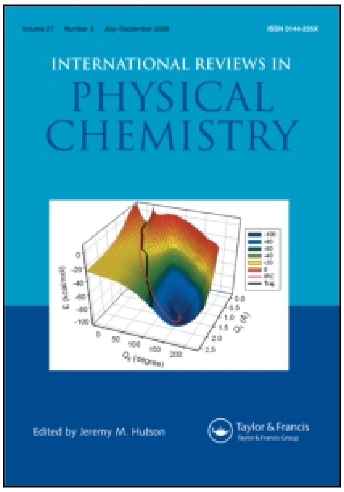

International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Classical trajectory calculations on gas-phase reactive collisions

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To cite this Article Mayne, Howard R.(1991) 'Classical trajectory calculations on gas-phase reactive collisions', International Reviews in Physical Chemistry, 10: 1, 107 — 121
To link to this Article: DOI: 10.1080/01442359109353255
URL: http://dx.doi.org/10.1080/01442359109353255

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1991, VOL. 10, NO. 1, 107–121

Classical trajectory calculations on gas-phase reactive collisions

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The recent (since 1983) literature on classical trajectory calculations on gas phase reactions is reviewed. It is seen that this continues to be a vigorous area of research, yielding considerable insight into the microscopic details of reaction mechanisms, as well as being a relatively simple means of calculating cross-sections and rate constants. The necessary theoretical background is touched upon briefly, and several caveats are pointed out.

A few model reactions continue to be the subject of intensive activity, most notably the reactions $H+H_2 \rightarrow H_2+H$ and $F+H_2 \rightarrow FH+H$, the prototypical thermoneutral and exoergic systems respectively. These reactions are unusual in that their potential energy surfaces are relatively well known. For this reason, among others, comparisons of quantum and classical dynamics on these systems are common.

Recent advances in quantum mechanical scattering theory have greatly increased the feasibility of exact calculations for the transfer of H atoms between heavier atoms. Spurred by this development, the number of classical treatments of light-atom transfer has increased dramatically. This work is considered here in some detail.

Largely due to recent breakthroughs in experimental technique, there has been a renewal of interest in the influence of reactant vibration and rotation on reactivity. Many trajectory studies reflect this interest.

Other topics include the treatment of reactions dominated by long-range attraction, in which the traditional Langevin approach has often been found wanting, non-adiabatic reactions, and collision-induced dissociation.

Finally, the one area in which the classical trajectory technique is still the only viable technique is in the treatment of polyatomic molecules. Recent calculations are summarized.

1. Introduction

The classical (or quasi-classical) trajectory approach to simulating gas-phase chemical reactions was pioneered 25 years ago by Porter, Karplus and Sharma [1]. It avoids the basis-set expansions of quantum mechanical methods (and the concomitant need for large computer storage) by assuming that the nuclei behave as classical particles. They move under the influence of the potential energy surface, $V(q)$, where q denotes the set of nuclear displacements. Once the initial conditions have been determined (see below), a trajectory is computed by numerically solving the dynamical equations of motion. Typically the equations of motion will be Hamilton's equations.

For an N-atom system, the classical Hamiltonian is a function of position, $\mathbf{q}=(q_{1x}, q_{1y}, q_{1z}, \ldots, q_{Nz})$ and the conjugate momenta, $\mathbf{p}=(p_{1x}, p_{1y}, p_{1z}, \ldots p_{Nz})$. It is given by

$$H(\mathbf{q}, \mathbf{p}) = \sum_{i=1}^{N} \sum_{\alpha=x,y,z} \frac{p_{i\alpha}^2}{2m_i} + V(\mathbf{q}).$$

with m_i the mass of the ith atom. Hamilton's equations are

$$\left.\begin{aligned} p_{i\alpha} &= -\frac{\partial H(\mathbf{q},\mathbf{p})}{\partial q_{i\alpha}} = -\frac{\partial V(\mathbf{q})}{\partial q_{i\alpha}} \\ q_{i\alpha} &= \frac{\partial H(\mathbf{q},\mathbf{p})}{\partial p_{i\alpha}} = \frac{p_{i\alpha}}{m_i} \end{aligned}\right\} \quad i=1,\dots N; \quad \alpha=x,y,z.$$

More compactly,

$$\mathbf{p}_i = -\nabla_i V; \qquad \mathbf{q}_i = \mathbf{p}_i/m_i, \qquad i=1,\dots N.$$

Removal of the centre of mass motion is advantageous for the case of two or three atoms [2], effectively reducing the system to a one- or two-particle system respectively. In the former case, the coordinate of interest is the internuclear separation, and the mass becomes the reduced mass, given by $\mu_{12}^{-1} = m_1^{-1} + m_2^{-1}$. In the latter, one coordinate becomes the internuclear displacement of the centre of mass of the diatom (12), $\mathbf{r} = \mathbf{q}_1 - \mathbf{q}_2$, with the reduced mass μ_{12}, the other becomes the displacement from the atom (3) to the diatom (12),

$$\mathbf{R} = \mathbf{q}_3 - \frac{m_1\mathbf{q}_1 + m_2\mathbf{q}_2}{m_1 + m_2},$$

with the reduced mass $\mu_{123}^{-1} = (m_1 + m_2)^{-1} + m_3^{-1}$. These are the usual Jacobi coordinates [1, 2]. Details of the computational methods required for solving the differential equations are reviewed elsewhere [2–6].

Selection of initial conditions for the trajectory depends on the nature of the problem under study. The impact parameter can be sampled either systematically [7] or by Monte Carlo methods, either 'crude' or 'stratified' [2, 5, 6]. Quantum mechanically, the state of a diatomic molecule is unambiguously determined by the vibrational, rotational and magnetic quantum numbers, v, j and m_j. Classically, v and j serve only to fix the energy of the molecule: the vibrational and rotational 'phases' must also be specified. That is, the location of the diatom is its vibrational cycle, as well as the spatial orientation of both the molecular frame and the angular momentum vector must be randomly selected. Efficient methods for doing this have been described [5, 6, 8, 9]. Selection of initial conditions for triatomic and more complicated molecules is still the subject of much research. Most practical algorithms are due to Schatz and co-workers [10–13].

The range of validity of the classical approximation is of course of paramount importance. It is usually assumed that classical mechanics will predict highly-averaged quantities (such as total reaction cross-section, or mean energy transfer) more accurately than very specific quantities (such as state-to-state cross-sections). Recent extremely detailed comparisons for $\mathrm{H} + \mathrm{H}_2$ (14) and $\mathrm{D} + \mathrm{H}_2$ [15, 16] seem to confirm this.

It is frequently believed that the greatest deficiency of classical mechanics lies in its inability to incorporate tunnelling phenomena, but rate constants calculated using classical mechanics on even such a light system as $\mathrm{H} + \mathrm{H}_2$ are usually in reasonable agreement both with experimental and with quantum results, if the low-temperature region is avoided [17].

Unfortunately another, potentially far more devastating, weakness of classical trajectories has recently come to light. Quantum mechanics always requires some zero-point energy in a vibrational mode; classical mechanics imposes no such restrictions.

Thus it is quite possible for classical mechanical calculations to have a reaction threshold at collision energies below the quantum threshold [18–20]. This has been dubbed 'adiabatic leak' [18, 19]. In studies of energy transfer in polyatomic molecules, this problem has been shown to be compounded by multiple 'leaks'. For instance, in a classical simulation of energy transfer in benzene [21], the $n=3$ overtone was found to have a linewidth ten times broader than that found in the experiment; the classical trajectories allow relaxation to occur much more rapidly than quantum mechanics does. Techniques for obviating this problem by adding constraints to the classical mechanics have recently been proposed [22, 23]. It remains to be seen how they perform in practice.

If only heavy atoms are involved, both the problems of tunnelling and adiabatic leak disappear, and classical trajectory results can be expected to be valid for most phenomena.

2. Scope of this review

A detailed summary of the computational methods employed in trajectory calculations was presented in the comprehensive review of Raff and Thompson [2]. The reader is referred to that excellent work for such technical matters. Their article also reviewed trajectory calculations up to 1983. We survey the literature since that date.

We are concerned here exclusively with three-dimensional bimolecular reactions in the gas phase; unimolecular decomposition is reviewed elsewhere [24]. In addition, we concentrate on calculations in which the dynamics is solved exclusively using classical mechanics, avoiding the less well-understood hierarchy of mixed classical-quantum dynamics [25]. Nor do we consider transition state or statistical theories of reaction. Excellent reviews of these approaches are available elsewhere [26, 27].

3. $H+H_2$

The hydrogen exchange reaction is the prototype for thermoneutral systems. It continues to be a popular candidate for trajectory calculations. One reason for this is undoubtedly the fact that this system is ideal both for quantum chemical calculations of the potential energy (since the system possesses only three electrons) and for quantum-mechanical dynamical calculations (because the lightness of the atoms involved results in large spacing between energy levels). Therefore direct comparison of quantum and classical mechanics is feasible for this reaction. Extremely detailed comparisons of state-to-state cross-sections have been made for $H+H_2$ [14] and $D+H_2$ [15] at low total angular momentum. The conclusion from these studies is that classical cross-sections are generally poor if compared with the state-to-state exact cross-section. Summation over product states usually improves the agreement.

Another attractive feature of the reaction is the large number of experiments which have been carried out [28]. These have prompted several recent trajectory studies. Blais and Truhlar [29–32] have performed detailed calculations on $H+D_2 \rightarrow HD(v',j')+H$ and $D+H_2$. In general, they find excellent agreement with experimental data. Blais *et al.* [33, 34] have also compared rate constant data from trajectories with experimental rate constants.

The effects of reactant vibration [35–39] and rotation [40–44] on this reaction have been investigated. The system has been used to investigate stereo chemical requirements for reaction [45, 46], and to compare 'insertion' and 'abstraction' mechanisms for reaction [47]. The effects of the bending potential on product state distributions have been considered in detail [48]. The reactive differential cross-sections for $H+H_2$ and $D+H_2$ at 0·65 eV translational energy have been compared using a Fourier moment method on two different potential energy surfaces [49]. The astrophysical implications of the reaction of 'hot' D with H_2 have been discussed [50].

4. $F+H_2$

The reaction $F+H_2 \rightarrow HF+H$ is a prototypical exoergic reaction. Its potential energy surface has recently been the subject of considerable controversy [51].

Of great recent interest have been the differential cross-sections in each product vibrational channel. Calculations of these for $F+H_2$ [52–55] and $F+D_2$ [56] have been carried out. Connor *et al.* [57] have used the angle-dependent line-of-centres model (ADLOC) to analyse the orientation dependence of the reaction. Ashton *et al.* [58] used a 'hybrid' (trajectory with pods [59]) method to obtain cross-sections and rate constants for $F+H_2$. Frost and Smith [60, 61] used another hybrid (trajectory + transition state theory) method for this same reaction.

5. Light atom transfer

The transfer of a light atom between heavy atoms has been the object of intensive research recently. One obvious motivation for studying such reactions is that they serve as a model for H atom (or proton or hydride) transfer in more complicated systems. A further source of interest is the prediction [62–67] that such reactions may exhibit reaction cross-sections and product attributes which oscillate as a function of translational energy.

The thermoneutral reaction $O(^3P)+HCl \rightarrow OH+Cl$ has been extremely well studied on a variety of model (mostly London–Eyring–Polanyi–Sato, LEPS) potential surfaces. In particular, the effects of reactant vibration [66] and rotation [68–72] (*vide infra*) have been studied. The exoergic reactions $O+HBr$ [73, 74] and $O+HI$ [75] have also been investigated.

Another well studied system is ClHCl [76]. It was the prototype reaction for oscillatory behaviour [62, 63], and has since been studied using a number of different potentials [64, 66–68, 76, 77]. It has been reported that reactant vibration amplifies oscillatory trends for this reaction [66]. The effect of reactant rotation (*vide infra*) has also been studied [67, 77, 78], as it was in the related IHI system [79].

A recent model study [80] using endoergic, exoergic and thermoneutral potentials has compared the enhancement of reaction rate constant for H atom transfer between heavy atoms by translational, vibrational and rotational energy.

6. Reactions dominated by long-range attraction

6.1. *Ion–molecule reactions*

In many cases, ion–molecule reactions involve several electronic potential energy surfaces, where non-adiabatic behaviour must be accounted for. Some studies in which this has been done are reviewed under 'Electronically non-adiabatic collisions'. Often, however, such reactions have been treated as if they took place on a single adiabatic surface. The reactions of B^+ [81], $C^+(^2P)$ [82, 83], $N^+(^3P)$ [84, 85] and $O^+(^4S)$ [86] with H_2 have been treated in this way, as has $O^+ + N_2$ [87].

For more complicated ion–molecule reactions, however, potential energy surfaces are seldom available. In such cases, it is usually assumed that the ion-dipole or ion–quadrupole attraction dominates the long-range dynamics, and that reaction will occur if this attraction is strong enough to 'capture' the reactants, enabling a complex to be formed. Whether, in fact, complex formation occurs can be determined by computing the trajectory of the reactant molecules, assuming they react if they approach to within some 'capture radius' [88]. This approach has been used for a variety of ion–dipole systems [89–95] and ion–quadrupole systems [96, 97]. The effect of induced dipole-induced dipole interaction has been investigated [98]. It has been demonstrated [99] that at high energy both the size of the collision partners and induced dipole interactions are important. Furthermore, the moment of inertia of the target molecule seems to affect the rate constant more than was previously believed [96, 97].

6.2. *Other reactions*

The reaction $O(^3P)+OH(^2\Pi)\leftrightarrows HO_2\rightarrow O_2+H$ is important in combustion and atmospheric chemistry. Formation of the HO_2 complex has been studied several times by trajectory methods [99–103]. The cross-section for low-energy complex formation for M + OH was found to be enhanced by OH rotation [104]. Several studies [99–101, 103] have emphasized that the decomposition back to reactants is significant, and therefore that rate constants based solely on complex formation will yield an overestimate to the true rate constant. Trajectory studies on the reverse reaction have also been performed [105–107].

The formation of ozone $O(^3P)+O_2(^3\Sigma_g^-)\rightleftarrows O_3$ has been studied on a new potential surface, and good agreement with experiment was reported [108, 109]. The isoelectronic reactions involving SO_2 are important in sulphur combustion, and have been studied [110, 111].

7. Other A + BC→AB + C reactions

The bimolecular atom–diatom exchange reaction, A + BC→AB + C, is still the most widely investigated by trajectories, as well as by other methods. One well studied example is Li + HF→LiF + H. The reaction is a prototype for alkali metal + hydrogen halide systems. The potential is extremely anisotropic, and this leads to pronounced orientational effects during the collision [112–114]. An accurate potential energy surface for this reaction has been developed, and trajectory calculations used [115–118] to compare cross-sections with experiment. In addition, the related reactions Li + HCl and Mg + HF [119, 120] have been studied recently. The effect of rotation on these reactions has also been of great interest [121–125] and some controversy [121, 123].

Largely owing to the relatively recent experimental success in preferentially orienting reactants [126], there has been a growing interest in understanding the spatial aspects of reaction dynamics; in particular, the geometry at the transition state. Recent calculations on Mg + HF [120] and on H + Li_2 [127] explore vector correlations for reactive collisions. The use of ADLOC to analyse the transition state of H + H_2 and F + H_2 reactions has already been alluded to, as has the contrast between insertion and abstraction in H + H_2. A pioneering study investigating the reactivity of aligned reactant molecules on a series of potentials, ranging from collinear to 'broadside' transition states, has been carried out [128] by Pattengill *et al.* Blais and Bernstein [129] looked at the reaction of initially oriented MeI with K to form KI (with Me treated as a pseudoatom).

There remains a lively interest in the possibility of forming bimodal product distributions via 'microscopic branching' [130]. It is proposed that this can occur when both atoms of a diatomic could react with the incoming atom, giving the possibility of a 'direct' reaction with the closer, or a 'migration' to react with the farther atom. This has been studied in detail for $F+I_2$ [131–133] and H+ICl [134, 135]. The alkali metal reactions $Li+Li_2$ [136], $Li+Na_2$ and $Na+K_2$ have been investigated to determine whether they react directly or via complex formation [137].

The mechanism for M+HX (M = alkaline earth metal, X = halogen) also involves two pathways. The X atom can be abstracted directly, or else the M can insert itself between the H and the X, in which case a complex is formed. The former seems to dominate [138, 139]. When the reaction does proceed via a complex, reactant rotation favours product formation, whereas reactant translation favours a return to reactants.

A well studied reaction in which both direct abstraction and insertion can occur is $O(^1D)+H_2 \rightarrow OH+H$. Reactant translation here seems to favour insertion, and enhances product vibration [140, 141]. Isotopic branching ratios for HD have also been studied [142]. A similar insertion-dominated reaction, $O(^1D)+HCl \rightarrow OH+Cl$, has been investigated by Schinke [143] on a fitted *ab initio* surface. The product attributes are reported to be in good agreement with experiment.

Several direct reactions, $A+H_2 \rightarrow AH+H$, have been studied using isotopic substitution. For all cases ($A = O(^3P)$ [144], Cl [145, 146], H [42, 45, 47]), it was found that the cross-section for abstracting a heavier hydrogen isotope is greater than for the lighter, with the ratio increasing with increasing translational energy. (The addition of rotation changes this, as discussed below.) A similar finding has been reported for $He+HD^+$ [147].

Some reactions of $C(^3P)$ have been reported: $C(^3P)+HI \rightarrow CH(^2P)+I$ [148], $C(^3P)+NO(^2P) \rightarrow CN(^2\Sigma^+)+O(^3P)$ [149] and $C(^3P)+N_2O \rightarrow CN+NO$ [150]. The dynamics of $O(^3P)+CS$ [151] and $O(^3P)+I_2$ [152] were also investigated recently. In the latter case, the transition from 'complex' to 'direct' collisions as the collision energy increases was explicitly described.

The $H'+HX$ reactions allow two distinct mechanisms, abstraction to form H_2 or exchange to form H'X. Both pathways are usually direct reactions. A study comparing the two pathways on a set of potentials in which the abstraction barrier was varied has been performed [153]. Detailed calculations of product energy distributions have been carried out for X = I [154, 155], Cl and Br [155]. A recent study of fast H(D) atoms with HF (DF) on an accurate potential surface reports good agreement with experiment [156].

Exchange reactions between rare gases have been investigated using pairwise-additive Morse potentials [157, 158]. Good agreement with experiment was reported in most cases. When agreement was found to be poor, the overly-soft Morse repulsive wall was implicated.

If several atoms are treated as a single pseudoatom, reactions of larger molecules can be considered. Such an approximation is only valid, of course, if the internal modes of the 'frozen' species do not contribute significantly to the reaction. It has been employed for the methyl group (Me) on several occasions: to treat hot atom reactions $T+HMe \rightarrow TH+Me$ [159], for halide abstraction, $H+XMe \rightarrow HX+Me$ [160–162], for $K+IMe \rightarrow KI+Me$ [129]. NO was recently treated as a pseudoatom in $C(^3P)+NNO \rightarrow CN+NO$ [163].

8. Collision-induced dissociation and three-body recombination

Collision-induced dissociation (CID), $AB+M \rightarrow A+B+M$, is a high-energy process of significance in the interstellar medium. Its reverse, thermolecular recombination, is a low-energy process, also of importance in the interstellar medium and the upper atmosphere. The difficulties involved in a quantum mechanical treatment of these events, in which both the discrete and continuum levels of the diatom must be included, are formidable [164]. Classical dynamics is an obvious choice for such systems. The application of trajectory methods to CID has been reviewed [165].

The dissociation rate constant for H_2 by inert Ar has been calculated [166–168] and found to be lower than when the third body is H [167]. The dissociation of H_2 by H out of specific (v,j) states was considered by Dove *et al.* [169, 170] who find vibration more efficient at promoting dissociation than rotation. The competition between reaction and dissociation has been investigated for $O(^3P)+H_2$ [171] and $He+H_2^+$ [172]. Trajectories have also been used to calculate rate constants for the recombination of Ar_2 [173] and Si_2 [174].

9. Electronically non-adiabatic reactions

In those cases where the dynamics cannot be adequately described by motion on a single adiabatic potential-energy surface, additional dynamical assumptions must be made. The pioneering technique is the trajectory surface hopping (TSH) method [175, 176] of Tully and co-workers. In these calculations, the classical trajectories are integrated on an adiabatic potential energy surface (typically generated by diatomics-in-molecules, DIM [177]) until they reach the vicinity of an avoided crossing. At this point, the probability of the trajectory hopping to another adiabatic surface is determined using a local Landau–Zener probability. When a hop occurs, the momenta must be adjusted to conserve energy [178]. Both the hopping and non-hopping trajectories are then further integrated on the appropriate adiabatic surface until they either hop again or reach the asymptotic region. If many hops occur along a single trajectory, different strategies [175, 176, 179] have been devised to avoid the necessity of following an excessive number of trajectories.

There are several variations to this basic technique. Determining the exact location of the avoided crossing has been the subject of some discussion [179–181]. Blais and Truhlar [182] avoid the local hop criterion by computing the semiclassical probability for *each* surface along the trajectory. Whenever the probability of being on the current surface drops below 0·5, a random number is generated to determine whether a hop should occur, and to which surface. The technique has been applied to quenching of Na* by H_2 [182] and the $H_2^+ + H_2$ system [183]. A similar procedure was recently proposed and tested by Parlant and Gislason [184]. Dunne *et al.* [185] have proposed a method in which the Liouville equation for the electronic density matrix is computed along the trajectory. Several of these approaches have been critically compared [183, 186].

Calculations using the TSH technique have been previously reviewed [2, 187]. Recent applications have been to the $H^+ + H_2$ [188–190], $H_2 + H_2^+$ [191], $Ar^+ + H_2$ [192], $He + H_2^+$ [193], $Cl^- + H_2$ [194, 195], and $H_2 + H_2^+$ [183, 196–201] systems where both reaction and charge transfer can occur, to charge transfer in $Ar + N_2^+(v)$ [202], to Na* quenching by H_2 (D_2) [182, 186, 203] and N_2 [204, 205], Li* quenching by $H_2(D_2)$ [206], and to ion-pair formation in $K + O_2$ [207, 208]. The reaction $O(^1D) + H_2 \rightarrow OH\ (^2\Pi) + H$ has been studied by a true TSH approach [209] and by a simplified approach [210]. Quenching [191, 211] and reaction [212] in $He(^1S) + H_2(^1\Sigma_u^+)$ have been investigated. Blais *et al.* [213] used TSH to investigate the effect of a conical intersection on collision-induced dissociation. In addition, some attempt has also been made to systematically vary parameters (such as the seam location) and study their effects on electronic branching ratios and product state distributions in non-adiabatic systems [214, 215].

10. The effect of reactant vibration

The field of vibrational excitation and its effect on reactivity was recently reviewed [216–218].

It is generally recognized that reactant vibration enhances reaction rates, and that this is especially marked in the case of 'late' potential energy barriers [219]. Since endoergic reactions are generally of this nature, the investigation of reactant vibration in such systems is clearly warranted. Sathyamurthy and co-workers have studied these effects for $He+H_2^+(v)$ [147, 220, 221]. The behaviour of the reaction's cone of acceptance as the vibrational energy was increased has been studied recently [222].

Highly vibrationally excited molecules occur in plasma discharges, and their relaxation rate is of importance in modelling these systems. Laganà and co-workers have made an exhaustive study of relaxation rates of H_2 (v) by H [36–39, 223] and of $N_2(v)$ by N [224]. Frost and Smith have also employed their hybrid (trajectories + transition state theory) method for both the former [225] and the latter [226] systems. Per collision, it is found that reactive collisions are more efficient quenchers of vibration than non-reactive vibrationally inelastic collisions.

Vibration has been found to amplify oscillatory behaviour in light atom transfer reactions [66, 69].

A pair of studies on the $OH+H_2 \rightarrow H_2O+H$ reaction showed that vibration in H_2 was more efficient in promoting reaction than was vibration in the spectator OH [227, 228]. Schatz and co-workers [229] also studied the reverse reaction. They found that bend motion in H_2O was most effective in enhancing reaction and the asymmetric stretch least effective.

In an ambitious study of the S_N2 reaction $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$ (in which the motion of all atoms was considered) Vande Linde and Hase [230] found that vibration in the C–Cl stretch enhanced reaction.

11. The effect of reactant rotation

In contrast to vibration, where thermal populations are dominated by the ground state, the rotational partition function for non-hydrogenic molecules is large. Therefore, for a full simulation and understanding of room-temperature rate constants, the dependence of the cross-section on reactant rotation must be included.

The last comprehensive review on the effect of rotational excitation was in 1983 [231]. Since then, there has been considerable activity in the field. In many reactions which proceed through a linear transition state, the reaction cross-section as a function of rotational quantum number, $\sigma(j)$, shows the same general trend: for low j, σ decreases, reaches a minimum and then increases for higher j values. This is usually most pronounced at collision energies near threshold. At higher energies, the decreasing part of the curve may not be in evidence at all. This has been ascribed to competing 'orientational' and 'energetic' effects [23]. These concepts have been recently refined [232]. It is also a function of the mass combination and the transition state bend force constant [232]. For a tight bend, the decrease will dominate; for a soft one, the increase will do so. Systematic studies of the effect of transition state geometry on reaction of rotationally excited species have been rare [128], and further work would be of great interest.

Previously-reported 'oscillatory' behaviour of the cross-section as a function of j in $Li+HF$ [121, 122] and $OH+H_2$ [233] has now been clearly demonstrated [123, 234] to be caused by 'bumps' or 'hollows' in the potential which are artifacts of the analytic fitting function. It has been suggested [234] that looking for such oscillatory $\sigma(j)$ behaviour be used as a diagnostic for testing new potentials for smoothness.

Among the systems which have been studied are $H+H_2$ [40–44], $O(^3P)+HCl$ [67, 71, 72, 235–237, H. R. Mayne, 1990, unpublished data], $O(^3P)+HBr$ [73], $O(^3P)+HI$ [75], $Cl+HCl$ [67, 71, 76–78], I +HI [79], $Be+HF$ [238], $F+H_2$ [239, 240], Na and F+IMe [162], $OH+H_2$ (both diatoms) [227, 228, 233, 234], $Li+HF$ [121, 122, 125], $Mg+HF$ [120], $C(^3P)+HI$ [148], $O(^3P)+CS$ [151]. While most of these calculations fit the $\sigma(j)$ pattern discussed above, several appear to be anomalous. For instance, Rayós *et al.* [151] see an increase with j followed by a decrease. There is obviously much to be learned even in such simple systems.

One particularly interesting aspect of rotational excitation is the 'rotational isotope effect' [42]. First reported in 1971 [242], this effect has been observed several times since [40, 42, 145, 242, 243]. The phenomenon occurs for $A+H_2 \rightarrow AH+H$ reactions with isotopically-substituted H atoms. In the absence of rotation, the heavier hydrogen isotope is always preferentially abstracted. However, as rotation increases, the lighter isotope becomes more reactive. The effect is found to hold for thermoneutral, endoergic and exoergic reactions [42]. An explanation has been proposed [42]. It appears [80] that rotation may be more efficient at promoting light-atom transfer than either vibration or translation. Recent calculations [H. R. Mayne, 1990, unpublished data] show that rotation always seems to enhance reaction of light isotopes over heavier ones.

12. Polyatomic systems

The classical trajectory approach has the great advantage that the computational requirements increase only linearly with the number of atoms involved. This is in marked contrast to the coupled-channels techniques of quantum reaction dynamics, where the computational effort increases rapidly with the number of states included. Therefore classical mechanics lends itself easily to calculations of reactions of polyatomic systems, but there are problems which may be particularly severe for such systems. First, classical mechanics does not describe eigenstates well for polyatomic molecules; energy can flow between normal modes. Fortunately progress is being made towards at least reasonable agreement, notably by Schatz and co-workers [10–13]. Second, as mentioned above, classical mechanics fails to respect the adiabatic barriers imposed by quantum mechanics. It appears that progrees towards removing this difficulty may now finally be at hand [22, 23]. Since basis-set expansion techniques lag far behind classical trajectories in their potential for polyatomic reactions, it is clear that further work on improving the application of trajectory calculations for such systems is warranted.

Several of the reactions of polyatomics treated recently have already been mentioned: the $OH+H_2 \rightleftarrows H_2O+H$ system [227–229, 233, 234], and the S_{N2} reaction $Cl^-+CH_3Cl \rightarrow ClCH_3+Cl^-$ [230]. Other systems studied have included the reaction $H+CO_2 \rightarrow CO+OH$ [244, 245], the $H+CH_3 \rightarrow CH_4$ recombination [246, 247] and $H+C_2H_4 \rightarrow C_2H_5$ recombination [248], as well as ion–molecule association reactions of Li^+ with $(CH_3)_2O$ [249] and of $Li^+(H_2O)$ with H_2O [250]. Raff [251] has considered the addition reaction of C_2H_4 and F_2 with all possible product channels included. He finds the major products to be CH_2CH_2F and CH_2CHF, and detects no $(CH_2F)_2$.

Noor Batcha *et al.* [252] carried out an interesting study on a model system designed to test the feasibility of six-centre reaction mechanisms using three diatoms. They found frequent metathesis rearrangement reactions with the third diatom acting as a 'third body', but no true six-centre events.

Acknowledgment

The author gratefully acknowledges Chifuru Noda's assistance in preparing the manuscript, and thanks those colleagues who generously provided reprints and preprints of their work.

References

[1] Karplus, M., Porter, R. N., and Sharma, R. D., 1965, *J. chem. Phys.*, **43**, 3259.
[2] Raff, L. M., and Thompson, D. L., 1985, *Theory of Chemical Reaction Dynamics*, Vol. 3, edited by M. Baer (Boca Raton: CRC Press), p. 1.
[3] Bunker, D. L., 1971, *Method Comput. Phys.*, **10**, 287.
[4] Porter, R. N., 1974, *Ann. Rev. phys. Chem.*, **25**, 317.
[5] Porter, R. N., and Raff, L. M., 1976, *Modern Theoretical Chemistry*, edited by W. H. Miller (New York: Plenum), p. 1.
[6] Truhlar, D. G., and Muckerman, J. T., 1979, *Atom-Molecule Collision Theory*, edited by R. B. Bernstein (New York: Plenum), p. 505.
[7] Barg, G. D., Kendall, G. M., and Toennies, J. P., 1976, *Chem. Phys.*, **16**, 243.
[8] Porter, R. N., Raff, L. M., and Miller, W. H., 1975, *J. chem. Phys.*, **63**, 2214.
[9] Eaker, C. W., 1959, *J. chem. Phys.*, **90**, 105.
[10] Schatz, G. C., 1983, *Top. Current Phys.*, **33**, 25.
[11] Eaker, C. W., and Schatz, G. C., 1984, *J. chem. Phys.*, **81**, 2394.
[12] Eaker, C. W., Schatz, G. C., De Leon, N., and Heller, E. J., 1984, *J. chem. Phys.*, **81**, 5913.
[13] Duchovic, R. J., and Schatz, G. C., 1986, *J. chem. Phys.*, **84**, 2239.
[14] Zhao, M., Mladenovic, M., Truhlar, D. G., Schwenke, D. W., Sun, Y., Kouri, D. J., and Blais, N. C., 1989, *J. Am. Chem. Soc.*, **111**, 852.
[15] Blais, N. C., Zhao, M., Mladenovic, M., Truhlar, D. G., Sun, Y., and Kouri, D. J., 1989, *J. chem. Phys.*, **91**, 1038.
[16] Blais, N. C., Zhao, M., Truhlar, D. G., Schwenke, D. W., and Kouri, D. J., 1990, *Chem. Phys. Lett.*, **166**, 11.
[17] Mayne, H. R., and Toennies, J. P., 1981, *J. chem. Phys.*, **75**, 1794.
[18] Schatz, G. C., 1983, *J. chem. Phys.*, **79**, 5386.
[19] Bowman, J. M., Lee, K.-T., and Walker, R. B., 1983, *J. chem. Phys.*, **79**, 3742.
[20] Mayne, H. R., 1986, *Chem. Phys. Lett.*, **130**, 249.
[21] Lu, D.-H., Hase, W. L., and Wolf, R. J., 1986, *J. chem. Phys.*, **85**, 4422.
[22] Bowman, J. M., Gazdy, B., and Sun, Q., 1989, *J. chem. Phys.*, **91**, 2859.
[23] Miller, W. H., Hase, W. L., and Darling, C. L., 1989, *J. chem. Phys.*, **91**, 2863.
[24] Hase, W. L., 1986, *J. phys. Chem.*, **90**, 365.
[25] Connor, J. N. L., 1979, *Comp. Phys. Comm.*, **17**, 117.
[26] Truhlar, D. G., Hase, W. L., and Hynes, J. T., 1983, *J. phys. Chem.*, **87**, 2664.
[27] Truhlar, D. G., Isaacson, A. D., and Garrett, B. C., 1985, *Theory of Chemical Reaction Dynamics*, Vol. 4, edited by M. Baer (Boca Raton: CRC Press), p. 65.
[28] Valentin, J. J., and Phillips, D. L., 1989, *Advances in Gas Phase Photochemistry and Kinetics*, volume 2, *Bimolecular Collisions*, edited by M. N. R. Ashfold and J. E. Baggott (London: Royal Society of Chemistry), p. 1.
[29] Blais, N. C., and Truhlar, D. G., 1983, *Chem. Phys. Lett.*, **102**, 120.
[30] Blais, N. C., and Truhlar, D. G., 1985, *J. chem. Phys.*, **83**, 2201.
[31] Blais, N. C., and Truhlar, D. G., 1989, *Chem. Phys. Lett.*, **162**, 503.
[32] Blais, N. C., and Truhlar, D. G., 1988, *J. chem. Phys.*, **88**, 5457.
[33] Blais, N. C., Truhlar, D. G., and Garrett, B. C., 1983, *J. chem. Phys.*, **78**, 2363.
[34] Blais, N. C., Truhlar, D. G., and Garrett, B. C., 1982, *J. chem. Phys.*, **76**, 2768.
[35] Schechter, I., Kosloff, R., and Levine, R. D., 1985, *Chem. Phys. Lett.*, **121**, 297.

[36] Laganà, A., 1986, *Int. J. Chem. Kin.*, **18,** 1009.
[37] Garcia, E., and Laganà, A., 1986, *Chem. Phys. Lett.*, **123,** 365.
[38] Garcia, E., and Laganà, A., 1986, *J. phys. Chem.*, **90,** 987.
[39] Laganà, A., 1989, *Non Equilibrium Processes in Partially Ionized Gases*, edited by M. Capitelli (New York: Plenum) (in the press).
[40] Boonenberg, C. A., and Mayne, H. R., 1984, *Chem. Phys. Lett.*, **108,** 67.
[41] Mayne, H. R., and Minick, S. K., 1987, *J. phys. Chem.*, **91,** 1400.
[42] Mayne, H. R., 1988, *J. phys. Chem.*, **92,** 6289.
[43] Sathyamurthy, N., and Toennies, J. P., 1988, *Chem. Phys. Lett.*, **143,** 323.
[44] Aoiz, F. J., Herrero, V. J., and Sáez, V., 1989, *Chem. Phys. Lett.*, **161,** 270.
[45] Schechter, I., and Levine, R. D., 1986, *Int. J. chem. Kin.*, **18,** 1023.
[46] Blais, N. C., Bernstein, R. B., and Levine, R. D., 1985, *J. phys. Chem.*, **89,** 10.
[47] Schechter, I., Kosloff, R., and Levine, R. D., 1986, *J. phys. Chem.*, **90,** 1006.
[48] Blais, N. C., Truhlar, D. G., and Garrett, B. C., 1985, *J. chem. Phys.*, **82,** 2300.
[49] Hillenbrand, E. A., Main, D. J., Jorgensen, A. D., and Gislason, E. A., 1984, *J. phys. Chem.*, **88,** 1358.
[50] Mayne, H. R., and Prasad, S. S., 1986, *Int. J. chem. Kin.*, **18,** 977.
[51] Schaefer III, H. F., 1985, *J. phys. Chem.*, **89,** 5336.
[52] Blais, N. C., and Truhlar, D. G., 1982, *J. chem. Phys.*, **76,** 4490.
[53] Ron, S., Baer, M., and Pollak, E., 1983, *J. chem. Phys.*, **78,** 4414.
[54] Takayanagi, T., and Sato, S., 1988, *Chem. Phys. Lett.*, **144,** 191.
[55] Budenholzer, F. E., and Jeng, D. C., 1989, *Chem. Phys. Lett.*, **156,** 411.
[56] Ron, S., Pollak, E., and Baer, M., 1983, *J. chem. Phys.*, **79,** 5204.
[57] Connor, J. N. L., Whitehead, J. C., and Jakubetz, W., 1987, *J. chem. Soc. Farad. Trans.* II, **83,** 1703.
[58] Ashton, C. J., Muckerman, J. T., and Schubert, F. E., 1984, *J. chem. Phys.*, **81,** 5786.
[59] Pollak, E., 1985, *Theory of Chemical Reaction Dynamics*, Vol. 3, edited by M. Baer (Boca Raton: CRC Press), p. 123.
[60] Frost, R. J., and Smith, I. W. M., 1988, *J. chem. Soc. Farad. Trans* II, **84,** 1824.
[61] Frost, R. J., and Smith, I. W. M., 1988, *J. chem. Soc. Farad. Trans* II, **84,** 1837.
[62] Baer, M., and Last, I., 1985, *Chem. Phys. Lett.*, **119,** 393.
[63] Last, I., and Baer, M., 1987, *J. chem. Phys.*, **86,** 5534.
[64] Persky, A., and Kornweitz, H., 1987, *J. phys. Chem.*, **91,** 5496.
[65] Persky, A., and Kornweitz, H., 1989, *Chem. Phys. Lett.*, **159,** 134.
[66] Kornweitz, H., and Persky, A., 1989, *Chem. Phys.*, **132,** 153.
[67] Kornweitz, H., Broida, M., and Persky, A., *J. phys. Chem.*, **93,** 251.
[68] Persky, A., and Kornweitz, H., 1989, *Chem. Phys.*, **130,** 129.
[69] Persky, A., and Broida, M., 1984, *J. chem. Phys.*, **81,** 4352.
[70] Persky, A., and Kornweitz, H., 1986, *Chem. Phys. Lett.*, **127,** 609.
[71] Persky, A., and Kornweitz, H., 1987, *J. phys. Chem.*, **91,** 5472.
[72] Loesch, H., 1987, *Chem. Phys.*, **112,** 85.
[73] Broida, M., Tamir, M., and Persky, A., 1986, *Chem. Phys.*, **110,** 83.
[74] McKendrick, K. G., Rakestraw, D. J., Zhang, R., and Zare, R. N., 1988, *J. phys. Chem.*, **92,** 5530.
[75] Persky, A., and Broida, M., 1987, *Chem. Phys.*, **114,** 85.
[76] Connor, J. N. L., and Jakubetz, W., 1989, *Supercomputer Algorithms for Reactivity, Dynamics, and Kinetics of Small Molecules*, edited by A. Laganà (Dordrecht: Kluwer), p. 395.
[77] Amaee, B., Connor, J. N. L., Whitehead, J. C., Jakubetz, W., and Schatz, G. C., 1987, *Faraday Disc. Chem. Soc.*, **84,** 387.
[78] Last, I., and Baer, M., 1986, *Int. J. quant. Chem.*, **29,** 1067.
[79] Last, I., and Shima, Y., 1986, *Chem. Phys.*, **110,** 287.
[80] Mayne, H. R., 1990, *J. Am. chem. Soc.* (in the press).
[81] Klimo, V., Tiňo, J., and Urban, J., 1989, *Chem. Phys.*, **137,** 33.
[82] González, M., and Aguilar, A., 1989, *Chem. Phys.*, **132,** 443.
[83] González, M., Aguilar, A., and Virgili, J., 1985, *Chem. Phys. Lett.*, **113,** 187.
[84] González, M., Aguilar, A., and Sayós, R., 1989, *Chem. Phys.*, **132,** 137.
[85] González, M., Aguilar, A., and Fernández, Y., 1986, *Chem. Phys.*, **104,** 57; Erratum: 1986, *Chem. Phys.*, **106,** 477.

[86] González, M., Aguilar, A., and Gilibert, M., 1989, *Chem. Phys.*, **131**, 335; González, M., Aguilar, A., and Gilibert, M., 1989, *Chem. Phys.*, **131**, 347.

[87] Hopper, D. G., 1982, *J. chem. Phys.*, **77**, 314.

[88] Su, T., and Chesnavich, W. J., 1982, *J. chem. Phys.*, **76**, 5183.

[89] Su, T., and Hu, S., 1985, *J. chem. Phys.*, **82**, 2164.

[90] Su, T., and Hu, S., 1986, *J. chem. Phys.*, **84**, 774.

[91] Su, T., 1988, *J. chem. Phys.*, **88**, 4102. Erratum, 1988, *J. chem. Phys.*, **89**, 5355. See also Turulski, J., and Niedzielski, J., 1989, *J. chem. Phys.*, **91**, 3795; Su, T., 1989, *J. chem. Phys.*, **91**, 3796.

[92] Bei, H. C., Bhowmik, P. K., and Su, T., 1989, *J. chem. Phys.*, **90**, 7046.

[93] Markoviĉ, N., and Nordholm, S., 1989, *Chem. Phys.*, **135**, 109.

[94] Turulski, J., and Niedzielski, J., 1989, *Chem. Phys.*, **137**, 191.

[95] Viggiano, A., A., Morris, R. A., Dale, F., Paulson, J. F., Giles, K., Smith, D., and Su, T., 1990, *J. chem. Phys.*, **93**, 1149.

[96] Bhowmik, P. K., and Su, T., 1986, *J. chem. Phys.*, **84**, 1432.

[97] Mendaš I, and Milutinoviĉ, P., 1989, *Chem. Phys.*, **134**, 47.

[98] Hu, S., and Su, T., 1986, *J. chem. Phys.*, **85**, 3127.

[99] Miller, J. A., 1986, *J. chem. Phys.*, **84**, 6170.

[100] Quintales, L. A. M., Varandas, A. J. C., and Alvariño, J. M., 1988, *J. phys. Chem.*, **92**, 4552.

[101] Varandas, A. J. C., 1988, *J. molec Struct.* (*Theochem.*), **166**, 59.

[102] Markoviĉ, N., Nyman, G., and Nordholm, S., 1989, *Chem. Phys. Lett.*, **159**, 435.

[103] Davidsson, J., and Nyman, G., 1990, *J. chem. Phys.*, **92**, 2407; **92**, 2415.

[104] Howard, R. E., Mansker, L., and Thompson, D. L., 1986, *Chem. Phys. Lett.*, **127**, 399.

[105] Kleinermanns, K., and Schinke, R., 1984, *J. chem. Phys.*, **80**, 1440.

[106] Ju, G.-Z., Feng, D.-C., Cai, Z.-T., and Deng, C.-H., 1988, *Theor. Chim. Acta*, **74**, 403.

[107] Kleinermanns, K., Linnebach, E., and Pohl, M., 1989, *J. chem. Phys.*, **91**, 2181.

[108] Pais, A. A. C. C., and Varandas, A. J. C., 1988, *J. molec. Struct.* (*Theochem.*), **166**, 335.

[109] Varandas, A. J. C., and Pais, A. A. C. C., 1988, *Molec. Phys.*, **65**, 843.

[110] Craven, W., and Murrell, J. N., 1987, *J. chem. Soc. Farad. Trans.* II, **83**, 1733.

[111] Murrell, J. N., Cravern, W., and Farantos, S. C., 1983, *Molec. Phys.*, **49**, 1077.

[112] Alvariño, J. M., Basterrechea, F. J., Hernandez, M. L., and Laganà, A., 1985, *J. molec. Struct.* (*Theochem.*), **120**, 187.

[113] Alvariño, J. M., Basterrechea, F. J., and Laganà, A., 1986, *Molec. Phys.*, **59**, 559.

[114] Alvariño, J. M., Garcia, E., and Laganà, A., 1989, *Supercomputer Algorithms for Reactivity, Dynamics and Kinetics of Small Molecules*, edited by A. Laganà (Dordrecht: Kluwer), p. 383.

[115] Alvariño, J. M., Casavecchia, P., Gervasi, O., and Laganà, A., 1982, *J. chem. Phys.*, **77**, 6341.

[116] Alvariño, J. M., Hernandez, M. L., Garcia, E., and Laganà, A., 1986, *J. chem. Phys.*, **84**, 3059.

[117] Laganà, A., and Garcia, E., 1987, *Chem. Phys. Lett.*, **139**, 140.

[118] Laganà, A., Palmieri, P., Alvariño, J. M., and Garcia, E., 1990, *J. chem. Phys.* (submitted).

[119] Alvariño, J. M., and Laganà, A., 1990, *Chem. Phys. Lett.*, **168**, 441.

[120] Garcia, E., Ciccarelli, L., and Laganà, A., 1987, *Theor. Chim. Acta*, **72**, 253.

[121] Noor Batcha, I., and Sathyamurthy, N., 1982, *J. Am. chem. Soc.*, **104**, 1766.

[122] Noor Batcha, I., and Sathyamurthy, N., 1983, *Chem. Phys.*, **77**, 67.

[123] Loesch, H., 1986, *Chem. Phys.*, **104**, 213.

[124] Palmieri, P., Garcia, E., and Laganà, A., 1988, *J. chem. Phys.*, **88**, 181.

[125] Grote, W., Hoffmeister, M., Schleysing, R., Zerhau-Dreihoefer, H., and Loesch, H. J., 1988, *Selectivity in Chemical Reactions*, edited by J. C. Whitehead, (Dordrecht: Kluwer), p. 47.

[126] Parker, D. H., and Bernstein, R. B., 1989, *Ann. Rev. Phys. Chem.*, **40**, 561.

[127] Kim, S. K., and Herschbach, D. R., 1987, *Faraday Disc. Chem. Soc.*, **84**, 159.

[128] Pattengill, M. D., Zare, R. N., and Jaffe, R. L., 1987, *J. phys. Chem.*, **91**, 5489.

[129] Blais, N. C., and Bernstein, R. B., 1986, *J. chem. Phys.*, **85**, 7030.

[130] Polanyi, J. C., Schreiber, J. L., and Skrlac, W. J., 1979, *Faraday Disc. Chem. Soc.*, **67**, 66.

[131] Fletcher, I. W., and Whitehead, J. C., 1984, *J. chem. Soc. Farad. Trans.* II, **80,** 985.
[132] Urrecha, M. I., Castaño, F., and Iturbe, J., 1986, *J. chem. Soc. Farad. Trans.* II, **82,** 1077.
[133] Keane, N. W., Whitehead, J. C., and Grice, R., 1989, *J. chem. Soc. Farad. Trans.* II, **85,** 1081.
[134] Alvariño, J. M., and Quintales, L. M., *J. molec. Struct.*, **142,** 521.
[135] Alvariño, J. V., and Laganà, A., *J. phys. Chem.*, **91,** 5487.
[136] Morais, V. M. F., and Varandas, A. J. C., 1989, *J. chem. Soc. Farad. Trans.* II, **85,** 1.
[137] Morais, V. M. F., and Varandas, A. J. C., 1987, *J. chem. Soc. Farad. Trans.* II, **83,** 2247.
[138] Chapman, S., 1984, *J. chem. Phys.*, **81,** 262.
[139] Jaffe, R. L., Pattengill, M. D., Mascarello, F. G., and Zare, R. N., 1987, *J. chem. Phys.*, **86,** 6150.
[140] Aker, P. M., Sloan, J. J., and Wright, J. S., 1986, *Chem. Phys.*, **110,** 275.
[141] Dunne, L. J., and Murrell, J. N., 1983, *Molec. Phys.*, **50,** 635.
[142] Fitzcharles, M. S., and Schatz, G. C., 1986, *J. phys. Chem.*, **90,** 3634.
[143] Schinke, R., 1984, *J. chem. Phys.*, **80,** 5510.
[144] Broida, M., and Persky, A., 1984, *J. chem. Phys.*, **80,** 3687.
[145] Persky, A., Rubin, R., and Broida, M., 1983, *J. chem. Phys.*, **79,** 3279.
[146] Persky, A., and Broida, M., 1986, *J. chem. Phys.*, **84,** 2653.
[147] Bhalla, K. C., and Sathyamurthy, N., 1989, *Chem. Phys. Lett.*, **160,** 432.
[148] Nishiyama, N., Sekiya, N., and Nishimura, Y., 1988, *Chem. Phys.*, **123,** 359.
[149] Halvick, P., and Rayez, J. C., 1989, *Chem. Phys.*, **131,** 375.
[150] Bouachir, R., Rayez, M. T., Duguay, B., and Rayez, J. C., 1984, *Chem. Phys.*, **90,** 325.
[151] Sayós, R., Gonzáles, and Aguilar, A., 1990, *Chem. Phys.*, **141,** 401.
[152] Kosmas, A. M., and Williams, R. J., 1990, *Chem. Phys.*, **140,** 413.
[153] Sudhakara, M. P., and Raff, L. M., 1985, **95,** 165.
[154] González, M., and Sayós, R., 1989, *Chem. Phys. Lett.*, **164,** 643.
[155] Aker, P. M., and Valentini, J. J., 1990, *Israel J. Chem.*, **30,** 157.
[156] Schatz, G. C., 1987, *J. chem. Phys.*, **86,** 6738.
[157] Gettys, N. S., Raff, L. M., and Thompson, D. L., 1988, *J. phys. Chem.*, **92,** 5270.
[158] Turner, R. A., Raff, L. M., and Thompson, D. L., 1984, *J. chem. Phys.*, **80,** 3189.
[159] Valencich, T., 1983, *J. chem. Phys.*, **79,** 671.
[160] Sayós, R., Aguilar, A., Lucas, J. M., Solé, A., and Virgili, J., 1985, *Chem. Phys.*, **93,** 265.
[161] Sayós, R., González, M., and Aguilar, A., 1985, *Chem. Phys.*, **98,** 409.
[162] Menéndez, M., Bañares, L., González-Ureña, A., and Whitehead, J. C., 1988, *J. chem. Soc. Farad. Trans.* II, **84,** 1765.
[163] Bouachir, R., Rayez, M. T., Duguay, B., and Rayez, J. C., 1984, *Chem. Phys.*, **90,** 325.
[164] Leforestier, C., 1986, *The Theory of Chemical Reaction Dynamics*, edited by D. C. Clary (Dordrecht: Reidel), p. 235.
[165] Kuntz, P. J., 1979, *Atom–Molecule Collision Theory*, edited by R. B. Bernstein (New York: Plenum), p. 669.
[166] Blais, N. C., and Truhlar, D. G., 1982, *Astrophys. J.*, **258,** L79.
[167] Blais, N. C., and Truhlar, D. G., 1983, *J. chem. Phys.*, **78,** 2388.
[168] Haug, K., Truhlar, D. G., and Blais, N. C., 1987, *J. chem. Phys.*, **86,** 2697.
[169] Dove, J. E., Mandy, M. E., Sathyamurthy, N., and Joseph, T., 1986, *Chem. Phys. Lett.*, **127,** 1.
[170] Dove, J. E., and Mandy, M. E., 1986, *Int. J. chem. Kin.*, **18,** 993.
[171] Alfassi, Z. B., and Baer, M., 1981, *Chem. Phys.*, **63,** 275.
[172] Kumar, S., and Sathyamurthy, N., 1989, *Chem. Phys.*, **137,** 25.
[173] Howard, R. E., Planck, T. L., Trussell, S. R., and Saadevandi, B., 1987, *Chem. Phys. Lett.*, **142,** 33.
[174] Martin, D. L., Thompson, D. L., and Raff, L. M., *J. chem. Phys.*, **84,** 4426.
[175] Preston, R. K., and Tully, J. C., 1971, *J. chem. Phys.*, **54,** 4297.
[176] Tully, J. C., and Preston, R. K., 1971, *J. chem. Phys.*, **55,** 562.
[177] Kuntz, P. J., 1979, *Atom–Molecule Collision Theory*, edited by R. B. Bernstein (New York: Plenum), p. 505.
[178] Miller, W. H., and George, T. F., 1972, *J. chem. Phys.*, **56,** 5637.
[179] Stine, J. R., and Muckerman, J. T., 1976, *J. chem. Phys.*, **65,** 3975.
[180] Mead, C. A., and Truhlar, D. G., 1986, *J. chem. Phys.*, **84,** 1055.

[181] Stine, J. R., and Muckerman, J. T., 1986, *J. chem. Phys.*, **84,** 1056.
[182] Blais, N. C., and Truhlar, D. G., 1983, *J. chem. Phys.*, **79,** 1334.
[183] Stine, J. R., and Muckerman, J. T., 1987, *J. phys. Chem.*, **91,** 459.
[184] Parlant, G., and Gislason, E. A., 1989, *J. chem. Phys.*, **91,** 4416.
[185] Dunne, L. J., Murrell, J. N., and Stamper, J. G., 1984, *Chem. Phys. Lett.*, **112,** 497.
[186] Eaker, C. W., 1987, *J. chem. Phys.*, **87,** 4532.
[187] Kleyn, A. W., Los, J., and Gislason, E. A., 1982, *Phys. Rep.*, **90,** 1.
[188] Schlier, Ch., Nowotny, U., and Teloy, E., 1987, *Chem. Phys.*, **111,** 401.
[189] Niedner, G., Noll, M., Toennies, J. P., and Schlier, Ch., 1987, *J. chem. Phys.*, **87,** 2685.
[190] Schlier, Ch., and Vix, U., 1987, *Chem. Phys.*, **113,** 211.
[191] Farantos, S. C., Murrell, J. N., and Carter, S., 1984, *Chem. Phys. Lett.*, **108,** 367.
[192] Chapman, S., 1985, *J. chem. Phys.*, **82,** 4033.
[193] Sizun, M., and Gislason, E. A., 1989, *J. chem. Phys.*, **91,** 4603.
[194] Sizun, M., Gislason, E. A., and Parlant, G., 1986, *Chem. Phys.*, **107,** 311.
[195] Sizun, M., Parlant, G., and Gislason, E. A., 1989, *Chem. Phys.*, **133,** 251.
[196] Eaker, C. W., and Schatz, G. C., 1988, *J. chem. Phys.*, **89,** 6713.
[197] Badenhoop, J. K., Schatz, G. C., and Eaker, C. W., **87,** 5317.
[198] Eaker, C. W., and Schatz, G. C., 1985, *J. phys. Chem.*, **89,** 2612.
[199] Eaker, C. W., and Muzyka, J. L., 1985, *Chem. Phys. Lett.*, **119,** 169.
[200] Schatz, G. C., Badenhoop, J. K., and Eaker, C. W., 1987, *Int. J. quant. Chem.*, **31,** 57.
[201] Eaker, C. W., and Schatz, G. C., 1986, *Chem. Phys. Lett.*, **127,** 343.
[202] Parlant, G., and Gislason, E. A., 1989, *J. chem. Phys.*, **91,** 5359.
[203] Truhlar, D. G., Duff, J. W., Blais, N. C., Tully, J. C., and Garrett, B. C., 1982, *J. chem. Phys.*, **77,** 764.
[204] Achirel, P., and Habitz, P., 1983, *Chem. Phys.*, **78,** 213.
[205] Poppe, D., Papierowska-Kaminski, D., and Bonačič-Koutecký, 1987, *J. chem. Phys.*, **86,** 822.
[206] Eaker, C. W., 1988, *J. phys. Chem.*, **92,** 3858.
[207] Parlant, G., Schröder, M., and Goursaud, S., 1983, *Chem. Phys.*, **75,** 175.
[208] Goursaud, S., and Parlant, G., 1983, *Chem. Phys. Lett.*, **102,** 192.
[209] Kuntz, P. J., Niefer, B. I., and Sloan, J. J., 1988, *J. chem. Phys.*, **88,** 3629.
[210] Dunne, L. J., 1989, *Chem. Phys. Lett.*, **158,** 533.
[211] Farantos, S. C., 1985, *Molec. Phys.*, **54,** 835.
[212] Farantos, S. C., 1986, *Molec. Phys.*, **59,** 1273.
[213] Blais, N. C., Truhlar, D. G., and Mead, C. A., 1988, *J. chem. Phys.*, **89,** 6204.
[214] Mayne, H. R., Polanyi, J. C., and Tully, J. C., 1985, *J. chem. Phys.*, **82,** 161.
[215] Mayne, H. R., and Polanyi, J. C., 1985, *J. chem. Phys.*, **82,** 170.
[216] Leone, S. R., 1985, *Ann. Rev. Phys. Chem.*, **35,** 109.
[217] Kneba, M., and Wolfrum, J., 1980, *Ann. Rev. Phys. Chem.*, **31,** 47.
[218] Smith, I. W. M., 1985, *Chem. Soc. Rev.*, **14,** 141.
[219] Polanyi, J. C., 1987, *Science*, **236,** 680.
[220] Joseph, T., and Sathyamurthy, N., 1984, *J. chem. Phys.*, **80,** 5332.
[221] Joseph, T., and Sathyamurthy, N.,1987, *J. chem. Phys.*, **86,** 704.
[222] Schechter, I., and Levine, R. D., 1989, *J. phys. Chem.*, **93,** 7973.
[223] Gorse, C., Capitelli, M., Bacal, M., Bretagne, J., and Laganà, A., 1987, *Chem. Phys.*, **117,** 177.
[224] Laganà, A., Garcia, E., and Ciccarelli, L., 1987, *J. Phys. Chem.*, **91,** 312.
[225] Frost, R. J., and Smith, I. W. M., 1987, *Chem. Phys.*, **117,** 421.
[226] Frost, R. J., and Smith, I. W. M., 1987, *Chem. Phys. Lett.*, **140,** 499.
[227] Schatz, G. C., 1981, *J. chem. Phys.*, **74,** 1133.
[228] Brown, N. J., and Rashed, O., 1985, *J. chem. Phys.*, **82,** 5506. Erratum, 1985, *J. chem. Phys.*, **84,** 545.
[229] Schatz, G. C., Colton, M. C., and Grant, J. L., 1984, *J. phys. Chem.*, **88,** 2971.
[230] Vande Linde, S. R., and Hase, W. L., 1989, *J. Am. Chem. Soc.*, **111,** 2349.
[231] Sathyamurthy, N., 1983, *Chem. Rev.*, **83,** 601.
[232] Harrison, J. A., and Mayne, H. R., 1989, *Chem. Phys. Lett.*, **158,** 356.
[233] Harrison, J. A., and Mayne, H. R., 1987, *J. chem. Phys.*, **87,** 3698.
[234] Harrison, J. A., and Mayne, H. R., 1988, *J. chem. Phys.*, **88,** 7424.

[235] Kornweitz, H., Persky, A., and Levine, R. D., 1986, *Chem. Phys. Lett.*, 1986, **128,** 443.
[236] Mayne, H. R., and Harrison, J. A., 1987, *Chem. Phys. Lett.*, **133,** 185.
[237] Kornweitz, H., Persky, A., and Levine, R. D., 1987, *Chem. Phys. Lett.*, **133,** 187.
[238] Alvariño, J. M., and Laganà, A., 1988, *Chem. Phys. Lett.*, **144,** 558.
[239] Walker, R. B., Blais, N. C., and Truhlar, D. G., 1984, *J. chem. Phys.*, **80,** 246.
[240] Harrison, J. A., Isakson, L. J., and Mayne, H. R., 1989, *J. chem. Phys.*, **91,** 6906.
[241] Muckerman, J. T., 1971, *J. chem. Phys.*, **54,** 1155.
[242] Muckerman, J. T., 1981, *Theoretical Chemistry, Theory of Scattering. Papers in Honor of Henry Eyring*, Vol. 6A, edited by D. Henderson (New York: Academic), p. 1.
[243] Persky, A., 1979, *J. chem. Phys.*, **70,** 3910.
[244] Schatz, G. C., Fitzcharles, M. S., and Harding, L. B., 1987, *Faraday Disc. Chem. Soc.*, **84,** 359.
[245] Schatz, G. C., and Fitzcharles, M. S., 1988, *Selectivity in Chemical Reactions*, edited by J. C. Whitehead (Dordrecht: Kluwer), p. 523.
[246] Duchovic, R. J., and Hase, W. L., 1984, *Chem. Phys. Lett.*, **110,** 474.
[247] Duchovic, R. J., and Hase, W. L., 1985, *J. chem. Phys.*, **82,** 3599.
[248] Swamy, K. N., and Hase, W. L., 1983, *J. phys. Chem.*, **87,** 4715.
[249] Vande Linde, S. R., Mondro, S. L., and Hase, W. L., 1987, *J. chem. Phys.*, **86,** 1348.
[250] Swamy, K. N., and Hase, W. L., 1984, *J. Am. chem. Soc.*, **106,** 4071.
[251] Raff, L. M., 1988, *J. phys. Chem.*, **92,** 141.
[252] Noor Batcha, I., Thareja, S., and Sathyamurthy, N., 1987, *J. phys. Chem.*, **91,** 2171.