^{-13}$	295	Exp.	<i>c</i>
	$(4 \pm 3.5) \times 10^{-13}$	355	Exp.	<i>c</i>
	$(11 \pm 6) \times 10^{-13}$	390	Exp.	<i>c</i>
	12×10^{-13}	300	Exp.	<i>d</i>
	$(93 \pm 53) \times 10^{-13}$	300	Theor.	<i>e</i>
	$(721 \pm 244) \times 10^{-13}$	1000	Theor.	<i>e</i>
	$(15 \pm 5) \times 10^{-13}$	333	Theor.	<i>f</i>
	$(150 \pm 38) \times 10^{-13}$	1000	Theor.	<i>f</i>

^a Arnoldi and Wolfrum (1976); ^b Arnoldi *et al.* (1975); ^c Macdonald and Moore (1980); ^d Kneba (1977); ^e Brown (1977); ^f Smith (1977).

and more recent *ab initio* calculations by Botschwina and Meyer (1976) and Dunning (1981) do not agree with these results.

Further attempts to obtain information on details of the potential energy surface of the Cl—H—Cl system were made by observing the behaviour of vibrationally excited HCl molecules in the presence of Cl atoms. The open electronic shell as well as the spin-orbit components of the ground state chlorine atom provide several effective pathways for vibrational energy transfer in electronically adiabatic and nonadiabatic collisions (Smith, 1976). The experimental data were compared with the results of classical trajectory studies on various LEPS potential surfaces. Calculations using reaction barrier heights from 40 to 25 kJ mol⁻¹ predict vibrational relaxation rate coefficients much smaller than the experimental data. In contrast, calculations employing surfaces with a small potential energy well are in better accord with the experiments. The best agreement with the experimentally observed rates was obtained with a barrier height around 4 kJ mol⁻¹ (Smith, 1975). However, an experimental study by Kneba and Wolfrum (1979) using isotopically selective vibrational excitation of H³⁵Cl ($\nu = 1$) and mass spectrometric detection of H³⁷Cl formed during the reaction



demonstrated that this reaction is more than a factor of 10³ faster than the thermal reaction at 298 K. The large vibrational rate enhancement together with the confirmation of the low HCl ($\nu = 0$) exchange rate strongly supports the earlier determined (Klein *et al.*, 1964) barrier height of about 36 kJ mol⁻¹. The experiments were performed using an arrangement shown schematically in Fig. 3. It consists of a discharge-flow reactor with

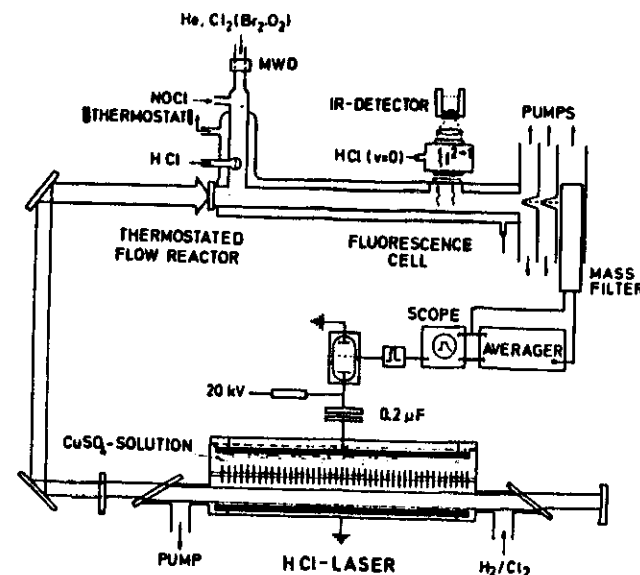
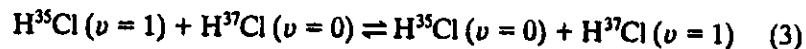


Fig. 3. Schematic of an experimental arrangement for time-resolved mass spectrometric detection of infrared laser-induced reaction products (Kneba and Wolfrum, 1979). MWD = Microwave Discharge.

laser excited infrared fluorescence detection coupled by a molecular beam sampling system to a quadrupole mass spectrometer for direct observation of the laser-induced reaction products. During the experiment the intensity of a certain m/e peak is followed as a function of time starting with the onset of the laser pulse. A signal is obtained during the transit time of the laser pulse through a volume of 10 mm diameter and 150 mm length at the sampling nozzle. The narrow line width infrared radiation from a chemical HCl laser can be used for the isotopically selective vibrational excitation of HCl molecules. This technique allows the investigation of isotopic exchange reactions without the need for isotopically enriched starting material. In a mixture containing HCl and chlorine atoms in their natural isotopic abundance (³⁵Cl:³⁷Cl = 75.53:24.47) a chemical laser operated

with a natural $\text{Cl}_2 + \text{H}_2$ mixture will excite predominantly H^{35}Cl molecules into the $\nu = 1$ state. If the rate of isotope exchange reaction can compete with the nonreactive vibrational deactivation of $\text{HCl} (\nu = 1)$ by Cl atoms, the thermal exchange reaction and the fast $V-V$ energy exchange process



Reaction (2) can directly be observed by measuring the amount of H^{37}Cl over the natural abundance ratio formed after the laser pulse. Using a computer model for the coupled rate equations of the elementary steps involved, the measurements can be simulated by varying k_2 as the unknown parameter. The measured temperature dependence of the calculated k_2 rates is shown in Fig. 4. An Arrhenius activation energy $E_a = 10.8 \text{ kJ mol}^{-1}$ can be derived from the slope of the curve. The $V-V$ energy transfer rate k_3 was taken to be independent of temperature between 250 and 358 K in these calculations. The data obtained for k_2 can be compared with the results for the vibrational deactivation of $\text{HCl} (\nu = 1)$

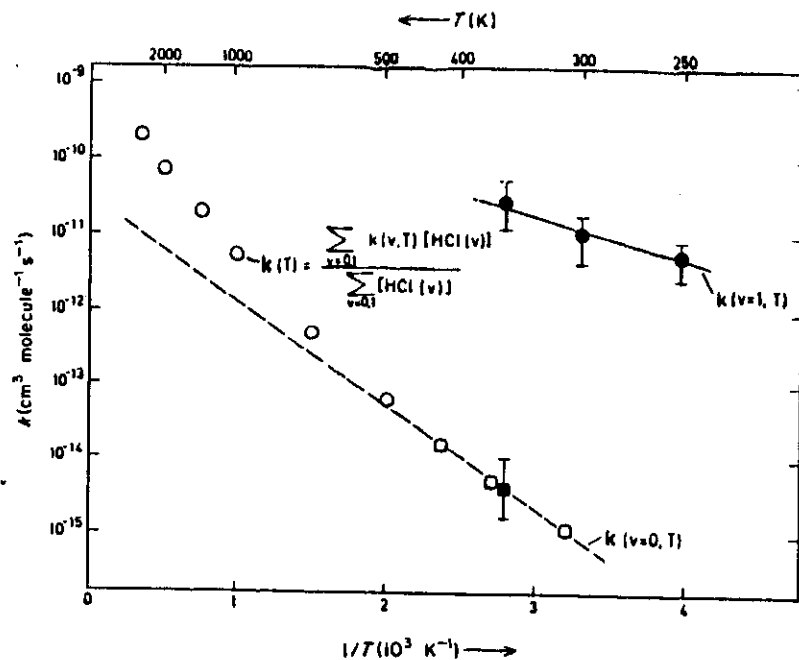


Fig. 4. Contributions from $\text{HCl} (\nu = 0, 1)$ to the thermal rate of reaction (2) (Kneba and Wolfrum, 1979). Top curve, $\text{HCl} (\nu = 1) + \text{Cl}' \rightarrow \text{Cl} + \text{HCl}' (\nu = 1, 0)$. Bottom curve, $\text{HCl} (\nu = 0) + \text{Cl}' \rightarrow \text{Cl} + \text{HCl}' (\nu = 0)$.

by Cl atoms. At room temperature the rate for the hydrogen atom exchange reaction k_2 is nearly double the relaxation rate. This difference becomes larger with higher temperatures. Thus, a significant amount of the reactive collisions must be vibrationally adiabatic. Because of the large rate enhancement after single quantum excitation, the contribution from $\text{HCl} (\nu = 1)$ to the thermal rate constant is expected to induce a substantial curvature in the Arrhenius graph (Fig. 4). The deactivation of $\text{HCl} (\nu = 1)$ as a result of the $V-E$ energy transfer process



i.e. via electronically nonadiabatic collisions, contributes only about 1% to the fast vibrational deactivation of $\text{HCl} (\nu = 1)$ by Cl atoms as expected from the fact that $\text{DCl} (\nu = 1)$ is relaxed less rapidly than $\text{HCl} (\nu = 1)$ by Cl atoms (Brown *et al.*, 1975b).

The result obtained in the direct investigation of Reaction (2) clearly demonstrates that it is a problematic procedure to construct potential surfaces for a particular system by adjusting the potential barrier used to describe the system until agreement between experimental and calculated rate constants for vibrational relaxation processes are obtained. It now seems worthwhile to carry out quantum mechanical and trajectory calculations on more recent potentials for the $\text{Cl} + \text{HCl} (\nu)$ system to see whether

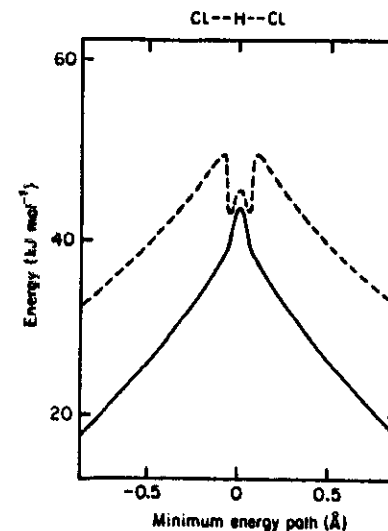


Fig. 5. Profile of the potential energy along the minimum energy path for the collinear $\text{Cl}-\text{H}-\text{Cl}$ surface (Adapted from Dunning, 1981). —, potential; ---, potential zero-point energy.

specific quantum effects are responsible for the conflicting results. An interesting new inversion procedure that uses detailed vibrational and total rate coefficient data to obtain potential energy surfaces for chemical reactions is given by Connor *et al.* (1980). Fig. 5 shows a new calculated collinear potential energy surface for the ClHCl-system. Along the minimum energy path, the decrease in zero point energy in the direction of the saddle point more than compensates for the increase in the potential energy. The reaction bottleneck is located 0.05 \AA away from the saddle point with a vibrationally adiabatic barrier about 4 kJ mol^{-1} higher than that at the saddle point.

(b) *The reaction $H, D + HCl(v)$.* In the $H + HCl$ system one has to consider two possible pathways, the hydrogen atom exchange and the hydrogen atom abstraction. Experimental rate constant data for the forward and backward thermal reactions $H + HCl \rightleftharpoons H_2 + Cl$ are now in good agreement with each other. Semi-empirical potential energy surfaces combined with trajectory calculations yielded rate constants in reasonable agreement with the experiments. The situation for the hydrogen atom exchange is less satisfying. The reported thermal rate constants for this reaction are very contradictory. In a static photochemical experiment, DeVries and Klein (1964) showed that the abstraction and exchange pathways have about equal importance at room temperature. The result was later confirmed in flow tube measurements (Klein and Veltmann, 1978). By contrast, Wood (1972) and Miller and Gordon (1982) in photochemical experiments, as well as Endo and Glass (1976) in thermostatted flow reactor studies, found the activation energy for H atom exchange higher than that for abstraction. The theoretical studies exhibit a similar discrepancy. While LEPS calculations give potential wells between -15 and -40 kJ mol^{-1} for the $H + Cl + H$ complex, the quantum mechanical *ab initio* treatment gives a barrier for exchange between 40 and 110 kJ mol^{-1} (for a review see Weston, 1979).

Vibrationally excited $HCl(v)$ molecules can be consumed by H or D atoms in electronically adiabatic processes either by thermoneutral hydrogen atom exchange, the slightly exothermic hydrogen atom abstraction reaction, or in nonreactive collisions. Figure 6 shows an experimental arrangement for the observation of these elementary processes. HCl molecules in the vibrational ground state are mixed with atoms in a discharge flow reactor. The decay of the laser excited $HCl(v)$ is followed by infrared fluorescence. To distinguish between reactive and inelastic pathways, it is necessary to measure the absolute consumption of reactants or formation of products. This is achieved here by measuring the absolute concentration of the vibrational excited molecules using the rapid equilibration between the $HCl(v)$ levels and a measurement of the relative population in the

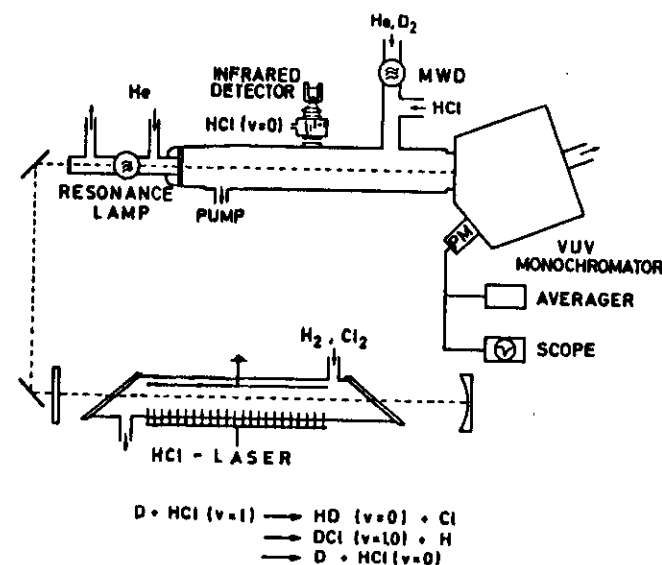


Fig. 6. Discharge-flow system for simultaneous time-resolved detection of the concentrations of reacting atoms and infrared laser excited $HCl(v)$ molecules (Arnoldi and Wolfrum, 1976). MWD = Microwave Discharge.

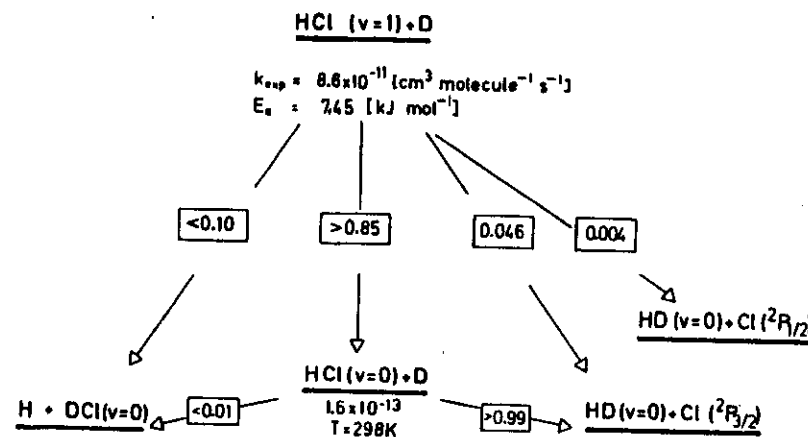


Fig. 7. Experimental results for the different channels of the $D + HCl(v = 0, 1)$ reaction (literature see text).

levels $\nu = 1$ and $\nu = 2$ as function of time. The concentrations of the reacting atoms are followed by time resolved atomic resonance absorption. Figure 7 summarizes the results for the $D + HCl (\nu = 1)$ system. Thus, the nonreactive relaxation, and not the hydrogen atom exchange or abstraction reaction, is mainly responsible for the high $HCl (\nu = 1)$ deactivation rate, contrary to predictions from theoretical calculations (Wilkins, 1975; Thompson *et al.*, 1975, 1976; Valencich *et al.*, 1977). The reason for the poor success of the theoretical calculations is obviously the fact that it is not possible to obtain a two parameter LEPS surface that can reproduce both the higher barrier for the exchange and the lower barrier for the abstraction reaction simultaneously. A high energy barrier of about 200 kJ mol^{-1} with respect to hydrogen atom exchange was also predicted by *ab initio* calculations on the $H + HF \rightarrow HF + H$ reaction, and was confirmed in recent experiments. The high energy barrier is surprising for this thermoneutral exchange reaction; it is substantially higher than that for the endothermic $H + HF \rightarrow H_2 + F$ reaction path that energetically opens up for $HF (\nu = 3)$ molecules only (Bott and Heidner, 1978).

(c) *The reaction $O (^3P) + HCl (\nu)$.* Ground state oxygen atoms react relatively slowly with thermal HCl at room temperature. The rate of the reaction



has been measured directly by several methods up to temperatures of 720 K. As shown in Fig. 8 there is relatively good agreement among different investigations. Since the first vibrational level of HCl corresponds to 34.3 kJ mol^{-1} , the single quantum excitation should deliver enough energy to overcome the potential energy barrier of reaction (5). When $HCl (\nu = 1)$ molecules are generated in the flow system by absorption of the laser pulse, the decay of $HCl (\nu = 1)$ is significantly accelerated in the presence of oxygen atoms. However, the data given in Fig. 8 indicate that the reactive channel forming $OH + Cl$ gives only a small contribution to the rapid removal of $HCl (\nu = 1)$ by $O (^3P)$. This is in agreement with the faster $DCl (\nu = 1)$ decay rate observed (Brown *et al.*, 1975a). However, the rate enhancement is much less than the factor $\exp[-E(\nu = 1)/RT]$. Since the Arrhenius pre-exponential factor is not changed significantly by vibrational excitation, the contribution of $HCl (\nu = 1)$ molecules to the thermal reaction is small for most temperatures of interest. At 200 K thermally excited $HCl (\nu = 1)$ molecules contribute less than $10^{-3}\%$ and at 200 K about 10% to the total consumption of HCl by $O (^3P)$ atoms. This is also true for $HCl (\nu = 2)$ molecules. As shown by quasiclassical trajectory calculations (Brown and Smith, 1978), the remaining thermal activation energies for $HCl (\nu = 1, 2)$ are very similar. Despite an increase

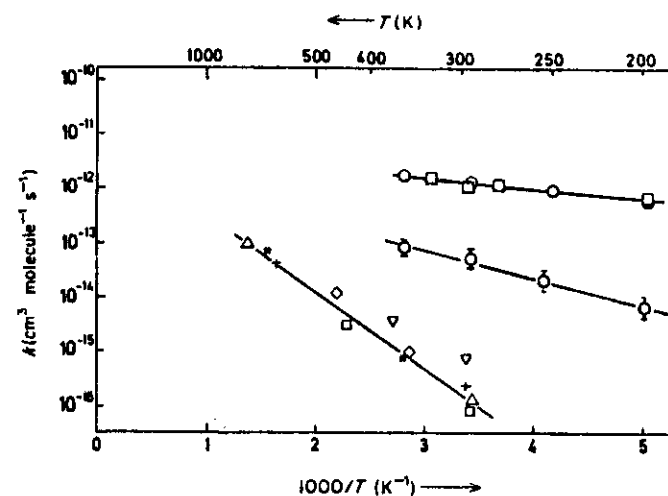


Fig. 8. Experimental data for the temperature dependence of the rates for vibrational relaxation and reaction of $HCl (\nu = 1, 0)$ with $O (^3P)$ atoms (Kneba and Wolfrum, 1978). Top curve, $O (^3P) + HCl (\nu = 1) \rightarrow O (^3P) + HCl (\nu = 0)$; middle curve, $O (^3P) + HCl (\nu = 1) \rightarrow OH + Cl (^2P_{3/2})$; bottom curve, $O (^3P) + HCl_{th} \rightarrow OH + Cl$.

by a factor around 10^4 in k_5 , the contribution from $HCl (\nu = 2)$ in the thermal reaction is below 10% up to 2000 K.

A theoretical model to explain the effective energy transfer in collisions involving P -state atoms as a result of electronically nonadiabatic curve crossing was given by Nikitin and Umanski (1972). As shown in Fig. 9, several potential surfaces exist for the interaction of $O (^3P)$ atoms with $HCl (\nu)$. At certain distances a nonadiabatic coupling between the different vibronic states is possible. The approach of the reactants $O (^3P)$ and HCl on a triplet surface, followed by a nonadiabatic transition to the singlet $HOCl$ surface as an intermediate complex, has been discussed as the possible origin of the potential energy barrier in this reaction. However, the fact that this crossing point appears necessarily to be lower than the saddle point of the lowest triplet surface is of course an artifact of the single coordinate correlation diagram. The experimental results on the reverse $Cl + OH (\nu \leq 9)$ reaction (Blackwell *et al.*, 1977) and the observed formation of $OH (\nu = 1)$ from $O (^3P) + HCl (\nu = 2)$ (Butler *et al.*, 1978) indicate that the chemical reaction occurs predominantly adiabatically vibronic on a triplet surface and does not proceed through a long-lived $HOCl$ complex. Detailed evaluations of the intermolecular potentials are

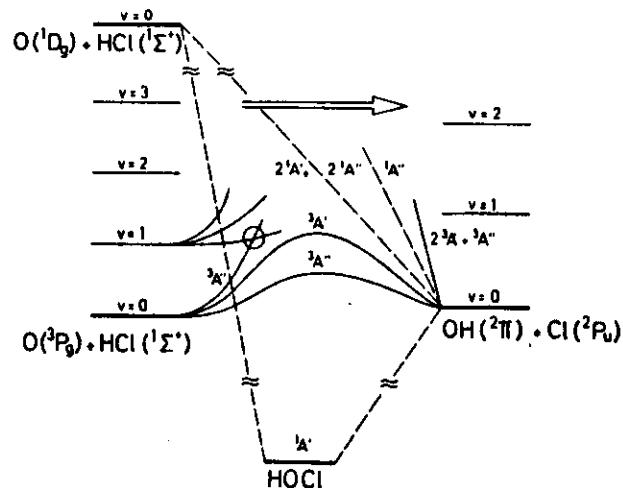
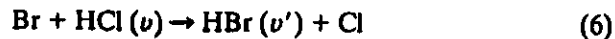


Fig. 9. Reaction and vibrational deactivation of HCl (ν) in collisions with O (3P).

still not available. The reaction $\text{Cl} + \text{OH}(\nu)$ increases by a factor of about 10 as ν increases from 1–9. There is evidence for the formation of $\text{H} + \text{OCl}$ from $\text{Cl} + \text{OH}(\nu = 4)$, probably via the HOCl intermediate.

2. Endothermic exchange reactions of the type $\text{Y} + \text{HX}(\nu)$

(a) *Investigations in 'bulk' systems.* For Y as the heavier halogen these reactions are endothermic. The reaction



has become a prototype for endothermic reactions whose rates are enhanced selectively by vibrational excitation. Relative rates of removal of HCl ($\nu = 1-4$) were measured using the infrared chemiluminescence depletion technique of Douglas *et al.* (1973, 1976). For HCl ($\nu = 4$) the reactive cross section for reaction with Br atoms was estimated as $1-4 \text{ \AA}^2$ from experiments performed in a cryo-pumped "arrested relaxation" chemiluminescence apparatus (Polanyi and Woodall, 1972) shown in Fig. 10. Vibrationally excited HCl is formed by the "pre-reaction" $\text{Cl} + \text{HI}$. The "depletion" of the emission intensity of the excited endothermic reactant in the presence of reactive atoms is monitored by an infrared grating spectrometer. This gives a measure of the steady state concentration of the reagent in each vibrational and rotational level. Relative reaction rates in different vibrational levels are obtained from the measured amount of population depletion relative to the undepleted spectrum. Absolute reaction rates were

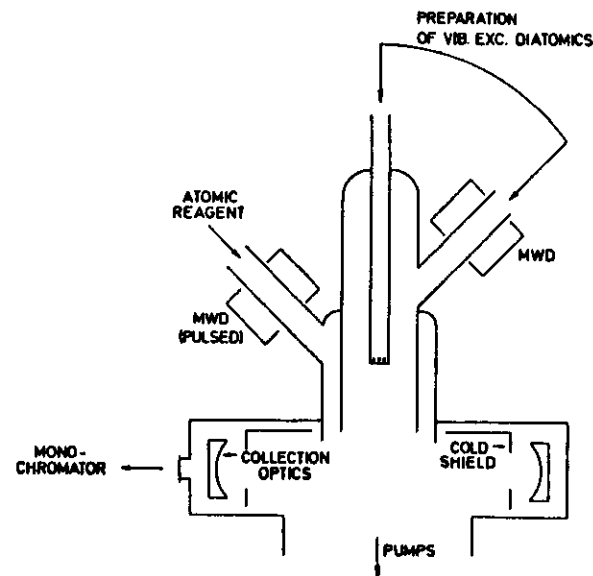


Fig. 10. Experimental arrangement for investigation of reactions of vibrationally excited molecules with the "arrested relaxation" technique (Adapted from Polanyi and Woodall, 1972). MWD = Microwave Discharge.

obtained from laser-induced infrared fluorescence experiments by observing the decay of HCl ($\nu = 1, 2$) in the presence of Br atoms. Figure 11 shows schematically the experimental set up used by Leone and Moore (1973) for direct excitation of HCl ($\nu = 2$) by a tunable optical parametric oscillator. The drastic augmentation of k_6 by vibrational excitation can be used for an isotopically selective stimulation of Reaction (6). As indicated in Fig. 12 the chemical HCl laser oscillates predominantly on H^{35}Cl , ($\nu = 1$) transitions. Therefore mainly $\text{H}^{35}\text{Cl}(\nu = 2)$ molecules are generated by the absorption of two photons via the steps $0 \rightarrow 1$ and $1 \rightarrow 2$. The isotopic selectivity was confirmed by mass spectrometric observation of Br^{35}Cl , formed by the fast reactions of ^{35}Cl atoms generated in reaction (6) with Br_2 present in the reaction mixture, with the nozzle beam sampling system shown in Fig. 3 (Arnoldi *et al.*, 1975). Another method of obtaining information on the $\text{HCl}(\nu = 2) + \text{Br}$ rate is the application of the principle of microscopic reversibility as discussed earlier. Combining the thermal rate constant for the $\text{Cl} + \text{HBr}$ reaction with the measured relative yields of HCl in different vibrational states gives a value for k_6 several times higher than the direct experimental result. However, more recent measure-

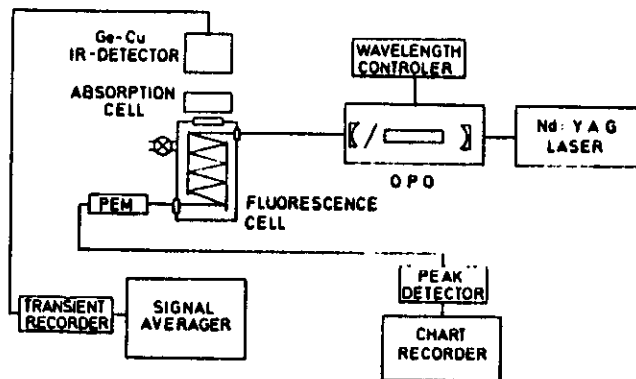


Fig. 11. Experimental apparatus for selective vibrational excitation using an optical parametric oscillator (Adapted from Leone and Moore, 1973). OPO = Optical Parametric Oscillator, PEM = Photoelectron Multiplier, IR = Infrared.

ments of the $\text{Cl} + \text{HBr}$ reaction (Zwier *et al.*, 1980) give higher relative yields in the $\text{HCl} (v = 2)$ state which will lower the calculated value for k_6 .

(b) *Investigations with molecular beams.* Molecular beam experiments allow one to perform kinetic studies involving vibrationally excited reactants under single collision conditions, where collisional relaxation does not significantly degrade the reactant and product experiments. Pruett *et al.* (1974, 1975) and Dispert *et al.* (1979) have investigated the vibrational as well as the translational and rotational energy dependence of the slightly endothermic reaction $\text{K} + \text{HCl} \rightarrow \text{KCl} + \text{H}$. Compared to ground state

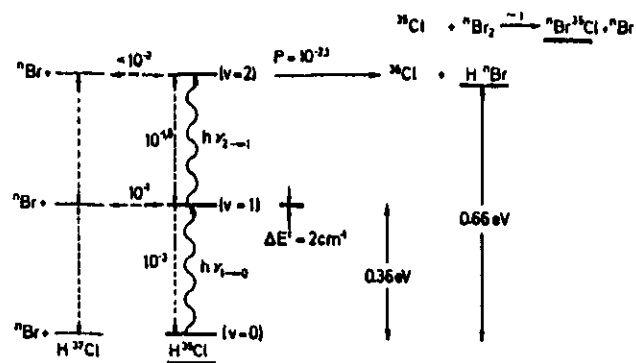


Fig. 12. Energy diagram for the reaction of Br atoms with isotopically selective excited HCl molecules. P denotes the probability of the collision process at room temperature (Arnoldi *et al.*, 1975).

HCl , the cross section for the reaction of $\text{HCl} (v = 1)$ is approximately a factor of 100 higher and roughly 10 times as large as if the same amount of energy were placed into relative translation. The reaction cross sections calculated by phase space theory (Truhlar, 1975) account within experimental error for the behaviour of the cross section at high initial translational energy and for the effect of initial vibrational excitation. Using thermal heating for the vibrational excitation of HCl and HF Heismann and Loesch (1982) found vibrational excitation more effective than translational energy in promoting the $\text{K} + \text{KCl} (v = 1)$ reaction up to collision energies of 48 kJ mol^{-1} and the $\text{K} + \text{HF} (v = 1)$ reaction up to 164 kJ mol^{-1} . At higher energies translation becomes more effective than vibration in surmounting the potential energy barrier of the reaction.

Another very elegant series of molecular beam experiments has been carried out by Zare and co-workers (1979) using selective laser excitation of HF coupled with laser-induced fluorescence detection of products. The apparatus is shown in Fig. 13. A beam of Sr atoms enters a scattering chamber containing HF at low pressure. The output of a pulsed grating tuned HF laser is directed perpendicular to the atom beam, preparing HF

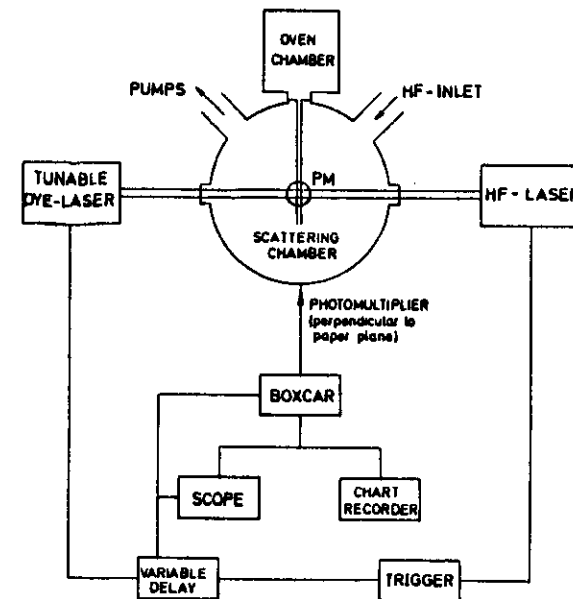


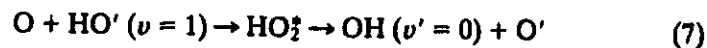
Fig. 13. Experimental arrangement for the investigation of reactions of vibrationally excited molecules under single-collision conditions using laser-induced fluorescence for product detection (Adapted from Zare, 1979). PM = Photomultiplier.

in the $\nu = 1, J = 1$ state. A half-wave Fresnel rhomb (ZnSe) is used to rotate the linear polarization vector of the laser emission. A tunable dye laser probes the SrF product internal state distribution. The reaction of vibrational ground state HF with Sr atoms scarcely proceeds, while HF ($\nu = 1$) reacts at least 104 times faster (Karny and Zare, 1978). Different SrF excitation spectra were obtained when the HF ($\nu = 1, J = 1$) molecule is preferentially oriented perpendicular or along the metal atom beam (Zare, 1979). The result indicates that the minimum energy path is a bent configuration (Balint-Kurti and Yardley, 1977).

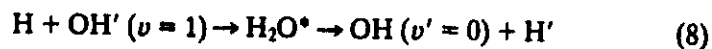
C. Reactions Proceeding Via Complex Formation

So far only direct reactions of atoms with diatomic molecules have been considered. Another possible pathway in this system is the formation of a quasibound intermediate reaction complex. The redissociation of this complex provides a very effective pathway for vibrational deactivation of diatomic molecules, e.g. $\text{NO}(\nu)$, $\text{O}_2(\nu) + \text{X}$ ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{O}$). The complex formation allows the application of statistical theories, such as the statistical adiabatic channel model (Troe, 1978; Quack, 1979).

Also the measured vibrational enhancement of the reaction rate of exchange reactions like

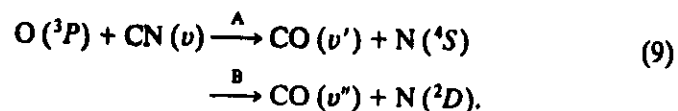


and



can be understood in this way (Spencer and Glass, 1976; Margitan *et al.*, 1975).

An interesting example in which complex and direct pathways can be observed simultaneously is the reaction



Channel A connects the reactants directly with ground state nitrogen atoms and CO, while channel B correlates with the electronic ground state of HCO radical as intermediate and with electronically excited nitrogen atoms and CO as products. To simulate the dynamics of Reaction (9) three dimensional classical trajectory calculations have been carried out using two different empirical adiabatic potential energy surfaces (Schmatjko and Wolfrum, 1975). Fig. 14 shows collinear cuts through the surfaces and two

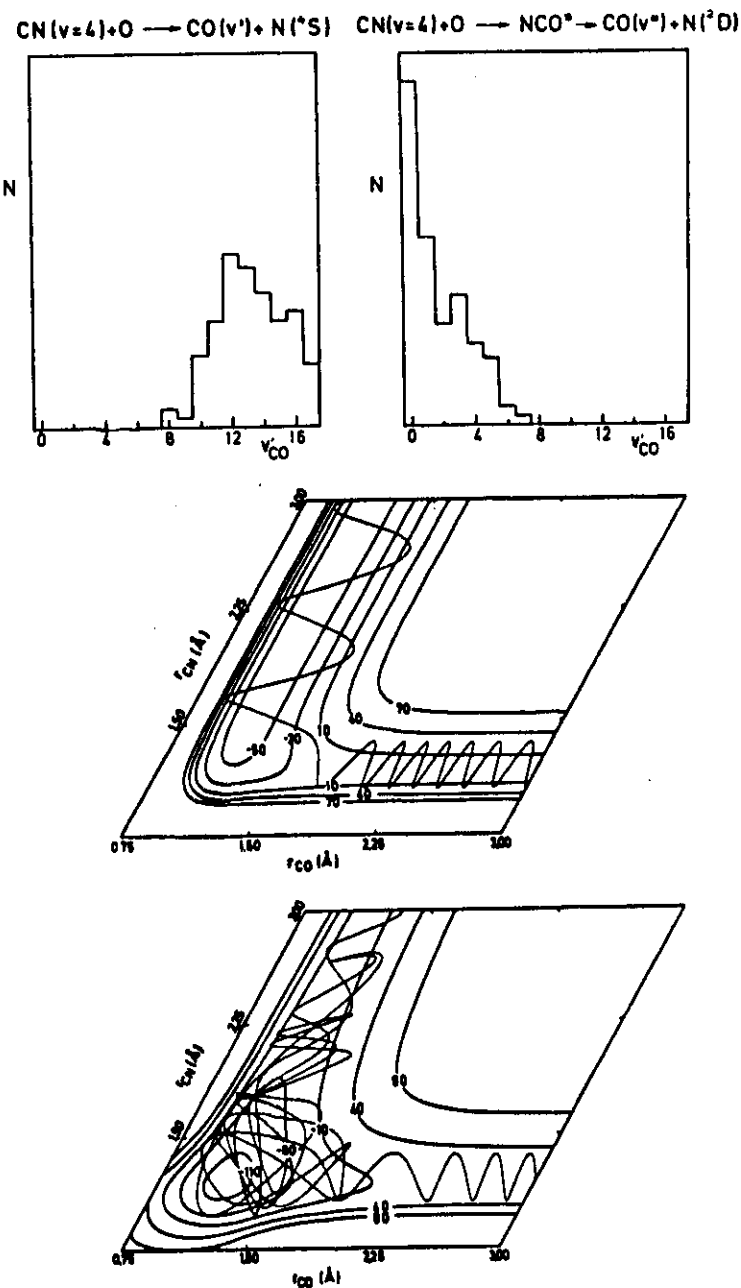


Fig. 14. Classical trajectories and product energy distributions for the reaction $\text{O}({}^3P) + \text{CN}(\nu = 4)$ calculated on empirical potential energy surfaces representing two direct and complex exothermic pathways (Schmatjko and Wolfrum, 1975).

typical trajectories for the reaction of vibrationally excited CN ($v = 4$) radicals. The trajectories demonstrate the quite different dynamical behaviour of the two pathways. The deep attractive "well" of the NCO ground state allows an effective energy exchange for several vibrational periods of the collision complex. The reaction energy can therefore be distributed in a more statistical way among the reaction products, while on the direct path a transformation mainly into vibrational excitation of the CO molecule occurs. Among other details the trajectory calculations can give a picture of how the vibrational excitation of CN (v) will influence the rate of the Reaction (9) on the two different pathways. On the complex path the reaction cross section decreases with increasing v_{CN} . This can be understood from the standpoint of unimolecular decomposition of the intermediate complex, which gives an increasing amount of redissociation into the reactants with increasing total energy. As discussed earlier, such collisions can provide a very effective way of vibrational deactivation. On the direct path the opposite trend is predicted. The increase in the reactive cross section with vibrational excitation can be rationalized by the "induced attraction" (Ding *et al.*, 1973). The barrier due to a repulsion between an attacking atom A and the molecule BC in the vibrational ground state will decrease for BC (v) in high vibrational levels, since in the limit (dissociation of BC) an attraction exists between the free atoms A and B. The opposing effects of vibrational excitation on the reactive cross sections for the exothermic direct and complex pathway will be enhanced in systems with higher potential energy barriers, and diminished for higher translational temperatures. Information about the relative importance of the two different exothermic pathways of Reaction (9) can be obtained by observation of the product energy distribution. Fig. 15 shows the primary CO (v) distribution formed in Reaction (9) measured by time resolved infrared spectroscopy using a CO-laser tunable down to the 1-0 band. (Schmatjko and Wolfrum, 1978). In agreement with the predictions of the trajectory calculations on path A the energy is predominantly channeled into CO vibrational excitation, so that a partial inversion in the population of higher vibrational states is created. On path B the formation of CO in low vibrational levels predominates. The energy is converted into the excitation of the metastable N (2D) atoms and relative translational energy of the products. Because more phase space is associated with states of relative translation, the vibrational state distribution of molecules produced by the decay of the transition complex decreases monotonically with increasing vibrational quantum number (Marcus, 1975). Figure 15 also shows the effect of increasing vibrational excitation of the CN radical on the product energy distribution. Only the direct channel A allows the conversion of about 50% of the reactant vibrational energy into product vibration. In

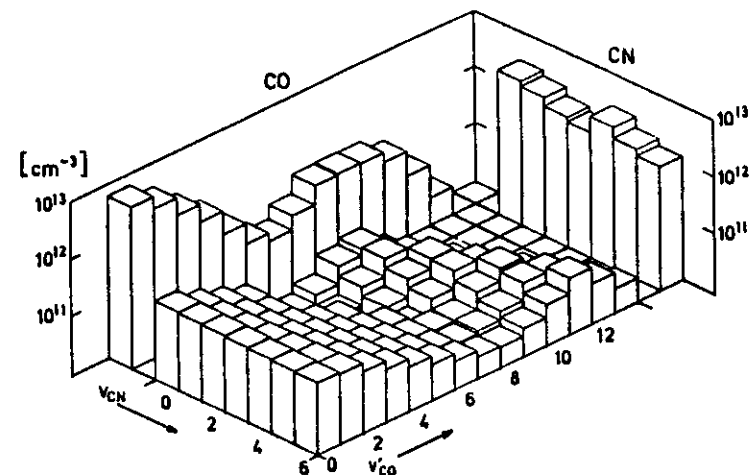


Fig. 15. Vibrational population of CO (v) formed in Reaction (9) as function of the initial vibrational state of the CN radical (Schmatjko and Wolfrum, 1978).

contrast, there is practically no "vibrational memory" for the complex channel B.

In some cases the electronic ground states of the collision partners and the triatomic complex do not correlate directly, e.g.



Here nonadiabatic processes on the "spin-forbidden" route as well as the competition of "spin-allowed" routes with higher potential barriers must be considered (McNeal *et al.*, 1974; Lewittes *et al.*, 1978).

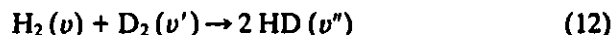
III. Reactions of Vibrationally Excited Diatomic and Triatomic Molecules

If one considers reactions involving four atoms, the simplest system is the interaction of two vibrationally excited diatomic molecules. Compared to elementary steps involving free atoms, reactions between molecules with closed electronic shells exhibit much higher potential energy barriers.

A. The System AB (ν) + CD (ν')

1. Reaction between vibrationally excited H₂ molecules

The simple 4-centre metathesis reaction



has a barrier height equal to several vibrational quanta, which makes it difficult experimentally to separate the detailed reactive processes from vibrational energy transfer. Early indirect shock tube studies on this prototype reaction have been mentioned above (Bauer, 1964). More direct investigations were also performed more recently by Bauer and coworkers. The stimulated Raman effect was used for laser optical pumping on H₂ (Bauer *et al.*, 1973). Vibrational ladder climbing steps have been assumed to explain the observed HD formation in experiments using thermal and stimulated Raman pumping of the hydrogen molecules. However, several investigations (Pratt and Rogers, 1976; Marteau *et al.*, 1978) show that only an atomic mechanism (see Fig. 2) can sufficiently well explain all the observations. The central focus in the controversy is that the ground electronic state H₂ + D₂ orbitals do not directly correlate with ground state 2HD for the expected square planar transition state. Extensive calculations of reaction pathways for several bimolecular transition state geometries by Brown and Silver (1978) have shown that the reaction barrier lies above the H₂ + 2H asymptote for each configuration. Calculations by Dixon *et al.* (1977) suggest a six centre, hexagonal transition state that can explain the experimental findings. However, calculations by Goddard and Csizmadia (1979) indicate that the lowest H₄ singlet excimer state probably lies less than 226 kJ mol⁻¹ above H₂ + H₂, and may thus serve as the transition state for concerted molecular H₂ + D₂ exchange.

Figure 16 shows a diagram of the experimental arrangement for the preparation of HD ($\nu = 5$) by cw intracavity dye laser excitation of the weak HD ($\nu = 0 \rightarrow 5$) overtone. The dye laser was tuned to the overtone resonances by optoacoustic detection, using the intracavity detection-cell. The reaction was followed by measurement of the D₂ photoproduct. Laser oscillations were limited to one or two longitudinal modes by using an uncoated quartz etalon and birefringent filter. The energy deposited per molecule (197 kJ mol⁻¹) is significantly larger than the 159 kJ mol⁻¹ calculated (Poulsen, 1970) as E_a for Reaction (12). However, no reaction products could be found in this experiment (Herman, 1980). The sensitivity of the experiment was high enough that the expected reaction yield was 100 times the D₂ detection limit, though it is not high enough to monitor either any trimolecular mechanism product HD ($\nu = 5$) + 2HD ($\nu = 0$), or

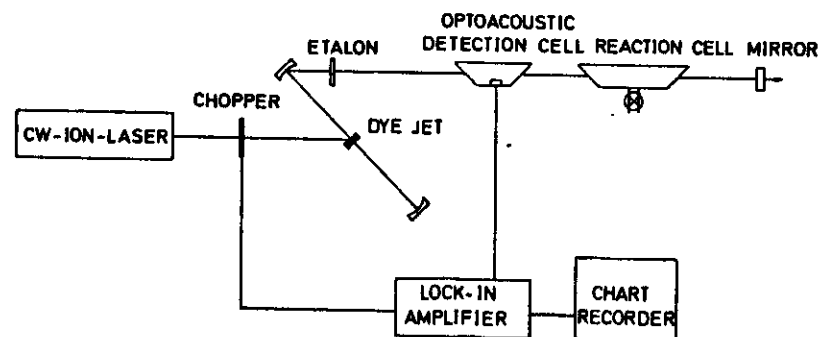


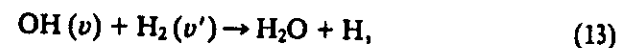
Fig. 16. Experimental arrangement for high vibrational overtone excitation by dye laser intracavity absorption (Adapted from Bray *et al.*, 1977; Herman, 1980).

the reaction between laser- and collisionally pumped reactants e.g., HD ($\nu = 2$) + HD ($\nu = 3$) reactions, which Poulsen (1970) has claimed are important in shock tube studies. However, as discussed in detail by Bauer (1979) neither the experimental nor theoretical investigations of this simple exchange reaction are beyond question. This holds also for such reactions involving hydrogen and hydrogen halides. For electronically excited halogens and interhalogens the effect of vibrational excitation in the reaction with H₂ could be studied more directly (Harris, 1977).

In early classical trajectory studies of 4-centre exchange reactions on model potential surfaces with a variable potential barrier location, Mok and Polanyi (1970) showed that substantial energy in excess of the barrier is required to induce significant reaction. The situation changes if one turns to reactions of diatomic radicals. Here atom transfer reactions such as AB (ν) + CD (ν') \rightarrow ABC + D with lower potential energy barriers become feasible.

2. The reaction OH (ν) + H₂ (ν')

In the reaction



single vibrational quantum excitation of one of the reactants already significantly exceeds the potential energy barrier. As one intuitively expects, and as shown by classical trajectory calculations (Raff, 1977), the reaction rate is further enhanced by vibrational excitation of the bond to be broken. H₂ ($\nu = 1$) is reported (Zellner and Steinert, 1981) to react 150 times more

rapidly than H_2 ($\nu = 0$), whereas for OH ($\nu = 1$) the enhancement is by less than a factor of 1.5 (Light and Matsumoto, 1978). For the specific case of H_2O formation there is no necessity for changing the OH bond length by vibration during the course of the abstraction reaction, because the OH bond distance remains almost constant going from OH to H_2O . An *ab initio* calculation on the potential energy surface for Reaction (13) was recently reported by Walch and Dunning (1980). Quasiclassical trajectory studies on this surface (Schatz and Elgersma, 1980; Schatz, 1981) show an interesting interplay between statistical and nonstatistical features in the product vibrational distribution. Excitation of OH ($\nu = 1$) leads to additional excitation of the H_2O stretch modes (001,011 etc.), perturbed by the reactive process. Excitation of H_2 ($\nu = 1$) causes additional excitation in all three H_2O modes.

In the low barrier $\text{OH} + \text{HBr} \rightarrow \text{H}_2\text{O} + \text{Br}$ reaction, acceleration by an order of magnitude is observed for OH ($\nu = 1$) (Spencer and Glass, 1977). A similar result is obtained for $\text{CN}(\nu) + \text{H}_2 \rightarrow \text{HCN} + \text{H}$ (Schacke *et al.*, 1977).

3. The reaction $\text{CO} + \text{OH}(\nu')$

A very interesting reaction in this series is the conversion of CO into CO_2 via



As discussed in Chapter 1 the measured thermal Arrhenius activation energy of the $\text{OH} + \text{CO}$ reaction shows a strong temperature variation, rising from E_a near zero below 300 K to 33.5 kJ mol^{-1} at temperatures in excess of 2000 K.

Experiments using vibrationally excited hydroxyl radicals in Reaction (14) do indicate that OH ($\nu = 1$) is quenched by CO at least as rapidly as it reacts with it. A rate enhancement of less than a factor of two was measured at 288 K (Spencer *et al.*, 1976). Vibrational excitation of the CO molecule should provide another clue to the microscopic mechanism of Reaction (14). The energy of the vibrational quanta in CO is comparable to the apparent activation energy observed at higher temperatures. Compared with OH radicals and other diatomic hydrides, the CO molecule has a much smaller dipole moment in the vibrational ground state. The change due to the dynamic dipole moment after vibrational excitation should therefore be more dramatic compared to those cases. Figure 17 shows an experimental set up for investigation of the $\text{CO}(\nu) + \text{OH}$ reaction (Dreier and Wolfrum, 1981). The experiments were performed using a discharge flow system coupled to a quadrupole mass spectrometer by a nozzle beam

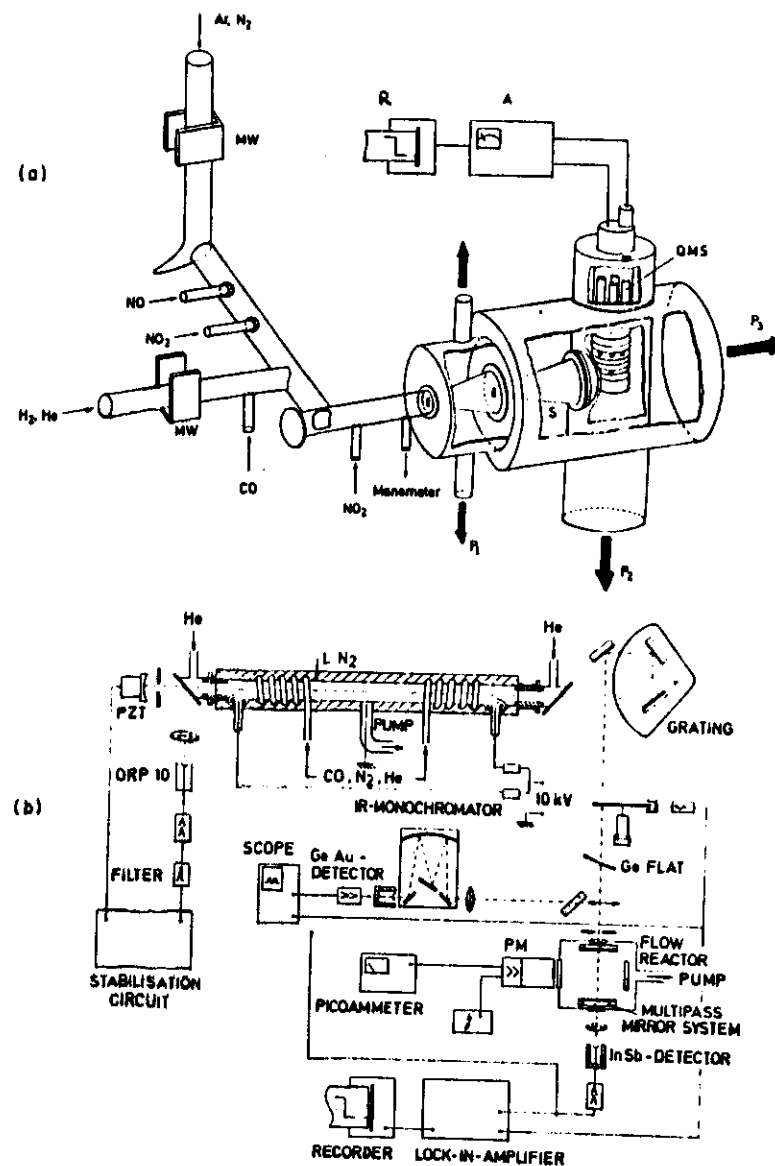
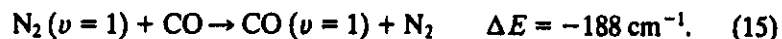


Fig. 17(a). Schematic of a discharge flow system coupled to a quadrupole mass spectrometer for investigation of the reaction $\text{CO}(\nu) + \text{OH}$. R = Chart Recorder, S = Scimmer, A = Amplifier, MW = Microwave Discharge.

(b). Schematic of the experimental arrangement for the determination of $\text{CO}(\nu)$ concentrations by infrared laser resonance absorption (Dreier and Wolfrum, 1981). PZT = Piezoelectric Translator, ORP10 = Infrared Detector, PM = Photomultiplier.

sampling system (Fig. 17a). Vibrational excitation of CO was achieved by energy transfer from vibrationally excited N₂ molecules



The vibrational and rotational temperatures of the reacting CO molecules could be determined directly by the arrangement shown in Fig. 17b.

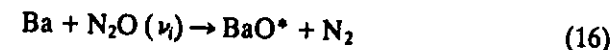
A stabilized cw-CO laser is employed as light source for infrared resonance absorption measurements. From the measured absolute population in the $\nu = 1-4$ CO vibrational levels the vibrational temperature of CO is monitored at different excitation levels of the N₂ molecules. At the same time the rotational and translational temperature of CO was kept at room temperature. With constant $T_T = T_R = 298 \text{ K}$, k_{14} decreases with increasing vibrational temperature of CO from $9 \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T_V^{\text{CO}} = 298 \text{ K}$ to $7.8 \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T_V^{\text{CO}} = 1800 \text{ K}$. Such a decrease could also directly be observed in the CN(ν) + O₂ → products reaction (Schacke *et al.*, 1973) and may be explained by an intermediate reaction complex. Here, as discussed earlier, with increasing internal excitation of the complex the rate of redissociation into the reactants increases, which results in a decreasing reaction rate if the cross section for the complex formation is not significantly enhanced by the vibrational excitation of the reactants. Vibrational rate enhancement can therefore not be used to explain the substantial non-Arrhenius behaviour of k_{14} . However, several calculations assuming the formation of a collision complex HOCO and different models for the transition state to form the products H + CO₂ can reproduce the measured experimental rate data and are used to extrapolate k_{14} data to higher temperatures. The presence of a potential well on the reaction surface before the system passes through the transition state, should result in strong coupling collisions leading to equilibrated distributions in the transition state. However, if the additional energy carried by the vibrationally excited CO molecules is equipartitioned among the degrees of freedom in the HOCO complex and the transition state, the measured rate for CO($\nu = 1$) should correspond to the thermal rate at a temperature of 830 K. The experiments described above show that $k_{14}(T = 830 \text{ K}) \approx 4 \times k_{14}(\nu = 1)$. Therefore it is questionable whether the presently discussed models for Reaction (14) can be used to describe the reaction over a wide temperature range.

Recent experiments (Jacobs *et al.*, 1983) show that relative translational energy of the reactants can induce a selective enhancement of the reaction rate in both directions. From such experiments, together with quasiclassical trajectory studies on *ab initio* calculated potential surfaces of the H + CO₂ (Peyerimhoff and Buenker, 1982) and HO + CO complex, one can expect to obtain a more direct picture of the microscopic dynamics of this reaction.

This should explain whether the reaction follows a pathway in which at high temperatures the relative translation of the reactants converted to a high rotational energy of the complex can open a new channel, or whether a second completely different direct pathway is dominant at high temperatures.

B. The System A + BCD (ν_i)

With the atom plus triatomic molecule reactions one encounters a fascinating aspect, the question of mode specific energy consumption in reactions of vibrationally excited molecules. Molecular beam studies of the

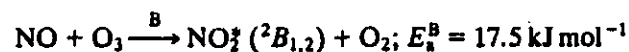
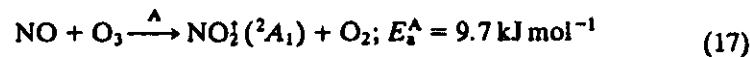


reaction suggest that the ν_2 -bending mode in N₂O acts as promoting mode and is more effective than an equivalent amount of translational energy (Wren and Menzinger, 1979). Similar results are obtained for the reactions of Sn and Group IIIb metal atoms with N₂O (Yokozeki and Menzinger, 1977; Manos and Parson, 1978). Because the ν_1 (N—O stretch) mode is in Fermi resonance with the asymmetric stretch vibration ν_3 in the triatomic molecule, trajectory studies of the O + CS₂ → CS + SO reaction (Schatz, 1979) indicate that the asymmetric stretch vibration ν_3 in the triatomic molecule may not be the promoting mode even though ν_3 appears to displace the molecule along the reaction coordinate. Quasi-classical calculations using a LEPS type potential energy surface for the O + CS₂ reaction and good action-angle variables (Schatz and Moser, 1978) show that, instead, the lower frequency mode ν_1 (symmetric stretch) couples most efficiently into the motion along the reaction coordinate, whereas the high frequency mode ν_3 tends to be vibrationally adiabatic at energies close to threshold. The product CS vibrational quantum number is always identical with the initial ν_3 quantum number, whereas the symmetric stretch ν_1 is highly nonadiabatic. The lowering in threshold by a (100) excitation is similar to that for (001), although the symmetric stretch quantum (100) is much smaller than the asymmetric (001) one. Also, the threshold for (500) is substantially lower than for (002), although the states are nearly degenerate. Experimental investigations of the exoergic reactions O + COS (ν_i) (Manning *et al.*, 1976; Kneba *et al.*, 1976), O + O₃ (ν_i) (West *et al.*, 1976, 1978b; Chekin *et al.*, 1979), and Pb + O₃ (Kurylo *et al.*, 1976), which have higher activation barriers, indicate that there is little or no coupling of vibrational energy to the reaction coordinate. Only a small fraction of the measured relaxation rate is due to the laser-enhanced reaction. This implies that these reactions with triatomic molecules are subject to similar

dynamic constraints as exoergic reactions of diatomic molecules, which tend to have the barrier in their entrance channel. The high relaxation rate may be explained by nonadiabatic transitions, as discussed earlier in connection with oxygen atom reactions.

C. The System AB (ν) + CDE (ν)

Activation energies comparable to the energy of the vibrational quanta of the reacting molecules can be expected in 5 atom systems for simple abstraction reactions involving at least one species with an unpaired electron. The exoergic reaction between nitric oxide and ozone looks very interesting in this respect. The reaction proceeds by two parallel paths to yield ground-state vibrationally excited (A) and electronically excited (B) NO₂ molecules



The spacings of the three vibrational modes in O₃ as well as the vibrational quantum in NO are comparable to the measured thermal activation energies. Both reactants can be vibrationally excited by molecular infrared lasers. For ozone a coincidence between the P (30) line of the CO₂ laser in the 9.6 μm band and the antisymmetric stretch vibration (001) exists. Nitric oxide has a near coincidence with the P (13) line in the Δν = 9–8 band at 5.3 μm of the CO laser. Because NO is a paramagnetic molecule, the NO absorption line can be "tuned" by a magnetic field in resonance with the laser line. Near infrared electronic chemiluminescence by NO₂[†] and vibrational emission by ground state NO₂[‡] near 3.6 μm facilitate study of both pathways. Significant rate enhancement in the two channels was originally demonstrated by Gordon and Lin (1973), by pumping the O₃ (001) vibrational level with a Q-switched CO₂ laser. Considerable discrepancies in the rate enhancement ratios $R_{\text{A}} = k_{\text{A}}^{\text{v}}/k_{\text{A}}$ and $R_{\text{B}} = k_{\text{B}}^{\text{v}}/k_{\text{B}}$ measured by different groups were reported (see Table VI). The specific roles of the directly pumped (001) stretching mode of O₃ (13.3 kJ mol⁻¹), strongly coupled with the (100) stretching mode (12.5 kJ mol⁻¹), and of the (010) bending mode (8.4 kJ mol⁻¹), excited by subsequent collisional relaxation, in promoting reactivity and the interplay of reaction and vibrational deactivation of ozone were also unclear. Most of these problems have been resolved by the work of Gordon *et al.* (1977) and Bar-Ziv *et al.* (1978) and by Hui and Cool (1978). By measuring the electronic chemiluminescence enhancement on pumping a measured fraction of O₃ molecules in the ν₃

Table VI. Rate enhancement factors for the reaction of NO molecules with ozone due to vibrational excitation in different modes

Reactants	Products	NO + O ₃ (010)	NO + O ₃ (001) or/and O ₃ (100)	NO(ν = 1) + O ₃ (000)
O ₂ (Σ _g ⁺) + NO(² A ₁)	22 ^g		6.0 ^g	18 ^g
	17.1 ± 4.3 ^b		7.0 ^g	22 ^g
	6		6.1 ^g	
O ₂ (Σ _g ⁺) + NO(² B ₁)	4.1 ± 2 ^b		5.0 ^g	
			5.3 ± 1 ^c	4.7 ± 2 ^c
			14.0 ^d	5.7 ± 1.4
			7.6 ⁺ 1.3	2.6 ⁺
			7.4 ^g	1.4

^g Gordon and Lin (1973); ^b Kurylo *et al.* (1974); ^c Gordon and Lin (1976); ^d Hui and Cool (1976); ⁺ Stephenson and Freund (1976); [†] Gordon *et al.* (1977); [‡] Hui and Cool (1978); ^Δ Gordon *et al.* (1981); [§] Stephenson and Freund (1976).

level immediately following the laser excitation, enhancement ratios are obtained. These can be compared with earlier measurements by Kurylo *et al.* (1974, 1975), involving vibrationally equilibrated ozone, where the ν_2 population predominates through the reaction. Thus, the bending and stretching vibrational modes make comparable contributions to the rate enhancement of reaction B. Measurements of the temperature dependence of reaction B in the temperature range 140–440 K, show a pre-exponential factor for the enhanced reaction essentially unchanged from the thermal value, and an effective reduction in E_a^B equivalent to only 42% of the O_3 (001) quantum energy. Similar results are obtained for reaction A. The measurements of Stephenson and Freund (1976a) on vibrational enhancement of the reaction rate by NO ($\nu = 1$) provided additional information for a dynamical interpretation. Thus, within present experimental error no marked dependence of the rate constant enhancement on specific initial vibrational modes is observed. Furthermore, neither O_3 nor NO vibrational energy is particularly effective in promoting the reactivity.

However, the interpretation of these "bulk" experiments is complicated by the rapid collision induced energy transfer in the ozone molecule (Rosen and Cool, 1975) and quenching of the NO_2^* product (van den Ende and Stolte, 1980). Quasiclassical trajectories on a series of model potentials restricted to one electronic surface have been carried out for Reaction (17) by Chapman (1981). While translational and vibrational energy have distinctive effects on the reaction, no mode specific enhancement of the reaction rate was observed for any model function. This is thought to result from the high degree of coupling of the internal coordinates to the reaction path and to the multidimensional curvature of the reaction coordinate. One cannot characterize one vibrational mode as directed generally along the reaction coordinate while the others lie orthogonal to it. In conclusion, the large amount of evidence accumulated on vibrational and translational effects in reactions A and B, and on the roles of the $^2\pi_{3/2,1/2}$ substates of NO (Redpath *et al.*, 1978) still appears to provide only limited help in deducing the nature of the hypersurfaces concerned. Important questions about surface-intersections that arise from consideration of the correlation diagrams cannot be answered. In view of the various accessible electronic states, also of the product molecules, a complete theoretical treatment does not appear possible in the near future.

The reactions $NO_2 + CO$ (Herman *et al.*, 1978), and $NO_2 \rightleftharpoons NO_2$ (Creel and Ross, 1976), have been stimulated by visible laser light radiation. Because of the complicated nature of the electronically excited states of NO_2 it is very difficult to specify the reacting state. Vibrational excitation of the NO_2 surely plays an important role in the measured rate enhancements. Further studies, though much less detailed, have been carried out

for the reactions $OH(\nu) + O_3$ (Streit and Johnston, 1976; Potter *et al.*, 1979) and $O_3(\nu_1) + SO$, $O_2(^1\Delta)$ (Kaldor *et al.*, 1974), $OH(\nu) + NO$, NO_2 (Jaffer and Smith, 1979), $AlO(\nu) + O_2$ (Felder and Fontijn, 1976).

IV. Reactions of Vibrationally Excited Polyatomic Molecules

A. Reactions Involving Chemically Stable Reactants

A great deal of interest in the chemistry involving bimolecular reactions of laser-generated vibrationally excited polyatomic molecules was triggered by the observation of Mayer *et al.* (1970) that infrared irradiation of a mixture of CH_3OH , CD_3OD , and Br_2 by a cw HF laser results in a significant enrichment of the CD_3OD isotopic compounds. However, more recent studies using a pulsed HF laser (Willis *et al.*, 1976) came to the conclusion that any reaction between CH_3OH and Br_2 induced by excitation of the OH stretching vibration must have a quantum yield less than 10^{-3} . Also, direct studies of the $Br + CH_3OH(\nu_1 = 1, 2)$ reaction showed no enhanced product formation, but fast vibrational relaxation of CH_3OH (Wolfrum, 1977). The observed isotopic enrichment may be explained by the kinetic isotope effect of the thermal reaction, which takes place by heating the gas mixture until the faster reacting component CH_3OH is consumed. Similarly, the vibrational specificity of CO_2 laser-induced reactions of N_2F_4 with NO, CO, SO_2 , N_2O , CH_4 (Basov *et al.*, 1974; Oraevsky *et al.*, 1977) could not be confirmed for the $N_2F_4 + NO$ reaction in experiments using pulsed lasers and time-resolved product detection (Clough and Kleinermanns, 1979).

Bimolecular reactions of boron compounds have been discussed as interesting examples demonstrating the potential application of vibrationally excited reactants in synthetic chemistry. An early investigation showed the conversion of diborane to icosaborane (Bachmann *et al.*, 1974). Further studies were made for $B(CH_3)_nBr_m + HBr$ (Bachmann *et al.*, 1975), $B_3H_6 + H_2S$, D_2S (Bachmann *et al.*, 1976) direct and sensitized reactions of boron trichloride with C_2H_2 (Karlov, 1974), H_2 (Rockwood and Hudson, 1975), C_2Cl_4 (Karlov, 1974), SiH_4 (Basov *et al.*, 1974), $COCl_2$ (Bachmann *et al.*, 1979), CH_4 (Schramm, 1979), decomposition and reaction of H_3BPF_3 (Lory *et al.*, 1975), D_3BPF_3 (Chien and Bauer, 1976) and $H_2S + N_2H_4$ (Bureiko *et al.*, 1981). Again no direct real-time identification and observation of the bimolecular elementary steps involving vibrationally excited molecules have been made. In some cases stable end products of the reactions could not be reproduced. Thus, for example, only lower boranes

and no $B_{20}H_{16}$ were found in more recent investigations of the CO_2 laser-induced reaction of B_2H_6 (Shatas *et al.*, 1978; Riley and Shatas, 1979).

Chemically more simple systems involving stable reactants are reactions between hydrogen halides and unsaturated hydrocarbons. Investigations of the reverse reactions, the corresponding dehydrohalogenates, show that a large part of the available reaction energy is found in vibrational levels of the products (Clough *et al.*, 1970; Berry, 1974; Bauer, 1978b; Quick and Wittig, 1978; West *et al.*, 1978a). However, no evidence for enhancement of the rate of addition of hydrogen halides to unsaturated hydrocarbons was found in direct experiments where one reactant was prepared in a high vibrational state by laser excitation of an overtone transition with the experimental apparatus shown in Fig. 16. The upper limit for rate constants of HCl ($\nu = 5, 6$) addition to several olefins and addition of HCl and HBr to C_2H_2 ($\nu_3 = 5$) was determined to be 10^{-1} to 10^{-3} of the pre-exponential factor of the corresponding thermal reactions (Herman and Marling, 1979). Similar results are reported for the HF ($\nu = 4$) with isobutene (Douglas and Moore, 1979) and HF (ν) with olefins (Bauer, 1978a) reactions.

The examples discussed here reveal that, analogous to the situation for smaller molecules, due to the relatively high potential energy barriers in reactions between two chemically stable species, preparation of the reactants and separation of vibrationally specific effects from thermal processes is a very difficult task. It also seems likely that simultaneous vibrational excitation of both reagents together with a controlled increase in the relative translational energy is often required to accelerate the reactions. This opens a wide field for further experimental investigations. The problem is somewhat simplified for reactions involving free atoms and vibrationally excited polyatomic molecules.

B. Reactions of Free Atoms with Polyatomic Molecules

1. Reactions with methane and methylbromide

Reactions of free atoms with methane and substituted methanes are good candidates for investigations of the behaviour of mode selective excited polyatomic molecules in lower vibrational levels. The problem of using a small vibrational rate enhancement in atomic reactions in the presence of rapid vibrational relaxation processes of the reacting molecules for selective product formation has been overcome by Manuccia *et al.* (1978) in some cases by a scheme shown in Fig. 18. To compensate for the high deactivation rate, the rate of vibrational excitation is also made very fast. If the concentration of excited molecules is sufficiently low, the relative rates can be

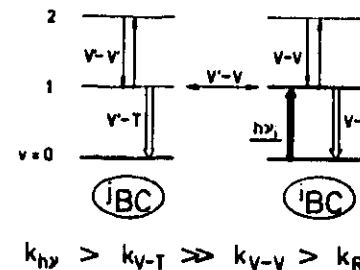
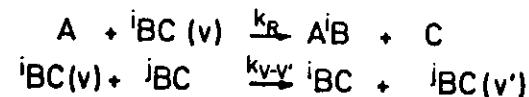
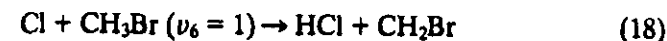
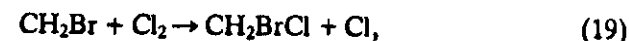


Fig. 18. Kinetic scheme for the measurement of small vibrational rate enhancements by saturation of the vibrational transition (Manuccia *et al.*, 1978).

adjusted to ensure saturation of the absorbing transition even within the power density level of a continuous infrared laser. For the reaction



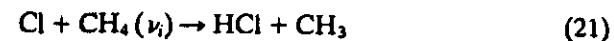
followed by



an enrichment for the ^{81}Br isotope of 5% in the stable end product CH_2BrCl was observed at 183 K (Manuccia *et al.*, 1978). Deuterium enrichment up to 72% was obtained by selective enhancement of the



reaction in $CH_2D_2 + CH_4$ mixtures (Hsu and Manuccia, 1978). The economics of such a process have also been discussed by Manuccia and Hsu (1979). Upper limits for the rate enhancements in the



reaction of <30 at 148 K for the ν_2, ν_4 bending and of $<10^3$ at 298 K for the ν_3 asymmetric stretching have been measured (Chesnokov *et al.*, 1975). No vibrational specific isotope effect could be determined in this reaction (Vijin *et al.*, 1975).

The reaction $CH_3 + H_2 \rightarrow CH_4 + H$ is one of the few examples where theoretical studies for reactions involving polyatomic molecules are available. Reactive cross sections for translational as well as vibrational excitation for both reactants and different modes of the CH_3 radical have been calculated (Chapman and Bunker, 1975). Vibration of H_2 strongly promotes

the reaction for all potentials used. Methyl vibration can suppress, enhance, or not influence the reaction, depending on the excited vibrational mode and the location of the potential energy barrier. Examination of the dynamics showed this to be the result of the ratio of the speed of the vibration over the relative molecular motion. The example shows that *a priori* predictions of mode-selective enhancements of reaction rates are very difficult to make.

2. Reactions with methylfluoride

In order to obtain information on a bimolecular chemical reaction of a polyatomic molecule, which is excited in a specific vibrational mode, one must first try to decouple the vibrational energy exchange from the removal of the excited molecule by interaction with the added reactant. Using a low partial pressure of the excited molecules, and spectral and time resolved detection of the infrared emission from the different excited modes, a direct observation of the energy flow is possible. For such investigations substituted methanes are well suited molecules. A great deal of information concerning vibration to vibration energy transfer has been obtained for the molecule CH_3F mainly due to the pioneering studies of Flynn and

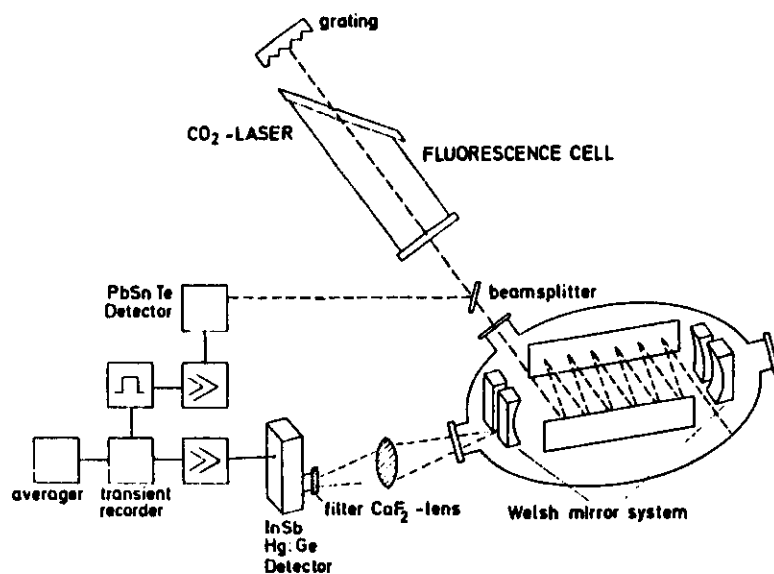


Fig. 19. Experimental arrangement for sensitive detection of CO_2 laser induced infrared fluorescence (Kneba *et al.*, 1980).

coworkers using laser induced infrared fluorescence, infrared double resonance and time resolved thermal lensing experiments (Sheorey and Flynn, 1980; Earl *et al.*, 1978). As shown in Fig. 19 a high detection sensitivity for the laser induced fluorescence can be achieved by a Welsh type mirror system (Welsh *et al.*, 1951, 1955) for the collection of infrared photons and two plane mirrors for multiple reflection of the exciting CO_2 -laser beam. Cooled LiF and MgF_2 windows, several interference filters, and Ge:Hg (4 K) and InSb (77 K) detections are used for time and spectral resolved fluorescence monitoring. The signal to noise ratio is improved by a transient recorder combined with a signal averaging system. As indicated in Fig. 20 several pathways of collision induced mode selective energy transfer have been observed by this arrangement (Kneba *et al.*, 1980). After single quantum excitation of the C—F stretching vibration ν_3 at 1049 cm^{-1} , vibrational energy is transferred first via "up the ladder" processes in the pumped ν_3 mode. Only four gas kinetic collisions are required in this nearly resonant vibration-to-vibration energy transfer process. Local Coriolis resonances between the $3\nu_3$ and the ν_4 level at high rotational states (Graner, 1979) allow a small fraction of the population in the $2\nu_3$ level to enter the ν_4 level. If the time resolved fluorescence signals are studied as a function of added inert gas pressure, with the partial pressure of CH_3F kept constant, the intensity of emission from the C—H bending (ν_6, ν_5, ν_2) and C—H stretching (ν_1, ν_4) levels increases drastically. This can be explained by another dominant pathway under these conditions. The intermode energy gaps between ν_3, ν_6 and ν_2, ν_5 are surmounted in collisions of the excited CH_3F (ν_3) molecules with inert gas atoms. Since the overtone $2\nu_2$ is in Fermi resonance with ν_1 an efficient population of the C—H stretching vibration is also possible. The experiments show that a "metastable" vibrational energy distribution with dominant population in the C—F stretching mode can be created after laser excitation. While the total vibrational energy in the excited CH_3F molecule remains nearly constant, the distribution can be changed in a mode selective way by collisions with inert gas atoms.

For the reaction



the rate is 30 times higher than the corresponding rate at thermal equilibrium at 373 K (Strunin *et al.*, 1976). Studies on the separation of ^{12}C , ^{13}C isotopes by this reaction indicate that the C—F vibration ν_3 excited by a laser is not effective (Molin *et al.*, 1978). No mode specific result, but an effective acceleration of the reaction with increasing vibrational temperature was found in a study using a stationary distribution among the vibrational levels in CH_3F (Krasnoperov *et al.*, 1979). In the exothermic

$D + CH_3F \rightarrow DF + CH_3$ reaction neither C—F nor C—H stretch vibrations help to accelerate the reaction. Effective vibrational deactivation of all vibrational modes is observed in the interaction of $O(^3P)$ atoms with CH_3F , C_2H_4 and CH_3CN (Kneba and Wolfrum, 1977).

3. Molecular beam studies

The effect of reactant translational and vibrational energy in the endothermic reaction



was studied in a crossed molecular beam experiment (Krajnovich *et al.*, 1982). Seeded supersonic beams of Br atoms and CF_3I molecules were crossed at right angles. Pulses from a high repetition rate CO_2 TEA laser were used to excite the CF_3I molecules after the molecular beam passed the source skimmer. The measured angular distributions shows that around 50% of the IBr product is forward scattered when CF_3I is vibrationally excited. This trend was also predicted in quasiclassical trajectory calculations (Perry *et al.*, 1974). Vibrational energy may allow larger impact parameter reactive collisions, which give rise to more forward scattering, when the collision energy is comparable to the barrier height, vibrational energy is more effective than additional translational energy in crossing the endothermic barrier. Most of the reactant vibrational energy is retained as product vibration. When the collision energy exceeds the barrier height several times, reactant vibrational energy appears to be less effective than an equivalent amount of additional translational energy in promoting the reaction. This suggests that the reaction barrier is lying along the approach coordinate (Polanyi and Sathyamurthy, 1979).

Preference for vibrational over translational energy has been found for the reactions



studied in a molecular beam apparatus (Sloane *et al.*, 1972), and



studied by the diffusion cloud technique (Eyal *et al.*, 1981). The observed inefficiency of additional translational energy is explained with a statistical reaction rate theory for very exothermic reactions with polyatomic molecules.

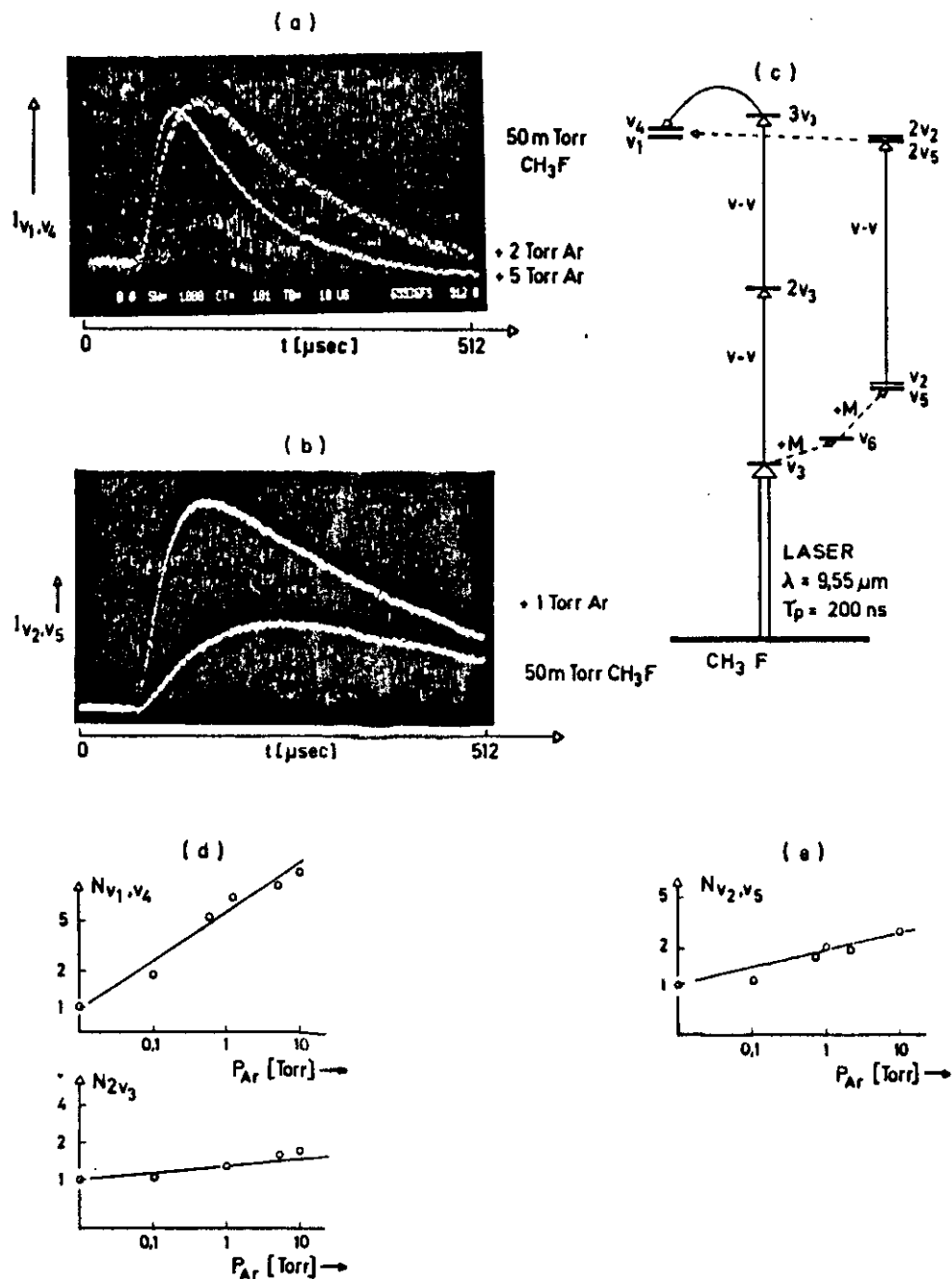


Fig. 20. Collision induced intramolecular energy transfer in CH_3F .

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References

- Anlauf, K. G., Maylotte, D. H., Polanyi, J. C. and Bernstein, R. B. (1969). *J. Chem. Phys.*, **51**, 5716.
- Arnoldi, D., Kaufmann, K. and Wolfrum, J. (1975). *Phys. Rev. Lett.*, **34**, 1597.
- Arnoldi, D. and Wolfrum, J. (1976). *Ber. Bunsenges. Phys. Chem.*, **80**, 892.
- Bachmann, H. R., Bachmann, F., Kompa, K. L., Nöth, H. and Rinck, R. (1976). *Chem. Ber.*, **109**, 3331.
- Bachmann, H. R., Nöth, H., Rinck, R. and Kompa, K. L. (1974). *Chem. Phys. Lett.*, **29**, 627.
- Bachmann, H. R., Nöth, H., Rinck, R. and Kompa, K. L. (1975). *Chem. Phys. Lett.*, **33**, 261.
- Bachmann, H. R., Rinck, R., Nöth, H. and Kompa, K. L. (1977). *Chem. Phys. Lett.*, **45**, 169.
- Bachmann, H. R., Nöth, H., Rinck, R. and Kompa, K. L. (1979). *J. Photochem.*, **10**, 433.
- Baer, M., Mayne, H. R., Khare, U. and Kouri, P. J. (1980). *Chem. Phys. Lett.*, **72**, 269.
- Balint-Kurti, G. G. and Yardley, R. N. (1977). *Faraday Discuss. Chem. Soc.*, **62**, 77.
- Bar-Ziv, E., Moy, J. and Gordon, R. J. (1978). *J. Chem. Phys.*, **68**, 1013.
- Basov, N. G., Oraevsky, A. N. and Pankratov, A. V. (1974). In *Chemical and Biochemical Applications of Lasers* (C. B. Moore, ed.) Vol. 1, pp. 203-29. Academic Press, New York.
- Bauer, S. H. and Resler, E. L. (1964). *Science*, **146**, 1045.
- Bauer, S. H. (1978a). In *Separation of Hydrogen Isotopes*, Am. Chem. Soc. Symp. Ser. 68 (H. K. Rae, ed.) p. 152. Washington DC.
- Bauer, S. H. (1978b). *Chem. Rev.*, **78**, 147.
- Bauer, S. H. (1979). *Annu. Rev. Chem.*, **30**, 271.
- Bauer, S. H., Ledermann, D. M., Resler, E. L. and Fisher, E. R. (1973). *Int. J. Chem. Kinet.*, **5**, 93.
- Berry, M. J. (1974). *J. Chem. Phys.*, **61**, 3114.

- Birely, J. H., Kasper, J. V. V., Hai, F. and Darnton, C. A. (1975). *Chem. Phys. Lett.*, **31**, 220.
- Blackwell, B. A., Polanyi, J. C. and Sloan, J. J. (1977). *Chem. Phys.*, **24**, 25.
- Botschwina, P. and Meyer, W. (1976). *Chem. Phys. Lett.*, **44**, 449.
- Bott, J. F. and Heidner, R. F. (1976). *J. Chem. Phys.*, **69**, 1544.
- Bott, J. F. and Heidner, R. F. (1978). *J. Chem. Phys.*, **68**, 1708.
- Bowman, J. M. and Lee, K. T. (1979). *Chem. Phys. Lett.*, **64**, 291.
- Bowman, J. M. and Lee, K. T. (1980). *J. Chem. Phys.*, **72**, 5071.
- Bray, R. G., Henke, W., Lin, S. K., Reddy, K. V. and Berry, M. J. (1977). *Chem. Phys. Lett.*, **47**, 213.
- Brown, R. D. H. (1977). *J. Phys. Chem.*, **81**, 479.
- Brown, R. D. H., Glass, G. P. and Smith, I. W. M. (1975a). *Chem. Phys. Lett.*, **32**, 517.
- Brown, R. D. H., Glass, G. P. and Smith, I. W. M. (1975b). *J. Chem. Soc. Faraday Trans. 2*, **71**, 1963.
- Brown, R. D. H. and Smith, I. W. M. (1978). *Int. J. Chem. Kinet.*, **10**, 1.
- Brown, N. J. and Silver, D. M. (1978). *J. Chem. Phys.*, **68**, 3607.
- Butler, J. E., Hudgens, J. W., Lin, M. C. and Smith, G. K. (1978). *Chem. Phys. Lett.*, **58**, 216.
- Bureiko, S. F., Burtsov, A. P., Goluber, N. S., Danilov, I. L. and Ladvischenko, Yu. M. (1981). *High Energy Chem.*, **14**, 282.
- Chapman, S. (1981). *J. Chem. Phys.*, **74**, 1001.
- Chapman, S. and Bunker, D. L. (1975). *J. Chem. Phys.*, **62**, 2890.
- Chekin, S. K., Ghershenzon, Y. M., Konoplyov, A. V. and Rozenshtein, V. B. (1979). *Chem. Phys. Lett.*, **68**, 386.
- Chesnokov, E. N., Strunin, V. P., Serdyuk, N. K. and Panfilov, V. N. (1975). *React. Kinet. Catal. Lett.*, **3**, 131.
- Chien, K. R. and Bauer, S. H. (1976). *J. Phys. Chem.*, **80**, 1405.
- Clary, D. C. and Connor, J. N. L. (1979). *Chem. Phys. Lett.*, **66**, 493.
- Clary, D. C. and Connor, J. N. L. (1980). *Chem. Phys.*, **48**, 175.
- Clary, D. C., Connor, J. N. L. and Edge, C. J. (1979). *Chem. Phys. Lett.*, **68**, 154.
- Clough, P. N. and Kleinermanns, K. (1979). unpublished results.
- Clough, P. N., Polanyi, J. C. and Taguchi, R. T. (1970). *Can. J. Chem.*, **48**, 2919.
- Connor, J. N. L., Jakubetz, W., Manz, J. and Whitehead, J. C. (1980). *J. Chem. Phys.*, **72**, 6209.
- Craig, N. C. and Moore, C. B. (1971). *J. Chem. Phys.*, **75**, 1622.
- Creel, C. L. and Ross, J. (1976). *J. Chem. Phys.*, **64**, 3560.
- DeVries, A. E. and Klein, F. S. (1964). *J. Chem. Phys.*, **41**, 3428.
- Ding, A. M. G., Kirsch, L. J., Perry, D. S., Polanyi, J. C. and Schreiber, J. L. (1973). *Faraday Discuss. Chem. Soc.*, **55**, 252.
- Dispert, H. H., Geis, M. W. and Brooks, P. R. (1979). *J. Chem. Phys.*, **70**, 5317.
- Dixon, D. A., Stevens, R. M. and Herschbach, D. R. (1977). *Faraday Discuss. Chem. Soc.*, **62**, 110.
- Doll, J. D., George, T. F. and Miller, W. H. (1973). *J. Chem. Phys.*, **58**, 1343.
- Douglas, D. J. and Moore, C. B. (1979). in *Laser-Induced Processes in Molecules* (K. L. Kompa and S. D. Smith, eds) p. 336. Springer, Heidelberg.
- Douglas, D. J., Polanyi, J. C. and Sloan, J. J. (1973). *J. Chem. Phys.*, **59**, 6679.
- Douglas, D. J., Polanyi, J. C. and Sloan, J. J. (1976). *Chem. Phys.*, **13**, 15.
- Dreier, T. and Wolfrum, J. (1981). *18th Symposium (International) on Combustion*, p. 801. The Combustion Institute, Pittsburgh.

- Dunning, T. H. (1981). *Annual Report Theoretical Chemistry Group*, Argonne National Laboratory.
- Earl, B. L., Gamss, L. A. and Ronn, A. M. (1978). *Acc. Chem. Res.*, **11**, 183.
- Elkowitz, E. B. and Wyatt, R. E. (1976). *Mol. Phys.*, **31**, 189.
- van den Ende, D. and Stolte, S. (1980). *Chem. Phys.*, **45**, 55.
- Endo, H. and Glass, G. P. (1976). *Chem. Phys. Lett.*, **44**, 180.
- Eyal, M., Grabiner, F. R., Agam, U. and Gamss, L. A. (1981). *J. Chem. Phys.*, **75**, 4396.
- Felder, W. and Fontijn, A. (1976). *J. Chem. Phys.*, **64**, 1977.
- Franck, J. and Eucken, A. (1933). *Z. physik. Chem. B*, **20**, 460.
- Garrett, B. C. and Truhlar, D. G. (1979). *Proc. Natl. Acad. Sci. USA*, **76**, 4755.
- Garrett, B. C. and Truhlar, D. G. (1980a). *J. Phys. Chem.*, **84**, 682 (E).
- Garrett, B. C. and Truhlar, D. G. (1980b). *J. Chem. Phys.*, **72**, 3460.
- Glass, G. P. and Chaturvedi, B. K. (1982). *J. Chem. Phys.*, **77**, 3478.
- Goddard, J. D. and Csizmadia, I. G. (1979). *Chem. Phys. Lett.*, **64**, 219.
- Gordon, E. B., Ivanov, B. I., Perminov, A. P., Balalacv, V. G., Ponomarev, A. N. and Fitatov, V. V. (1978). *Chem. Phys. Lett.*, **58**, 425.
- Gordon, R. J., Bar-Ziv, E. and Moy, J. (1981). *J. Chem. Phys.*, **68**, 1013.
- Gordon, R. J. and Lin, M. C. (1976). *J. Chem. Phys.*, **64**, 1058.
- Gordon, R. J. and Lin, M. C. (1973). *Chem. Phys. Lett.*, **22**, 262.
- Gordon, R. J., Moy, J. and Bar-Ziv, E. (1977). *J. Chem. Phys.*, **66**, 5439.
- Graner, G. (1979). *J. Phys. Chem.*, **83**, 1491.
- Gray, J. C., Truhlar, D. G., Clemens, L., Duff, J. W., Chappmann, F. M., Morrell, G. O. and Hayes, E. F. (1978). *J. Chem. Phys.*, **69**, 240.
- Harris, S. J. (1977). *J. Am. Chem. Soc.*, **99**, 5798.
- Heidner, R. F. and Kasper, J. V. V. (1972). *Chem. Phys. Lett.*, **15**, 179.
- Heismann, F. and Loesch, H. J. (1982). *Chem. Phys.* (to be published).
- Herman, I. P. (1980). *J. Chem. Phys.*, **72**, 5777.
- Herman, I. P., Mariella, R. P. and Javan, A. (1978). *J. Chem. Phys.*, **68**, 1070.
- Herman, I. P. and Marling, J. B. (1979). *J. Chem. Phys.*, **71**, 643.
- Hsu, D. S. Y. and Manuccia, T. J. (1978). *Appl. Phys. Lett.*, **33**, 915.
- Hui, K. K. and Cool, T. A. (1976). *12th Informal Conference on Photochemistry*. Abstract R 1, NBS Gaithersburg (Maryland, USA).
- Hui, K. K. and Cool, T. A. (1978). *J. Chem. Phys.*, **68**, 1022.
- Jacobs, A., Kleinermanns, K. and Wolfrum, J. (1983). (to be published).
- Jaffer, D. H. and Smith, I. W. M. (1979). *Faraday Discuss. Chem. Soc.*, **67**, 212.
- Kaldor, A., Braun, W. and Kurylo, M. J. (1974). *J. Chem. Phys.*, **61**, 2496.
- Kaplan, H., Levine, R. D. and Manz, J. (1976). *Chem. Phys.*, **12**, 447.
- Karlov, N. V. (1974). *Appl. Opt.*, **13**, 301.
- Karny, Z. and Zare, R. N. (1978). *J. Chem. Phys.*, **68**, 3360.
- Karplus, M., Porter, R. N. and Sharma, R. D. (1965). *J. Chem. Phys.*, **43**, 3259.
- Kleon, F. S., Persky, A. and Weston, R. E. (1964). *J. Chem. Phys.*, **41**, 1799.
- Klein, F. S. and Veltman, I. (1978). *J. Chem. Soc. Faraday Trans. 2*, **74**, 17.
- Kneba, M. (1977). *Thesis*. Univ. Göttingen.
- Kneba, M., Stender, R., Wellhausen, U. and Wolfrum, J. (1980). *J. Mol. Struct.*, **59**, 207.
- Kneba, M., Wagner, H. Gg. and Wolfrum, J. (1976). *Ber. Max-Planck-Institut für Strömungsforschung*, **23**, 1.
- Kneba, M., Wellhausen, U. and Wolfrum, J. (1979). *Ber. Bunsenges. Phys. Chem.*, **83**, 940.

- Kneba, M. and Wolfrum, J. (1978). *17th Symposium (International) on Combustion*, p. 497. The Combustion Institute, Pittsburgh.
- Kneba, M. and Wolfrum, J. (1977). *Ber. Bunsenges. Phys. Chem.*, **81**, 1275.
- Kneba, M. and Wolfrum, J. (1979). *J. Phys. Chem.*, **83**, 69.
- Krajnovich, D., Zhang, Z., Huisken, F., Shen, Y. R. and Lee, Y. T. (1982). In *Physics of Electronic and Atomic Collisions*, p. 733. North Holland, Amsterdam.
- Krasnoperov, L. N., Chesnokov, E. N. and Panfilov, V. N. (1979). *Chem. Phys.*, **42**, 345.
- Kuppermann, A., Schatz, G. C. and Dwyer, J. (1977). *Chem. Phys. Lett.*, **45**, 71.
- Kurylo, M. J., Braun, W., Abramowitz, S. A. and Krauss, M. (1976). *J. Res. Nat. Bur. Stand., Sect. A*, **80**, 167.
- Kurylo, M. J., Braun, W., Kaldor, A., Freund, S. M. and Wayne, R. P. (1974). *J. Photochem.*, **3**, 71.
- Kurylo, M. J., Braun, W., Xuan, C. N. and Kaldor, A. (1975). *J. Chem. Phys.*, **62**, 2065.
- Leone, S. R., Macdonald, R. G. and Moore, C. B. (1975). *J. Chem. Phys.*, **63**, 4735.
- Leone, S. R. and Moore, C. B. (1973). *Chem. Phys. Lett.*, **19**, 340.
- Letokhov, V. S. (1975). *Ann. Rev. Phys. Chem.*, **28**, 133.
- Levine, R. D. (1978). *Ann. Rev. Phys. Chem.*, **29**, 59.
- Lewittes, M. E., Davis, C. C. and McFarlane, R. A. (1978). *J. Chem. Phys.*, **69**, 1952.
- Light, G. C. (1978). *J. Chem. Phys.*, **68**, 2831.
- Light, G. C. and Matsumoto, J. H. (1978). *Chem. Phys. Lett.*, **58**, 578.
- London, F. C. (1928). *Probleme der Modernen Physik*, p. 104. Hirzel, Leipzig.
- Lory, E. R., Bauer, S. H. and Manuccia, T. (1975). *J. Phys. Chem.*, **79**, 545.
- Macdonald, R. G. and Moore, C. B. (1978). *J. Chem. Phys.*, **68**, 513.
- Manning, R. G., Braun, W. and Kurylo, M. J. (1976). *J. Chem. Phys.*, **65**, 2609.
- Manos, D. M. and Parson, J. M. (1978). *J. Chem. Phys.*, **69**, 231.
- Manuccia, T. J., Clark, M. D. and Lory, E. R. (1978). *J. Chem. Phys.*, **68**, 2271.
- Manuccia, T. J. and Hsu, D. S. Y. (1979). In *Laser-Induced Processes in Molecules* (K. L. Kompa and S. D. Smith, eds) p. 270. Springer, Heidelberg.
- Marcus, R. A. (1975). *J. Chem. Phys.*, **62**, 1372.
- Margitan, J. J., Kaufman, F. and Anderson, J. G. (1975). *Chem. Phys. Lett.*, **34**, 485.
- Marteau, C., Gaillard-Cusin, F. and James, H. (1978). *J. Chem. Phys.*, **75**, 491, 498.
- Mayne, H. R. (1979a). *Chem. Phys. Lett.*, **66**, 487.
- Mayne, H. R. (1979b). *Chem. Phys.*, **43**, 3259.
- Mayne, H. R. and Toennies, J. P. (1979). *J. Chem. Phys.*, **70**, 5314.
- Mayne, H. R. and Toennies, J. P. (1981). *J. Chem. Phys.*, **75**, 1794.
- Mayer, S. W., Kwok, M. A., Gross, R. W. F. and Spencer, D. J. (1970). *Appl. Phys. Lett.*, **17**, 516.
- McNeal, R. J., Whitson, M.E. Jr. and Cook, G. R. (1974). *J. Geophys. Res.*, **79**, 1527.
- Miller, J. C. and Gordon, R. J. (1983). *J. Chem. Phys.*, **78**, 3713.
- Mitchell, D. N. and LeRoy, D. J. (1973). *J. Chem. Phys.*, **58**, 3449.
- Mok, N. H. and Polanyi, J. C. (1970). *J. Chem. Phys.*, **53**, 4588.
- Molin, Yu. N., Panfilov, V. N. and Strunin, V. P. (1978). *Chem. Phys. Lett.*, **56**, 557.

- Nesbitt, D. J. and Leone, S. R. (1980). *J. Chem. Phys.*, **73**, 6182.
- Nikitin, E. E. and Umanski, S. Y. (1972). *Faraday Discuss. Chem. Soc.*, **53**, 1.
- Oraevsky, A. N., Pankratov, A. V., Skachkov, A. N. and Shabarskin, V. M. (1977). *Khim Vys. Energ.*, **11**, 152.
- Osherov, V. I., Ushakov, V. G. and Lomakin, L. A. (1978). *Chem. Phys. Lett.*, **55**, 513.
- Pechukas, P. and Pollak, E. (1979). *J. Chem. Phys.*, **71**, 2062.
- Perry, D. S., Polanyi, J. C. and Wilson Jr., C. W. (1974). *Chem. Phys.*, **3**, 317.
- Peyerimhof, S. D. and Buenker, R. J. (1982). *J. Chem. Phys.* (to be published).
- Polanyi, J. C. (1963). *J. Quant. Spectrosc. Radiat. Transfer*, **3**, 47.
- Polanyi, J. C. (1972). *Acc. Chem. Res.*, **5**, 161.
- Polanyi, J. C. and Sathyamurthy, N. (1979). *Chem. Phys.*, **37**, 259.
- Polanyi, J. C. and Woodall, K. B. (1972). *J. Chem. Phys.*, **57**, 1574.
- Pollak, E. (1981). *J. Chem. Phys.*, **74**, 5586; *Chem. Phys.*, **61**, 305; *Chem. Phys. Lett.*, **80**, 45; *J. Chem. Phys.*, **75**, 4435.
- Pollak, E. and Wyatt, R. E. (1983). *J. Chem. Phys.*, **78**, 4464.
- Porter, R. N. and Karplus, M. (1964). *J. Chem. Phys.*, **40**, 1105.
- Porter, R. N., Sims, L. B., Thompson, D. L. and Raff, L. M. (1973). *J. Chem. Phys.*, **58**, 2855.
- Potter, A. E. Jr., Coltharp, R. N. and Worley, S. D. (1979). *J. Chem. Phys.*, **54**, 992.
- Poulsen, L. L. (1970). *J. Chem. Phys.*, **53**, 1987.
- Pratt, G. and Rogers, D. (1976). *J. Chem. Soc. Faraday Trans. 1*, **72**, 1589.
- Pruett, J. G., Grabiner, F. R. and Brooks, P. R. (1974). *J. Chem. Phys.*, **60**, 3335.
- Pruett, J. G., Grabiner, F. R. and Brooks, P. R. (1975). *J. Chem. Phys.*, **63**, 1173.
- Pruett, J. G. and Zare, R. N. (1976). *J. Chem. Phys.*, **64**, 1774.
- Quack, M. (1979). *J. Phys. Chem.*, **83**, 150.
- Quick, C. E. Jr. and Wittig, C. (1978). *Chem. Phys.*, **32**, 75.
- Raff, L. M. (1977). *J. Chem. Phys.*, **44**, 1212.
- Raff, L. M., Simms, L. B., Thompson, D. L. and Porter, R. N. (1970). *J. Chem. Phys.*, **53**, 1606.
- Redmon, M. J. (1979). *Int. J. Quantum Chem., Symp.*, **13**, 559.
- Redpath, A. E., Menzinger, M. and Carrington, T. (1978). *Chem. Phys.*, **27**, 409.
- Ridley, B. A. and Smith, I. W. M. (1971). *Chem. Phys. Lett.*, **9**, 457.
- Riley, C. and Shatas, R. (1979). *J. Phys. Chem.*, **83**, 1679.
- Rockwood, S. D. and Hudson, J. W. (1975). *Chem. Phys. Lett.*, **34**, 542.
- Rosen, D. I. and Cool, T. R. (1975). *J. Chem. Phys.*, **62**, 466.
- Sato, S. (1955). *J. Chem. Phys.*, **23**, 592, 2465.
- Schacke, H., Schmatjko, K. J. and Wolfrum, J. (1973). *Ber. Bunsenges. Phys. Chem.*, **77**, 248.
- Schacke, H., Wagner, H. Gg. and Wolfrum, J. (1977). *Ber. Bunsenges. Phys. Chem.*, **81**, 670.
- Schatz, G. C. (1979). *Faraday Discuss. Chem. Soc.*, **67**, 140; *J. Chem. Phys.*, **71**, 542.
- Schatz, G. C. (1981). *J. Chem. Phys.*, **74**, 1133.
- Schatz, G. C. and Elgersma, H. (1980). *Chem. Phys. Lett.*, **73**, 21.
- Schatz, G. C. and Kuppermann, A. (1976). *J. Chem. Phys.*, **65**, 4668.
- Schatz, G. C. and Moser, M. D. (1978). *Chem. Phys.*, **35**, 239; *J. Chem. Phys.*, **68**, 1992.
- Schinke, R. and Lester, W. A. (1979). *J. Chem. Phys.*, **70**, 4893.
- Schmatjko, K. J. and Wolfrum, J. (1975). *Ber. Bunsenges. Phys. Chem.*, **79**, 69.
- Schmatjko, K. J. and Wolfrum, J. (1978). *Ber. Bunsenges. Phys. Chem.*, **83**, 419.
- Schramm, B. (1979). In *Laser-Induced Processes in Molecules* (K. L. Kompa and S. D. Smith, eds), p. 274. Springer, Heidelberg.
- Schultz, W. R. and LeRoy, D. J. (1965). *J. Chem. Phys.*, **42**, 3869.
- Shan, Y., Choi, B. H., Poe, R. T. and Tang, K. T. (1978). *Chem. Phys. Lett.*, **57**, 379.
- Shatas, S., Gregory, D., Shatas, R. and Riley, C. (1978). *Inorg. Chem.*, **17**, 163.
- Sheorey, R. S. and Flynn, G. W. (1980). *J. Chem. Phys.*, **72**, 1175.
- Siegbahn, P. and Liu, B. (1978). *J. Chem. Phys.*, **68**, 2457.
- Sims, L. B., Dosser, L. R. and Wilson, P. S. (1975). *Chem. Phys. Lett.*, **32**, 150.
- Slater, J. C. (1931). *Phys. Rev.*, **38**, 1109.
- Sloane, M., Tang, S. Y. and Ross, J. (1972). *J. Chem. Phys.*, **57**, 2745.
- Smith, I. W. M. (1975). *J. Chem. Soc., Faraday Trans. 2*, **71**, 1970.
- Smith, I. W. M. (1976). *Acc. Chem. Res.*, **9**, 161.
- Smith, I. W. M. (1977a). *Chem. Phys. Lett.*, **47**, 219.
- Smith, I. W. M. (1977b). *Chem. Phys.*, **20**, 437.
- Smith, I. W. M. and Wood, P. M. (1973). *Mol. Phys.*, **25**, 441.
- Spencer, J. E., Endo, H. and Glass, G. P. (1976). *16th Symposium (International) on Combustion*, p. 829. The Combustion Institute, Pittsburgh.
- Spencer, J. E. and Glass, G. P. (1976). *Chem. Phys.*, **15**, 35.
- Spencer, J. E. and Glass, G. P. (1977). *Int. J. Chem. Kinet.*, **9**, 111.
- Stedman, D. H., Steffenson, D. and Niki, H. (1970). *Chem. Phys. Lett.*, **7**, 173.
- Stephenson, J. C. and Freund, S. M. (1976a). *J. Chem. Phys.*, **65**, 4303.
- Stephenson, J. C. and Freund, S. M. (1976b). *Opt. Comm.*, **18**, 93.
- Streit, G. E. and Johnston, H. S. (1976). *J. Chem. Phys.*, **64**, 95.
- Strunin, V. P., Serdyuk, N. K., Chesnokov, E. N. and Panfilov, V. N. (1976). *React. Kinet. Catal. Lett.*, **5**, 37.
- Sun, J. C., Choi, B. H., Poe, R. T. and Tang, K. T. (1980). *Phys. Rev. Lett.*, **44**, 1211.
- Thompson, D. L., Suzukawa, H. H. and Raff, L. M. (1975). *J. Chem. Phys.*, **62**, 4727.
- Thompson, D. L., Suzukawa, H. H. and Raff, L. M. (1976). *J. Chem. Phys.*, **64**, 2269.
- Troe, J. (1978). *Annu. Rev. Phys. Chem.*, **29**, 223.
- Truhlar, D. G. (1975). *J. Am. Chem. Soc.*, **97**, 6310.
- Truhlar, D. G. and Horowitz, C. J. (1978). *J. Chem. Phys.*, **68**, 2460.
- Truhlar, D. G., Olson, P. C. and Parr, C. A. (1972). *J. Chem. Phys.*, **57**, 4479.
- Valenich, T., Hsieh, J., Kwan, J., Stewart, T. and Lenhardt, T. (1977). *Ber. Bunsenges. Phys. Chem.*, **81**, 131.
- Vijin, V. V., Mikheev, A. N., Petrov, A. K. and Molin, Yu. N. (1975). *React. Kinet. Catal. Lett.*, **3**, 79.
- Walch, S. P. and Dunning, T. H. (1980). *Chem. Phys. Lett.*, **72**, 1303.
- Walker, R. B., Steckel, E. B. and Light, J. C. (1978). *J. Chem. Phys.*, **69**, 2922.
- Welsh, H. L., Cumming, C. and Stansbury, E. J. (1951). *J. Opt. Soc. Am.*, **41**, 712.
- Welsh, H. L., Stansbury, E. J., Romanko, J. and Feldman, T. (1955). *J. Opt. Soc. Am.*, **45**, 338.
- West, G. A., Weston, R. E. and Flynn, G. W. (1976). *Chem. Phys. Lett.*, **42**, 488.
- West, G. A., Weston, R. E. Jr. and Flynn, G. W. (1978a). *Chem. Phys.*, **35**, 275.

- West, G. A., Weston, R. E. and Flynn, G. W. (1978b). *Chem. Phys. Lett.*, **56**, 429.
- Weston, R. E. (1979). *J. Phys. Chem.*, **83**, 61.
- Wilkins, R. L. (1975). *J. Chem. Phys.*, **63**, 534.
- Willis, C., Back, R. A., Corkum, R., McAlpine, R. P. and McClusky, F. K. (1976). *Chem. Phys. Lett.*, **38**, 336.
- Wolfrum, J. (1977a), *2nd Winter Colloquium on Laser Induced Chemistry*, pp. 84. Park City, Utah.
- Wolfrum, J. (1977b). *Ber. Bunsenges. Phys. Chem.*, **81**, 114.
- Wood, G. O. (1972). *J. Chem. Phys.*, **56**, 1723.
- Wren, D. J. and Menzinger, M. (1979). *Faraday Discuss. Chem. Soc.*, **67**, 97.
- Yokozeki, A. and Menzinger, M. (1977). *Chem. Phys.*, **20**, 9.
- Zare, R. N. (1979). In *Laser-Induced Processes in Molecules* (K. L. Kompa and S. D. Smith, eds) p. 225. Springer, Heidelberg.
- Zellner, R. and Steinert, W. (1981). *Chem. Phys. Lett.*, **81**, 568.
- Zwier, T. S., Bierbaum, V. M., Ellison, G. B. and Leone, S. R. (1980). *J. Chem. Phys.*, **72**, 5426.