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Effect of Reagent Rotation on Elementary Bimolecular Exchange Reactions

N. SATHYAMURTHY

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

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Contents

N. Sathyamurthy obtained his B.Sc. and M.Sc. degrees from Annamalai University in India in 1970 and 1972, respectively. He received his Ph.D. degree from Oklahoma State University in 1975. He was a research associate with Prof. J. C. Polanyi at the University of Toronto, Canada during 1975–1978. He joined the Chemistry Department at the Indian Institute of Technology Kanpur as a lecturer in 1978 and he continues there as an Assistant Professor since 1980. He was awarded the Young Scientist Medal from the Indian National Science Academy recently for his contributions in the area of Theoretical Molecular Reaction Dynamics.

I. Introduction

State-to-state reaction dynamics has been the focus of attention of much experimental and theoretical research in the last decade or so.[1] In addition to studying the effect of temperature on reaction rate, the influence of different forms of *reagent* energy (translation (T), vibration (V), rotation (R) and electronic) on reaction cross section (σ) and rate coefficient (k) has been studied for several elementary reactions in the gas phase. General effects of T and V on σ have become well identified and the reasons understood to a large extent.[2] For example, for an endothermic reaction or for an exothermic/neutral reaction with a substantial barrier, there is a threshold energy (T_{th}) above which σ increases to a maximum and then decreases[3] with increase in T. For a *substantially* endothermic reaction (i.e., $\Delta H° \geqslant 10$ kcal mol^{-1}) V enhances σ much more than T.[4] For exothermic reactions and for endothermic and neutral reactions under exoergic conditions (i.e., total energy (E) is above the barrier height (E_{b})) there is much less or little effect of increasing V on σ at constant T.[5] At a constant E, V is less effective than T in enhancing an exothermic reaction. These effects are related to the topological features (barrier height, barrier location, shape of the inner repulsive wall, etc.) of the potential-energy surfaces (PES) and detailed discussions can be found elsewhere.[4,6] The effect of changing V and T on other reaction attributes like product-energy distribution (PED) also has been fairly well documented.[7] In contrast, the effect of reagent rotation on reaction dynamics has been much less studied from both experimental and theoretical points of view and therefore has been much less understood. From an experimental point of view, the rotational energy levels of the reagent molecule(s) are closely spaced and hence rotational state selection becomes difficult. Also, the rotational relaxation is much faster than vibrational relaxation. As a result, requirements of collision-free conditions and measurable changes in the intensities of light emission for example are much more stringent. Theoretically, in addition to the phase space theory (PST)[8] approach, only quasiclassical trajectory (QCT) method[9] has been used extensively to study the effect of R on σ and k. The former is valid only if the outcomes are statistical and for most of the reactions, they are not. Discrepancies between "observations" (from experiments or computed from

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dynamical theories) and *statistical* predictions as analyzed through an information theoretical approach[5] illustrate the importance of the *dynamical* factors. The QCT approach suffers from the fact that apart from the limitations of classical mechanics[10] in following molecular collisions, the predictions are only as reliable as the quality of the PES used in the study. Except for a few systems like $H + H_2$ and $He + H_2^+$, ab initio PESs have not been calculated to chemical accuracy (± 0.5 kcal mol^{-1}) particularly for noncollinear geometries as the elaborate electronic structure calculations[11] have to be repeated for several geometries that are possible during the course of a collision. Similarly, the time-consuming QCT calculations have to be repeated for each choice of V, R, and T. In the absence of experimental results on the effect of rotation, the tendency therefore has been to select the initial rotational state (J) from an appropriate distribution in the theoretical studies of reaction dynamics. Also, from an interpretation point, the effect of V and T could be analyzed easily using a collinear model and therefore by plotting representative trajectories on the PES contours for an atom–diatom exchange reaction. For studying the effect of R on the other hand, three-dimensional representations are a must and therefore simple models have not emerged so far. Also, in the case of the rotational motion, angular momentum factors have to be taken into account in addition to the energy constraints.

In the last few years, new experimental techniques have been developed to study the explicit dependence of σ and k and other reaction attributes on the initial J of the reactants.[12] As a result, new theoretical results for specific J levels have also started appearing. In view of the above, we have undertaken to review what has been done so far on the effect of reagent rotation on various attributes for simple bimolecular exchange reactions. This is still a young field with few generalizations possible as yet. By necessity, most of the work till this date has been on reactions of the type

$$A + BC \rightarrow AB + C \qquad (R0)$$

We have covered the literature, with a few exceptions, until the end of 1982. Although we are aware of the studies on the effect of reagent rotation on vibrational energy transfer processes[13] and other chemical reactions like unimolecular,[14] collision-induced dissociation,[15] and photochemical[16] processes, we do not deal with them in this review.

II. Effect of Reagent Rotation on Reaction Cross Section and Rate Coefficient

A. Experimental Studies

The earliest method[17] developed by Polanyi and coworkers was to obtain information on the effect of R (as well as V and T) on the rate of an endothermic reaction by applying the *principle of detailed balance*[18] to the chemiluminescence data obtained for the reverse exothermic reaction. This was accomplished for the reactions

$$I + HCl \rightarrow IH + Cl \qquad (R1)$$

$$Cl + ClH \rightarrow Cl_2 + H \qquad (R2)$$

$$H + HF \rightarrow H_2 + F \qquad (R3)$$

Polanyi and co-workers[7a,d,12c] also introduced early direct methods for obtaining $k(J)$. The methods, termed fluorescence depletion (FD) and chemiluminescence depletion (CD) depended on the measurement, under arrested relaxation conditions of the relative depletion of the emission from various (v,J) levels in determining the dependence of k on J by FD for[7d]

$$F + HCl \rightarrow HF + Cl \qquad (R4)$$

and by CD for the reactions[7a,12c]

$$Na + ClH \rightarrow NaCl + H \qquad (R5)$$

$$Na + FH \rightarrow NaF + H \qquad (R6)$$

The advantage of this method is that an array of relative reaction rates from several J levels for different v states of the molecule could be obtained from a single experiment with a wide range of rotational energies (up to 12 kcal mol^{-1} of rotation in several vibrational levels). Despite a considerable scatter in the data it was evident that the detailed rate coefficient $k(J)$ at first diminished as J increased, thereafter $k(J)$ increased. The decline in $k(J)$ was attributed to diminution in the time that $A + B - C$ spent in a preferred orientation, and the subsequent enhancement to the effect of substantial rotational energy in carrying the system over the barrier (rotation could enhance collision energy on an early-barrier surface, or vibrational energy, through vibration–rotation interaction, on a late-barrier surface).[12c]

Another method available for rotational state selection was to use a quadrupole field in selecting the J states of a polar molecule as was done by Bernstein and co-workers[12b] for the reactions

$$K + FCs \rightarrow KF + Cs \qquad (R7)$$

$$K + FRb \rightarrow KF + Rb \qquad (R8)$$

Incidentally, these two reactions proceed through a long-lived complex and the variation of σ with J for these two reactions will be discussed separately.

A more recent method is to irradiate the beam/gas of a reactant using a laser of appropriate frequency to select the molecule in a particular J state. For example, in studying $\sigma(J)$ for the reaction

$$K + ClH \rightarrow KCl + H \qquad (R9)$$

Brooks and co-workers[12d] have used this technique. This method has been used[19,20] for studying $\sigma(J)$ for

$$K + FH \rightarrow KF + H \qquad (R10)$$

and its strontium analogue also. This method offers the advantage that by using a plane polarized light we can select further the orientation of the polar molecule as was done by Zare and co-workers[21] for

$$Sr + FH \rightarrow SrF + H \qquad (R11)$$

It obviously has the limitation that a laser of appropriate frequency for each J state and with a small enough line width has to be found. Also, the experiment has to be repeated for each J, v, and T.

None of the above mentioned methods are suitable for studying the effect of reagent rotation on reactions involving nonpolar molecules like H_2. In the particular case of H_2, the fact that ortho and para forms have only odd or even J states available, respectively, and that their relative ratios can be varied by varying the tem-

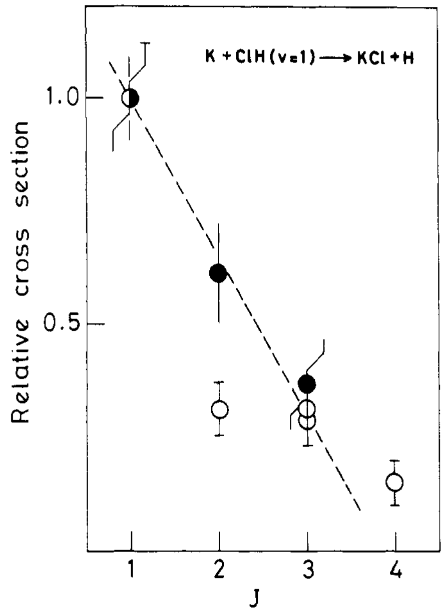

Figure 1. Total reactive cross sections for the formation of KCl from K + ClH (v = 1, J). Filled circles obtained by integrating angular distributions, open circles obtained from peak intensity measurements and are normalized at J = 1. Reproduced with permission from ref 12d. Copyright 1979, American Institute of Physics.

perature, has been made use of by Klein and Persky[12a] in studying the rate of the reaction

$$F + H_2 \rightarrow FH + H \qquad (R12)$$

They found that k decreased slightly with an increase in J for this reaction.

The different systems studied under different conditions by the various experimental methods are listed in Table I along with the major findings. The general qualitative result for *direct* reactions is that *molecular rotation inhibits reaction.* That is σ or k decreases initially with increase in J. We illustrate this for reaction R9 in Figure 1. Such a decrease is invariably followed by an increase in $\sigma(J)$ as has been shown by Loesch and co-workers[19] for (R10); this reiterates the earlier observation by Polanyi and co-workers[12c] of an initial decline followed by an enhancement in $k(J)$ for reactions (R4–R6).

The initial decline in σ or $k(J)$ for all these reactions has been interpreted generally as due to the fact that a particular orientation preferred for the reaction is disrupted by the rotational motion of the diatomic molecule. Ab initio PES studies have shown that barrier heights (E_b) for many reactions depend strongly on the angle of approach of atom A with respect to BC. For instance, for the reaction

$$H + H_2 \rightarrow H_2 + H \qquad (R13)$$

E_b is the lowest for the collinear approach.[22] However, for the reaction

$$Li + FH \rightarrow LiF + H \qquad (R14)$$

E_b is less for a sideways than for a head-on approach of Li to FH.[23] There is also direct experimental evidence[24,25] for a preferred orientation for reactions like

$$K + ICH_3 \rightarrow KI + CH_3 \qquad (R15)$$

$$M + I_2^* \rightarrow MI^* + I,\ M = In, Tl \qquad (R16)$$

The increase in $\sigma(J)$ and $k(J)$ following the initial decline could be due to further rotation bringing the molecule back to the favored orientation. Eventually, the molecule would be rotating fast enough for the incoming atom to see only a "blur" and therefore $\sigma(J)$ may level off and then start increasing due to an increase in the number of available product states arising from an increase in the total energy. Such a behavior is to be expected at least for reactions dominated by planar collisions as would be the case for example, for reactions of the type

$$H + HL \rightarrow HH + L \qquad (R17)$$

in which H and L represent heavy and light atoms, respectively. There are some instances[17,26] like reactions (R1–R3) and

$$D + DF \rightarrow D_2 + F \qquad (R18)$$

for which $k(J)$ increases initially and then decreases but this result was obtained at a constant $\langle E \rangle$ condition by applying the principle of "detailed balance" to chemiluminescence data for the reverse exothermic reaction and hence is not directly comparable with others listed in Table I.

In the case of reactions going through a *long-lived complex*, the only available experimental results[12b] are for reactions R7 and R8. The former, a slightly endothermic reaction, shows a 10–40% *increase* in the product yield for an increase in $\langle R \rangle$ of 2.4 kcal mol^{-1}, while the latter, an exothermic reaction shows a *decrease* in reactivity under identical conditions. For another slightly exothermic reaction[27,28]

$$H + HO \rightarrow H_2 + O\ (^1D) \qquad (R19)$$

which proceeds mostly (but not completely) through a long-lived complex, application of "detailed balance" to the laser-induced fluorescence PED data for the reverse reaction shows that high rotational excitation favors the reaction.

There is very little data available on the effect of J on σ or k for systems involving more than three atoms. For the reaction[28,29]

$$NO + OH \rightarrow NO_2 + H \qquad (R20)$$

application of detailed balance to PED for the reverse reaction shows that OH rotation favors reaction. Similarly for the reaction[30]

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (R21)$$

rotation in NO enhances the reaction cross section. In this particular case, the N end has been found to be 1.66 times more reactive than the O end. A related question on the effect of R on the reaction rate is its magnitude in comparison to that of V and T. Comparative results are available[7d,19,31,32] on the effect of V and T for reactions like (R9)–(R11) and

$$Ba + FH \rightarrow BaF + H \qquad (R22)$$

But for no single system are absolute results available as a function of V, R, and T under comparable conditions. Still, it *appears* that in general the effect of R on σ is less than that of V and T. Bernstein and co-workers[12b] have found that the relative efficiency of R in causing the reaction R7 is less than that of T. By a detailed statistical theoretical analysis, they attribute this to the centrifugal barrier effect and *not* to the in-

TABLE I. Experimental Results on the Effect of Reagent Rotation on Reaction Cross Section/Rate Coefficient

system	$\Delta H°$, kcal mol^{-1}	conditions[a]	finding	method[b]
			Direct Reactions $A + BC \rightarrow AB + C$	
$I + HCl \rightarrow IH + Cl$	+31.6	$v = 1$–4, $R = 0$–25, $\langle E \rangle = 33.9$	$k(J)$ *increases* initially and then decreases	application of detailed balance to chemiluminescence data for the exothermic reaction[17] (1969)
$Cl + ClH \rightarrow Cl_2 + H$	+45.1	$v = 3$, $R = 0$–10, $\langle E \rangle = 48.6$	$k(J)$ *increases* initially and then decreases	application of detailed balance to chemiluminescence data for the exothermic reaction[17] (1969)
$H + HF \rightarrow H_2 + F$	+31.5	$v = 1$–3, $J = 0$–20, $\langle E \rangle = 34.7$	$k(J)$ *increases* initially and then decreases	application of detailed balance to chemiluminescence data for the exothermic reaction[17] (1969)
$D + DF \rightarrow D_2 + F$	+31.2	$v = 1$–4, $J = 0$–15, $\langle E \rangle = 34.4$	$k(J)$ *increases* initially and then decreases	application of detailed balance to chemiluminescence data for the exothermic reaction[26] (1976)
$F + HCl \rightarrow FH + Cl$	−32.6	$v = 1$, $J = 0$–10	k *decreases* as $J{:}0 \rightarrow 2$ and then rises; $k(J) \sim 1.0 + 0.1\,J$ as $J{:}2 \rightarrow 6$ and *possibly* levels off	fluorescence depletion[7d] (1973)
$F + H_2 \rightarrow FH + H$	−31.5	$v = 0$, $J = 0$–3, $T_{\text{trans}}° = 175$–298 K	*slight* tendency for k to decrease with increase in J; $k_J/k_{J+1} \sim 1.08 + 0.03$	ortho/para mixture[12a] (1974)
$Na + ClH \rightarrow NaCl + H$	+4.2	$v = 1$–4, $J = 0$–19, ($R = 0$–13)	k *decreases* with increase in $J{:}0 \rightarrow 10$; increases with increase in $J{:}11 \rightarrow 19$;	chemiluminescence depletion[12c] (1978)
$Na + FH \rightarrow NaF + H$	+12.0	$v = 2$–4, $J = 0$–14, ($R = 0$–12)	k *decreases* with increase in $J{:}0 \rightarrow 7$; increases with increase in $J{:}7 \rightarrow 14$; $J_{\text{min}} = 7$, $R_{\text{min}} = 3$	chemiluminescence depletion[12c] (1978)
$K + ClH \rightarrow KCl + H$	+1	$v = 1$, $J = 1$–4	σ *decreases* by a factor of 2 as the $[J(J+1)]^{1/2}$ increases by $1\hbar$; *indication* that σ increases at a higher J	crossed molecular beams with effusive sources/laser excitation of the diatom[12d] (1979)
$Sr + FH \rightarrow SrF + H$	+6.4 ± 1.6	$v = 1$, $J = 1$–4	σ *decreases* as J increases from 1 to 3	crossed molecular beams with effusive sources/laser excitation of the diatom[20] (1981)
$K + FH \rightarrow KF + H$	+17	$v = 1$, $J = 0$–12, $T = 30.4$, 15.4	σ *decreases* with increase in J from 0 to 4; shallow minimum around $J = 5$–7 at the higher T; *increases* with increase in J for the lower T	crossed molecular beam[19a] using a supersonic nozzle and heating of the gas to get rotational excitation and HF laser to obtain vibrational excitation (1982)
		$v = 1$, $J = 5$–7, $T = 12.68$–30.4	$\sigma(J)$ increases at most T	beam/laser[19b] (1983)
			Complex Formation $A + BC \rightarrow AB + C$	
$K + FCs \rightarrow [KFCs] \rightarrow KF + Cs$	1.8	$v = 0$, low J and thermal J, $T = 3.4$–6.2	10–40% *increase* in product yield for an increase in $\langle R \rangle$ of 2.4 kcal mol^{-1}	molecular beam/quadrupole field[12b] (1978)
$K + FRb \rightarrow [KFRb] \rightarrow KF + Rb$	−1.5	$v = 0$, low J and thermal J, $J = 3$–6	*decrease* in reactivity with increase in $\langle R \rangle$ of 2.4 kcal mol^{-1}	molecular beam/quadrupole field[12b] (1978)
$H + HO \rightarrow H_2 + O(^1D)$	−2.9	$v = 0$, 1, $J = 0$–32	rotation favors reaction	application of detailed balance to laser-induced fluorescence data for the reverse reaction[27,28] (1979)
			Diatom–Diatom Reactions	
$NO + OH \rightarrow NO_2 + H$	+29.3 ± 0.5	$v = 0$, 1, $J = 0$–16, $E = 31.3 \pm 0.5$	rotation favors reaction	application of detailed balance to laser-induced fluorescence data for the reverse reaction[28,29] (1976)
			Diatom–Triatom Reactions	
$NO + O_3 \rightarrow NO_2 + O_2$	−9.9	v = thermal, $R = 0$–0.7	rotation enhances the reaction	beam-gas hexapole electric field[30] (1980)

[a] Energies in kcal mol^{-1}. [b] The year of publication is included in this column to highlight the chronological development in the field.

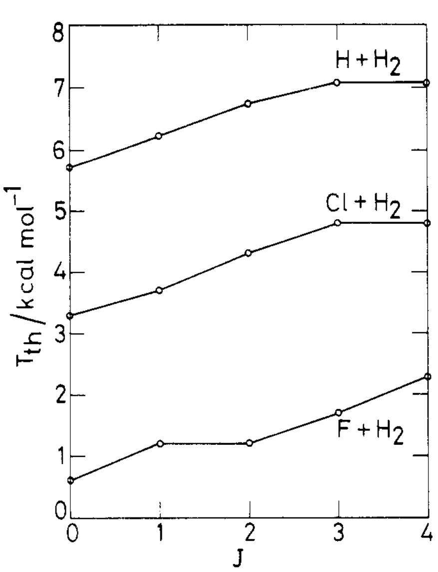

Figure 2. Translational threshold as a function of J obtained from QCT calculations[34,41,44] for M (H, F, Cl) + H_2 (v = 0).

complete energy randomization for the long-lived complex. Within the uncertainties of the experiments, R is approximately equivalent in importance to T in influencing the decay of the collision complex in reaction R8.

When the reaction rates[12c] for (R5) and (R6) are compared, the decline in $k(J)$ for the former is much steeper than for the latter. Similar results have been obtained[19a] for the potassium analogue of these two reactions. It is tempting to attribute this to the larger size of the Cl than the F atom. But this would be simple-minded as σ for these reactions is larger than their "collision cross sections".[33]

B. Theoretical Studies

None of the reactive systems for which σ or $k(J)$ has been investigated experimentally has been studied theoretically by using an accurate ab initio PES. However, some of them have been studied on semiempirical or empirical PES by the QCT method. Many systems for which no experimental results are available also have been investigated in this manner. A summary of such studies and their findings follows.

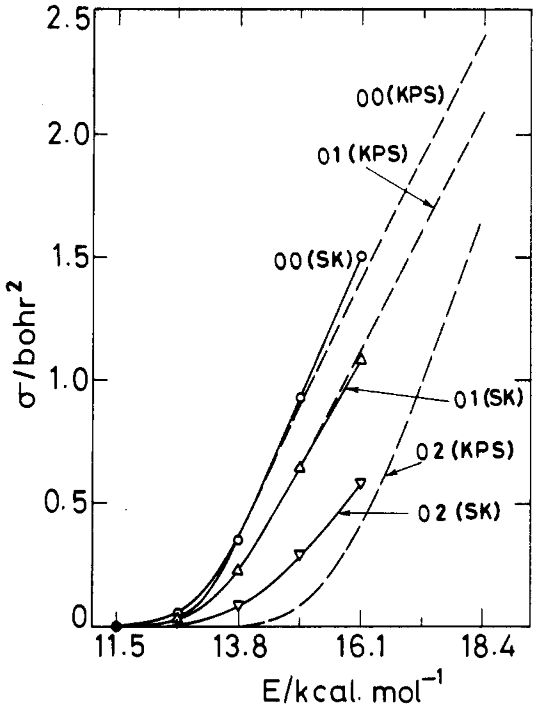

Figure 3. Comparison of quantum mechanical and quasiclassical trajectory results for H + H_2. SK stands for Schatz and Kuppermann;[36] KPS for Karplus, Porter, and Sharma.[34] The numbers 00, 01, etc. represent vJ levels of H_2. Reproduced with permission from ref 36. Copyright 1976, American Institute of Physics.

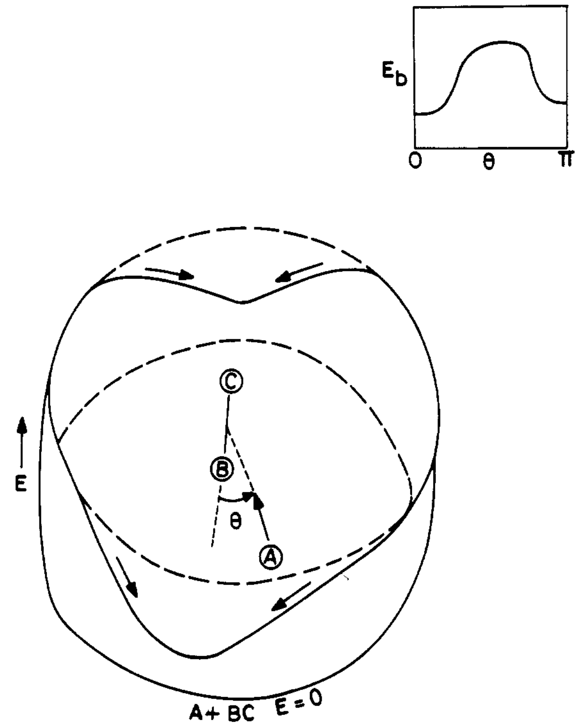

Figure 4. Schematic representation of the variation of E in polar coordinates. Collinear geometry is shown to be the most preferred. The arrows indicate the direction to which noncollinear trajectories would be "steered". The insert shows E_b as a function of θ in the linear scale, for a symmetric exchange reaction.

H + H_2. The simplest prototype bimolecular exchange reaction is between a hydrogen atom and a hydrogen molecule to yield another hydrogen atom and a hydrogen molecule (R13). The effect of J on σ for this reaction was studied first by Karplus, Porter, and Sharma[34] using the QCT method on a semiempirical Porter–Karplus[35] (PK) surface. The conclusion was that near threshold, reagent *rotation inhibits the reaction* and that T_{th} increases with increase in J as shown in Figure 2. The former finding has been subsequently confirmed by the full 3D quantal results of Schatz and Kuppermann[36] under identical conditions although the latter is not noticeable in the QM results, because of the non-zero QM probabilities below the classical threshold. The overall agreement between the QM and QCT results shown in Figure 3 lends credence to the applicability of the QCT method to a study of the effect of J on σ for simple bimolecular exchange reactions. The reason for the decline in $\sigma(J)$ is thought to be that the reaction R13 is most favored through the collinear configuration—that is, E_b for the reaction is the lowest when the H atom (A) approaches the H_2 molecule (BC) at θ = 0° (or 180°) and increases with increase in θ. At a constant $R_{A,BC}$, the energy vs. θ plot would look like that shown in Figure 4. Here, the asymptotic A + BC is taken to have an E = 0. Actual collisions would originate at different θ but all of them would be steered toward the collinear "alignment". If

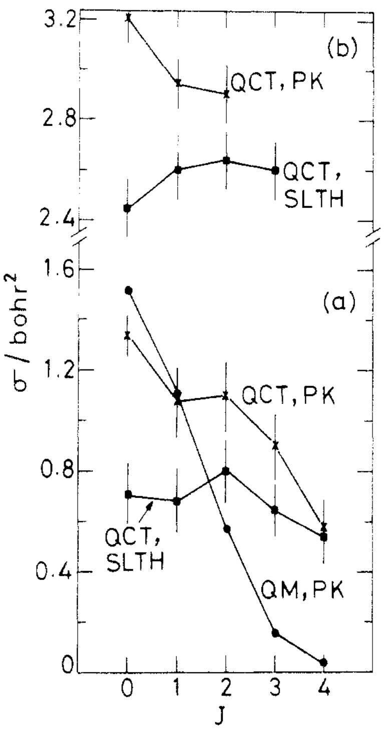

Figure 5. Integral reaction cross section for H + H_2 (v = 0) as a function of J. QM, PK represents the quantum mechanical results on the PK surface. QCT, PK and QCT, SLTH represent the QCT results on the PK and SLTH surfaces, respectively. Error bars represent 2σ Monte Carlo error estimates. (a) T = 9.844 kcal mol^{-1}; (b) T = 14.95 kcal mol^{-1}. Reproduced with permission from ref 38b. Copyright 1981, American Institute of Physics.

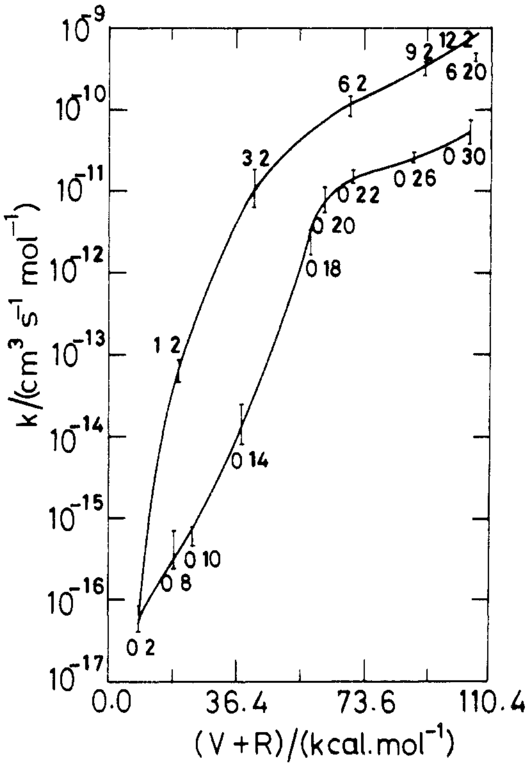

Figure 6. Rate coefficient at $T_{\mathrm{trans}}°$ = 300 K for the H + H_2 reaction as a function of the internal energy, obtained by QCT calculations.[39] The numbers on the curves indicate the vJ values. Error bars correspond to 1σ Monte Carlo error estimate. The curves have been drawn by hand to aid visualization. Reproduced with permission from ref 39. Copyright 1981, Plenum Publishing Corp.

the BC molecule is allowed to rotate, the *alignment effect* is opposed and a lower number of collisions would lead to reaction. As a result, σ decreases, more so with more rotation. But at a certain J, if the directions are right, the rotational *angular* velocity would compensate for the orbital *angular* velocity of the approaching atom and σ would return (after the initial decline) to the J = 0 value. In the absence of strong interactions, the $\langle J\rangle$ at which this is expected can be shown (appendix) to be

$$\langle J\rangle = 4\pi(2T/\mu_{\mathrm{A,BC}})^{1/2}(\mu_{\mathrm{BC}}/h)(r_{\mathrm{BC}}^2/b_{\max}) \qquad (1)$$

At T = 12.84 kcal mol^{-1}, $b_{\max}$ = 1–2 Å, and $\langle r_{\mathrm{BC}}\rangle \sim 0.75$ Å, σ_J is expected to return to the σ_0 value at J = 5–10. Unfortunately, available data do not allow a verification of this prediction. Similarly, the data are not adequate to test the $T^{1/2}$ and $\mu_{\mathrm{BC}}/(\mu_{\mathrm{A,BC}})^{1/2}$ dependence of $\langle J\rangle$.

At energies substantially above threshold, σ reaches a limiting value and is nearly insensitive to J in the range 0–5. This is probably because the "alignment effect" is not important as the total energy available to the system is well above the barrier for noncollinear reaction. Also at a higher T, there is not sufficient time for the molecule BC to rotate away from the preferred alignment. The rotation period for H_2, $(2.7 \times 10^{-13})/[J(J+1)]^{1/2}$ for J = 5 for example, equals $\sim 5 \times 10^{-14}$ s and is comparable to the collision time of $4\text{–}8 \times 10^{-14}$ s.

A chemically accurate PES has become available[22] in recent years for reaction R22 and it has been successfully fitted to an analytic function by Truhlar and Horowitz.[37] The dynamics of the reaction on this SLTH surface has been studied by Barg, Mayne, and Toennies[38b] and the results are compared with those on the PK surface in Figure 5. At T = 9.844 kcal mol^{-1} for v = 0, $\sigma(J)$ is distinctly different on the two surfaces showing that collision dynamics is very sensitive to the changes in PES and that the J dependence of σ could be a valuable probe in deciding the similarity (or lack thereof) between two surfaces. On the SLTH surface, there is very little variation in σ with change in J from 0 through 4. This means that the explanation for the rotational inhibition for the reaction on the PK surface in terms of the "alignment effect" could be simpleminded. The origin of the differences in the J dependence of σ on the two surfaces is not clear. At a higher energy of T = 14.95 kcal mol^{-1} also, σ is less on the SLTH than on the PK surface and is insensitive to variation in J in the range 0–3.

A much more extensive study of the effect of J (and v) on k at $T_{\mathrm{trans}}°$ = 300 K for the reaction on the SLTH surface has been carried out recently by Blais and Truhlar.[39] While the earlier studies[33,38] had been restricted to J = 0–5, these authors have varied J from 2 to 30 for v = 0 and found a dramatic increase in k with increase in J, the increase being larger at lower J's, in the energy scale as shown in Figure 6. Although no explanation was given by the authors, several factors would be important. One is that with increase in the reagent energy, the number of available product states increases. Although T is near threshold, E is well above E_{b} and the alignment effect would not be significant. Also, with increase in J, the Coriolis force would become increasingly important and the bond would be stretched with the effect that the molecule would behave as if it is vibrationally excited. It must be stressed that the

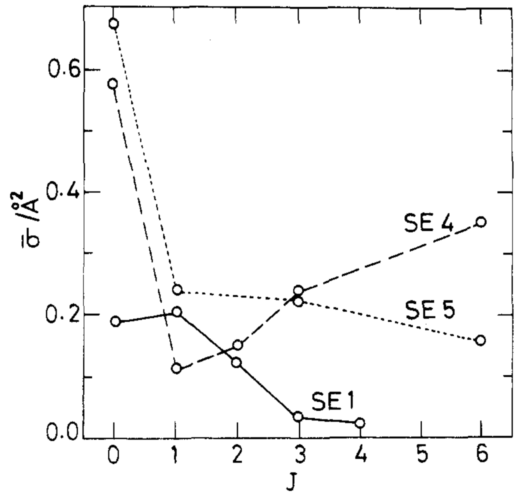

Figure 7. Thermal average cross section as a function of J for the $F + H_2$ ($v = 0$) reaction on three different PES.[40] Reproduced with permission from ref 40. Copyright 1977, Chemical Society, London.

increase in k observed by Blais and Truhlar does not contradict the insensitivity noted by Barg et al. (on the SLTH surface) as the ranges of J investigated by the two teams are almost mutually exclusive: 2–30 with $J = 3$ and 4 omitted and 0–4, respectively. Blais and Truhlar have also compared the effect of reagent rotation with that of vibrational excitation and found that the dependence of k on v is qualitatively similar; but at any given internal energy, *vibration is much more effective than rotation in causing the reaction* as may be seen from Figure 6 presumably because vibration helps in "cutting the corner" and reaching the product valley. This reasoning is supported by the fact that the average product vibration increases much more with increase in reagent vibration than rotation (see section III). It must be added that the effect of J on k becomes less important with increase in v. This would go against our interpretation of the increasing $k(J)$ in terms of the Coriolis force. The fact that, for the same internal energy, redistribution between V and R changes the k means that dynamical effects are important and/or rotational angular momentum factor plays an important role in reaction R13.

$F + H_2$, D_2, HD. The most extensively studied reaction from the point of view of the effect of reagent rotation and its dependence on the PES is (R12). An excellent summary of the results for this reaction up to 1977 has been given by Polanyi and Schreiber;[40] it has been updated by Muckerman.[41] Thermally averaged reaction cross section $\bar{\sigma}$ ($v = 0$, $T_{\text{trans}}{}^{\circ} = 300$ K) as obtained by the QCT method on three different LEPS surfaces by Polanyi and Schreiber are plotted as a function of J in Figure 7. Except on one surface on which $\bar{\sigma}_{J=0} \sim \bar{\sigma}_{J=1}$, $\bar{\sigma}_{J=0}$ is the highest of all $\bar{\sigma}_J$'s meaning that *rotation inhibits reaction*. Only on one surface, SE4, $\bar{\sigma}$ rises with increase in J after the initial decline with J going from 0 to 1. Incidentally, all these forms of $\bar{\sigma}(J)$ are in disagreement with the only experimental observation[12a] for this reaction that k decreases slightly with increase in J. It is certainly clear that the J dependence of $\bar{\sigma}$ is strongly dependent on the choice of PES. Then the question is which are the characteristic features of the PES that govern the variation of $\bar{\sigma}$ with J. Polanyi and Schreiber pointed out that in general a maximum in $\bar{\sigma}$ is observed at $J = 1$ for surfaces (SE1) having no well and a minimum at $J = 1$ for surfaces with a shallow well (SE4, SE5) in the entry valley. They explained the slight enhancement of J in going from 0 to 1 on the SE1 surface as due to the FHH system being able to maintain the collinearity throughout the collision and this being the energetically most favored geometry leads to reaction. Similarly, they attributed the greater reactivity of the SE5 surface due to the fact that, a well of ~1 kcal mol^{-1} depth in the entry channel accelerates a trajectory with $J = 3$ such that the approach time is small enough to prevent BC from going away from the preferred alignment. The *same* trajectory (i.e., identical initial conditions) is nonreactive on the SE1 which does not have the well. These explanations are of limited validity as for $H + H_2$, there is no potential well (except for the van der Waals interaction) in the entrance channel in either of the PK and SLTH surfaces and yet the $\sigma(J)$ on the two surfaces differ markedly—steady decline on the former and nearly flat curve on the latter, near threshold. Still, the fact remains that $\sigma(J)$ is sensitive to the choice of PES—more so than many of the other reaction attributes, for example the average product vibrational energy ($\langle V' \rangle$). All the three surfaces (SE1, SE4, SE5) give nearly the same $\langle V' \rangle$ but dramatically different $\bar{\sigma}(J)$. On what is considered the best surface for (R12), Muckerman-5, Muckerman[41] has found from QCT studies that at $T = 3$ kcal mol^{-1} and $v = 0$ for H_2, σ decreases significantly with increase in J from 0 to 4. The same trend has been observed for k in the $T_{\text{trans}}{}^{\circ}$ range 250–450 K. There is an increase in T_{th} as J increases from 0 to 4, as shown in Figure 2. The decline in σ and $k(J)$ has been found for the deuterium analogue also. The Arrhenius activation energy increases steadily with increase in J from 0 to 4 for both reactions, emphasizing that rotation inhibits reaction. The trend in the Arrhenius frequency factor with variation in J is however, erratic.

Interestingly, $\sigma(J)$ for the reaction[41]

$$F + HD\ (v = 0, J) \rightarrow FH + D \qquad (R23)$$

at $T = 3$ kcal mol^{-1} peaks at $J = 3$, while it declines dramatically for $0 < J \leqslant 4$ under identical conditions for the reaction

$$F + HD\ (v = 0, J) \rightarrow FD + H \qquad (R24)$$

the difference arising from the asymmetry of the rotor. Values of k for the two reactions in the $T_{\text{trans}}{}^{\circ}$ range 150–1000 K show the same trend. The branching ratio, $\Gamma = \sigma(\text{HF})/\sigma(\text{DF})$ is strongly dependent on J. At $J = 0$ and 1, DF is formed in preference over HF ($\Gamma < 1$) mainly because of the larger mass for D resulting in a wider and less skewed product channel in the scaled and skewed coordinates.[42] Further increase in J to 2–4 results in an increase in Γ as the lighter H atom sweeps a much larger volume during rotation than D due to the center of mass being shifted towards the heavier D. This means D is shielded by H with increasing rotation and the reactivity is larger for the H end.

The above results clearly indicate that the kinematic (mass) factors play an important role in rotation influencing an exchange reaction. A systematic study of the dependence of $k(J)$ or $\sigma(J)$ on various mass combinations of A, B, and C atoms is clearly warranted. Such a study has been carried out by Davidson and

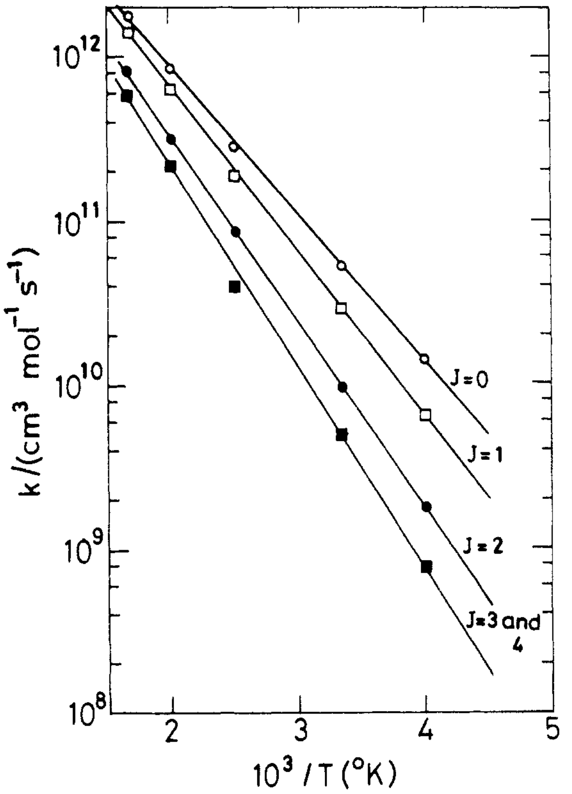

Figure 8. Rate coefficient as a function of $1/T_{trans}°$ for different J for the reaction $Cl + H_2$ ($v = 0$) as obtained by QCT calculations.[44] Reproduced with permission from ref 44. Copyright 1977, American Institute of Physics.

Polanyi[43] and the results remain to be published. However, we can speculate on the effect of the kinematic factors on $\sigma(J)$ based on qualitative arguments; a brief summary of our expectations and the "observations" is presented later in the review.

$Cl + H_2$, D_2, HD. The effect of reagent rotation on the chlorine analogue of the reaction (R12):

$$Cl + H_2 \rightarrow ClH + H \qquad (R25)$$

has been investigated in detail by Persky[44] for $v = 0$, $J = 0$–4 at $T = T_{th} - 12$ kcal mol^{-1} using the QCT technique on an LEPS surface. Although this reaction is slightly endothermic, the results are very similar to that of (R12) and (R13) in that the excitation function, $\sigma(T)$ has qualitatively the same shape for all J; near threshold, σ decreases with increase in J from 0 to 3 and then levels off for $J = 4$; T_{th} increases with J and the increase is almost the same as that for reaction R13 as shown in Figure 2. Therefore, this is another example where *rotation hinders the reaction* and the additional energy in the form of reagent rotation is not available for crossing the barrier. The fact that the decline in $\sigma(J)$ is mostly due to a decrease in b_{max} with increasing J for $T < 8$ kcal mol^{-1} emphasizes that orbital angular momentum (L) factors also play an important role in deciding the collisional outcome.

The effect of J on σ is reflected on the J dependence of k as illustrated in Figure 8. The state-selected rate constant decreases with increase in J from 0 through 3 and then stays constant for $J = 3$ and 4 in the range $T_{trans}° = 250$–600 K.

QCT results of Persky (for $v = 0$) on the deuterium analogue of (R25):

$$Cl + D_2 \rightarrow ClD + D \qquad (R26)$$

show qualitatively the same J dependence of σ and k. But the striking feature of the result is that σ depends on J and not on R emphasizing the importance of *rotational angular momentum.*

Persky has also investigated the effect of J on the reactions

$$Cl + HD \rightarrow ClH + D \qquad (R27)$$

$$Cl + DH \rightarrow ClD + H \qquad (R28)$$

for $v = 0$, $J = 0$–4 at $T = T_{th} - 15$ kcal mol^{-1}. While J affects the formation of both HCl and DCl, the effect is much more pronounced for the latter. The branching ratio $\Gamma = \sigma(HCl)/\sigma(DCl)$ increases considerably with J except between $J = 0$ and $J = 1$ where it decreases slightly. For a given J, $\Gamma > 1$ for low T but it decreases with increase in T. The value of T at which inversion in the branching ratio occurs (i.e., $\Gamma = 1$) increases with increasing J. At low energies the preferential formation of HCl over DCl with increasing J is explained, as for the fluorine analogue (see above) on the basis of the center of mass being shifted towards D and the H end of the rotating DH molecule sweeping a much larger volume than the D end.

H + HBr, Br + HBr. The bromine analogue of the reaction (R12):

$$Br + H_2 \rightarrow BrH + H \qquad (R29)$$

would be substantially endothermic and it would be interesting to know the effect of J on σ and k for this reaction. Unfortunately, to the best of our knowledge, it has not been the subject of any QCT study so far. However, the reverse reaction

$$H + HBr \rightarrow H_2 + Br \qquad (R30)$$

has been studied[45] on a semiempirical valence-bond surface of Raff et al.[46] for $v = 0$ and $J = 0$, 3, and 8 at $T = 0.738$–73.8 kcal mol^{-1}. The dependence of σ on J varies with T and is erratic and often within the statistical error estimates. Therefore, no conclusion could be drawn. However, White and Thompson[47] reported later that the $k(J)$ increases for $v = 2$ at $T_{trans}° = 1000$ K. Recently, Mayne and Polanyi[48] have also investigated the $\sigma(J)$ for this reaction on an LEPS surface of Parr and Kuppermann.[49] For HBr ($v = 0$), $T = 6$ kcal mol^{-1}, σ decreases from 0.61 Å^2 for $J = 0$ to 0.45 Å^2 for $J = 3$ and 6 and increases slightly to 0.56 Å^2 for $J = 9$. Unfortunately, these variations are within the statistical error estimates and therefore prevent us from drawing any conclusion. However, these authors have established the existence of the "alignment effect" by correlating the variation in E_b with θ for the LEPS and a BEBO[50] (bond-energy-bond-order) surface, to the variation of the reaction probability with θ. These authors also find the deuterium isotope effects for this reaction to be insensitive to a change in J from 0 to 6.

White[45] found the rotation ($J = 0, 4, 6$) to have no noticeable effect on the exchange reaction

$$H + BrH \rightarrow HBr + H \qquad (R31)$$

also for $v = 0$. But, as for the abstraction, for $v = 2$, at $T_{trans}° = 1000$ K, k increases[47] with J showing that the effect of J depends on the vibrational state also among other factors. One reason for this is that vibration enhances endothermic and to a less extent thermoneutral reactions and as a result the σ values are

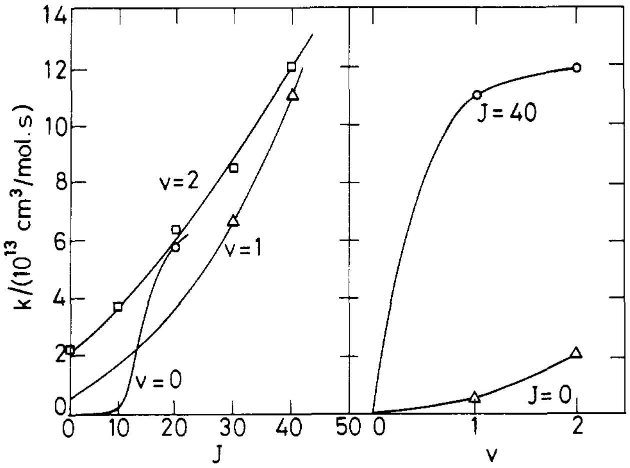

Figure 9. Rate coefficient at $T_{trans}° = 1000$ K as a function of v and J for the reaction Br + HBr → BrH + Br as obtained from QCT calculations.[47] Reproduced with permission from ref 47. Copyright 1974, American Institute of Physics.

large enough for the variation in σ with J to become noticeable only for non-zero v, unless an enormous (unrealistic) number of trajectories are run to keep the error estimates very small. In any case, the *cooperative effect* of reagent vibration and rotation on another exchange reaction

$$\mathrm{Br + HBr \rightarrow BrH + Br} \qquad \text{(R32)}$$

is illustrated in Figure 9a. For $v = 0$, k is insensitive to $J \leqslant 10$, but increases dramatically when J is increased to 20. For $v = 1$ and 2, *k increases* steeply with increasing J up to $J = 40$. The dramatic *enhancement* of the reaction rate by *reagent rotation* is illustrated by comparing it with vibrational enhancement for this reaction in Figure 9b. These results have a strong implication to vibrational relaxation. "When a large amount of rotational energy is present in the reactant molecule, the contribution from the atom-exchange mechanism to the vibrational relaxation is greatly enhanced at the expense of the nonreactive mechanism."[47] We must add that this system is unique in that it belongs to the mass combination H + LH (H = heavy; L = light) that results in long-lived complexes due to multiple collisions as the incoming and the outgoing atoms are particularly heavy.

F + HCl. A related reaction, (R4), has a similar mass combination but is exothermic. QCT studies[7d] on an LEPS surface for this reaction do not show any noticeable effect in k (at 780 K for $v = 1$) with increase in J from 0 to 10 but a further increase in J results in an increase in k. All we can say at this point is that this is not in disagreement with the experimental results which suggest a decline in $k(J)$ followed by an increase in the range $J = 0$–10.

H + Cl$_2$, H + Br$_2$, H + O$_2$. Polanyi and co-workers[7d] had tried to infer on the effect of R on k for the reaction

$$\mathrm{H + Cl_2 \rightarrow HCl + Cl} \qquad \text{(R33)}$$

by analyzing $\langle R \rangle$ in all collisions and in reactive collisions ($\langle R \rangle_r$) only. At $v = 0$, $T_{trans}° = 300$, 2650 K and $T_{rot}° = 300$, 1700 K, $\langle R \rangle_r = \langle R \rangle$ meaning that reagent rotation has little effect on reaction. But at $T_{vib}° = 1700$ K $= T_{rot}°$ and $T_{trans}° = 300$ K, $\langle R \rangle_r > \langle R \rangle$ which implies that *when accompanied by vibration, reagent rotation enhances the reaction rate.* Connor et al.[81] however find that for the same reaction for $v = 0$ at $T = 2.3$ kcal mol^{-1}, $\sigma(J)$ decreases initially, as J is increased from 0 through 10 and 20, and then increases with an increase in J through 100.

White[45] had investigated $\sigma(J)$ for the bromine analogue:

$$\mathrm{H + Br_2 \rightarrow HBr + Br} \qquad \text{(R34)}$$

and found that for $v = 0$ and $T = 0$–74.2 kcal mol^{-1}, changing J (0, 15, and 35) had little influence on σ, similar to the conclusion[7d] for (R33).

A similar reaction (from the mass combination point of view) that has drawn considerable attention is[51-53]

$$\mathrm{H + O_2 \rightarrow HO + O} \qquad \text{(R35)}$$

This reaction is different from all the reactions discussed so far in that despite its overall endothermicity (~14 kcal mol^{-1}), there is a deep potential well (of depth ~46 kcal mol^{-1}). The first QCT study of this reaction was by Gauss[51] who used a modified LEPS surface which could model a bent intermediate. For $v = 0$, 4, and 6 at $E = 18$–33 kcal mol^{-1}, σ was indistinguishable for $J = 1$ and 21 meaning that reagent rotation has little effect on σ for this reaction.

However, recently Miller[52] has computed a large number of trajectories on an ab initio surface[54] having nearly the same endothermicity and potential-well depth and published the k values for the reaction (R35) and its deuterium analogue in the $T_{trans}°$ range 250–2500 K. He has computed σ for $v = 0$–4, $J = 1$, 13, 19, 25, 37, 45, 55, and 69 at $T = 0$–50 kcal mol^{-1}. Except for $v = 0$ for which the $\sigma(T)$ for the lower J's cross each other, in general, σ increases with increase in J. This means that *rotation helps reaction.* This is further evident from the fact that for $v = 0$, 1, and 2, T_{th} *decreases* with increase in J. We must add, however, that for $v = 3$ and 4, T_{th} is much lower for $J = 1$ than for higher J values. Similarly for $J \geqslant 37$, T_{th} is independent of J as well as v. Another striking result is that for large J, the $\sigma(T)$ increases rapidly above T_{th}; much more rapidly than for the low J values. Miller points out that the O$_2$ molecules having large rotational angular momentum, at very low collision energies do not allow the trajectories to enter into the interaction region. If this is the case, he should have observed an overall decline in $\sigma(J)$! A detailed comparison of the increase in σ with increase in the available energy to the system, shows that at very low energies (<5 kcal mol^{-1}) all three forms of energy (T, V, R) are equal in their efficiency in causing the reaction. At higher energies, R and V are much more efficient than T. At intermediate energies, $\Delta\sigma/\Delta R > \Delta\sigma/\Delta V > \Delta\sigma/\Delta T$. All the available results for the reaction

$$\mathrm{D + O_2 \rightarrow DO + O} \qquad \text{(R36)}$$

show essentially the same dependence on J as for reaction R35.

Results of yet another QCT study[53] of reaction R35 have been reported recently. The authors have used an empirical surface[55] and investigated the effect of repartitioning of reactant energy to a limited extent. At $T = 3.7$ kcal mol^{-1}, $v = 6$, $J = 1$ and $v = 0$, $J = 79$ lead to nearly the same σ meaning that one is not preferred over the other. However, at $E = 40.5$ kcal mol^{-1} for $v = 6$, $J = 1$ at $T = 12.65$ kcal mol^{-1}, $\sigma = 0.25$ Å^2 while at the same E for $v = 6$, $J = 48$, $T = 3.7$ kcal mol^{-1}, σ

= 0.97 Å^2. Clearly, at a fixed total energy, *reagent rotation is more efficient than translation* for this reaction.

Na + Na$_2$. The effect of repartitioning of energy between V and R on σ has been studied for the reaction

$$Na + Na_2 \rightarrow Na_2 + Na \qquad (R37)$$

by Gelb and Alper.[56] At higher values of T, σ is unaffected by interconverting R and V at a fixed T; but for the lower values of T, *σ increases with increase in R at the expense of V.* The authors have explained this by pointing out that a rotating atom has a much better chance of reorienting itself to a favorable orientation for reaction at the lower energies. This is the converse of what is usually stated for explaining the decline in $\sigma(J)$! In any case, we must add that this is also a reaction having a deep potential well in its PES.

O + H$_2$. The reaction between a singlet oxygen atom and a hydrogen molecule

$$O(^1D) + H_2 \rightarrow OH + H \qquad (R38)$$

also involves a deep potential well corresponding to H_2O. Schinke and Lester,[57] using an ab initio surface[58] find that for v = 0, at T = 0.25–5 kcal mol^{-1}, change in J from 0 through 3 causes *very little change* in σ in spite of long-lived trajectories and the product vibrational energy distribution being nearly "statistical".

The effect of J on σ for the analogous reaction involving a triplet oxygen atom is also of interest. This reaction is slightly endothermic, has no significant potential well and has the collinear configuration as the most preferred geometry for the reaction, with an E_b of ~13 kcal mol^{-1}. Johnson and Winter,[59] using an LEPS surface found that there is in general an *enhancement of reaction by rotation.* To be specific, for v = 0, T = 8.5–25 kcal mol^{-1}, σ increases with increase in J from 0 through 4. At the higher energies $\sigma_{J=0} \sim \sigma_{J=1}$. For v = 1, T = 4–25 kcal mol^{-1}, σ increases as J increases from 0 to 3 but then there is a drop in σ as J is increased to 4. On an ab initio surface, Schinke and Lester[60] find that at $T = T_{th}$ – 30 kcal mol^{-1} (T_{th} = 10, 4, and 1 kcal mol^{-1}, respectively, for v = 0, 1, and 2), σ increases as J increases from 0 through 3 (6 in the case of v = 0) except that below 18 kcal mol^{-1} there is a maximum at J = 1. There are other small variations in this trend but they are all within the statistical error estimates. This *enhancement of reaction cross section by rotational excitation* for this *direct* reaction defies our earlier explanations of the decline in $\sigma(J)$ in terms of the "orientation alignment". For this reaction, E_b increases dramatically as the O–H–H angle decreases below 180° as shown in Figure 10. The variation is steeper for the LEPS and one would have expected a sharp decline in $\sigma(J)$ on this surface.

Li + FH. Recently, we[61] have been studying the effect of J on reaction R14. We have deferred discussion of it until now in the review as this deserves special attention. This is a prototype alkali–hydrogen halide exchange reaction for which a reasonable ab initio surface[23] is available, in a convenient form[62] for use in dynamical studies. Experimentally, σ or $k(J)$ has been studied for the Na, K, and Sr analogues and also for HCl as the diatom in the case of Na and K. Therefore, we could compare qualitatively our results on reaction R14 with those of other alkali–hydrogen halide reactions and our predictions could provide an incentive for the experimentalist to study this particular reaction.

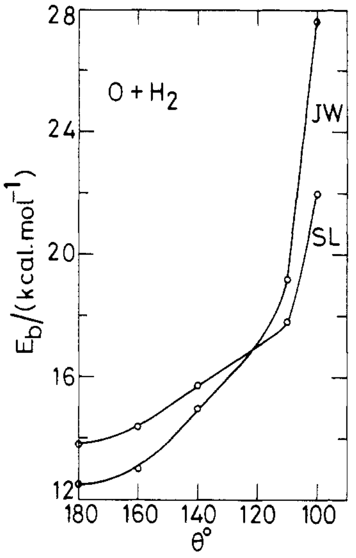

Figure 10. Barrier height as a function of the approach angle for the reaction O + H_2 on two different PES. JW stands for Johnson and Winter[59] and SL for Schinke and Lester.[60]

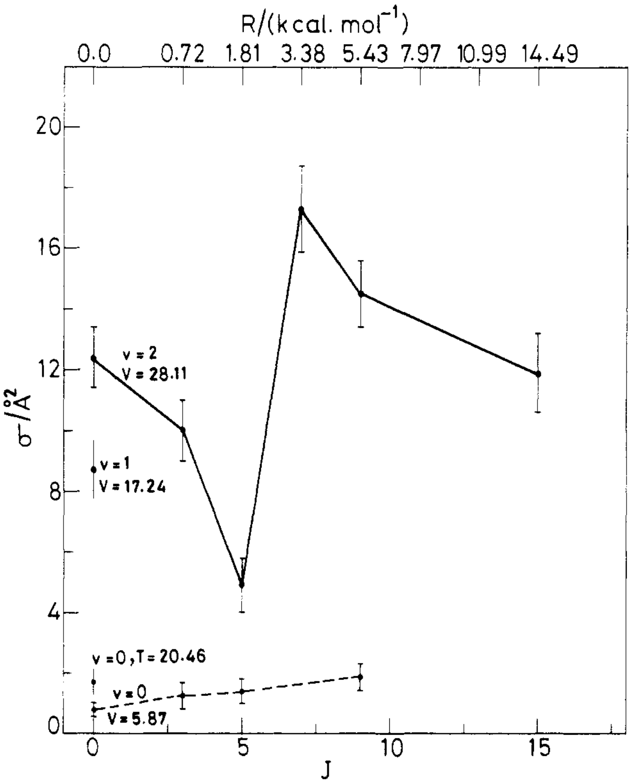

Figure 11. Reaction cross section as a function of J for the reaction Li + FH (v = 0, 2) at T = 8.7 kcal mol^{-1} as obtained from QCT calculations[61] on an ab initio surface. Also included are results at v = 0, T = 20.46 kcal mol^{-1} and v = 1, T = 8.7 kcal mol^{-1} to illustrate the comparative effect of V, R, and T. Energy values are in kcal mol^{-1}.

We chose to study the effect of J on σ at T = 8.7 kcal mol^{-1} as at this energy, for v = 0, molecular beam results are available for σ and product angular distribution (PAD). Therefore, we could check on the reliability of the ab initio PES[62] by comparing the calculated σ and PAD with the experimental results. We have found the agreement between theory and experiment to be good for these results. We have also investigated $\sigma(J)$ for v = 0 and 2 at T = 8.7 kcal mol^{-1} and the results are shown in Figure 11. Variation in σ with J, for v = 0,

TABLE II. Reaction Probability as a Function of the Approach Angle θ for Different J Values for the Reaction Li + FH ($v = 2$, J) → LiF + H[a]

J	θ 0°	θ 90°	θ 180°	random in 0–π
0	0.92	0.94	0.0	0.81
5	0.0	0.28	0.96	0.19
9	0.90	0.72	0.98	0.84

[a] $T = 8.7$ kcal mol^{-1} in the impact parameter range 1–1.5 Å. $\theta = 0°$ corresponds to the Li-F-H collinear configuration.

falls within the statistical error estimates to prevent any definite conclusion on the detailed effect of J. Nevertheless, the overall effect of R ($J = 0$–9) on σ is an enhancement better than that of T but less than that of V as may be seen from the values of $\Delta\sigma/\Delta R = 0.19$, $\Delta\sigma/\Delta T = 0.06$, and $\Delta\sigma/\Delta V = 0.69$. The order of magnitude difference in efficiency between V and T is due to the *sudden* nature of the surface for this system.

For $v = 2$ at $T = 8.7$ kcal mol^{-1}, σ *decreases* monotonically with increase in J from 0 through 5. Subsequent increase in J to 7 results in a sharp increase in σ, so much that *under these conditions, reagent rotation is nearly four times more efficient than vibration* in causing the reaction. Further increase in J to 9 and 15 results in a decline followed by a *possible* leveling off to nearly the same value of σ as for $J = 0$. In a preliminary communication[61] of our results, we had attributed the initial decline in $\sigma(J)$ to the disruption of the preferred orientation. This particular reaction has the lowest E_b when Li approaches FH at an LiFH angle of 75° from the H end. We *had* attributed the increase in σ to vibration–rotation coupling resulting in the HF bond stretch and the molecule behaving as if it has been vibrationally excited. Such an explanation was proposed first by Polanyi and co-workers.[12c] We reiterated the same explanation on the basis of the fact that for $v = 0$, there is only a slight increase in σ with increase in J; but for $v = 2$, the change is substantial. Although we realize that this evidence is not strong enough to justify this explanation, it remains a fact that there is a cooperative enhancement of σ by v and J. Another possibility is that at $v = 0$, the behavior is statistical and at a higher v, it is not. There is some support for this from the product angular distribution.

We have studied the orientation dependence of the reaction probability in the impact parameter range 1–1.5 Å, and the results are given in Table II for $v = 2$, $J = 0, 5, 9$. For $J = 0$, most of the reaction takes place when the F end of the molecule is oriented towards the incoming Li atom. For $J = 5$, initial approach at the F end does not lead to reaction as by the time Li approaches F, H comes in between and the collision becomes nonreactive. Similarly the collision that starts at the H end leads to reaction as H gets out of the way when Li approaches F. Therefore, the real difference between the results for $J = 0$ and 5 stems from the broadside attack (of Li on FH) that has the lowest E_b. Obviously, rotation ($J = 0$–5) disrupts the preferred orientation leading to a decline in $\sigma(J)$. Further details of this effect are currently under investigation.

Our explanation in the earlier part of the review that just as the molecule rotates away from the preferred orientation for small J, it should also return to the preferred orientation for a reasonably larger J is perhaps what is responsible for the increase in σ with increase in J from 5 to 7. We find from Table II that the initial orientations that become nonreactive for $J = 5$ become reactive for $J = 9$. Rotational velocity greater than a particular value has no influence on the orientation alignment and the molecule appears as a *blur*. This would explain the leveling off in σ, with $J = 9$–15.

It must be added that Polanyi and Sathyamurthy[4b] had investigated the effect of R on three model endothermic surfaces. Although they did not investigate the detailed J dependence of σ, they computed σ over a range of V at $T = 6$ kcal mol^{-1} for $T_{\rm rot}° = 300$ K and 1500 K. They found that reagent rotation enhanced the reaction cross section. This was corroborated by the fact that $\langle R \rangle$ for reactive trajectories increased from ~0.7 kcal mol^{-1} to 3.5–3.7 kcal mol^{-1} on surfaces IIS and IIHS and from 1.2 kcal mol^{-1} to 3.8 kcal mol^{-1} on I,IIG when $T_{\rm rot}°$ increased from 300 K to 1500 K. Here I and II refer to the saddle point in the entrance and exit channel respectively; S and G stand for *sudden* and *gradual*, indicating the way the reagent channel transforms into the product channel. Surface IIHS has a larger E_b than IIS; otherwise, they have similar characteristics. A striking observation made by them was that even when increase in T brought about a reduction in σ (on IIS and IIHS), R was helpful to reaction implying that on all three surfaces R was behaving like V, perhaps through vibration–rotation interaction. This is in marked contrast to the results obtained by Hodgson and Polanyi[63] on model I and II type surfaces. In the narrow (V, R, T) range investigated, a slight enhancement and a marked decline in σ were observed on the I and II surfaces, respectively, for an increase in R of 2 kcal mol^{-1}.

So far our discussion has been restricted to the effect of reagent rotation on the reaction cross section for atom–diatom exchange reaction. Schatz[64] has reported recently on the effect of rotational excitation on σ for a diatom–diatom reaction:

$$\mathrm{OH}\ (v = 0, J_1) + \mathrm{H_2}\ (v = 0, J_2) \rightarrow \mathrm{H_2O} + \mathrm{H} \qquad \text{(R39)}$$

As either of the reactants is rotationally excited, σ decreases; the decrease is more when H_2 is excited than when OH is. Perhaps the reason is that in the case of an excited OH, the reacting atom O remains relatively stationary. Schatz compares this result with the little effect of J on k for the reaction R31.

C. Taking Stock

From the above discussion of QCT results on a variety of (model) systems, it is clear that

(i) for most of the *direct* collisions, near threshold, *rotation inhibits reaction* for low J; further increase in J results in an increase followed by a *possible* leveling off of σ and k. At well above $T_{\rm th}$, σ becomes insensitive to small changes in J. As J becomes substantially large, rotation enhances reaction. Similarly, there is some amount of cooperative effect between v and J. At low v, changes in $\sigma(J)$ are invariably within the statistical error estimates; but for larger v, the changes are substantial.

(ii) for most of the *indirect* collisions arising from the presence of a deep potential well or the H + LH mass combination, *rotation enhances reaction.* At a constant E, when the energy is repartitioned between T and R,

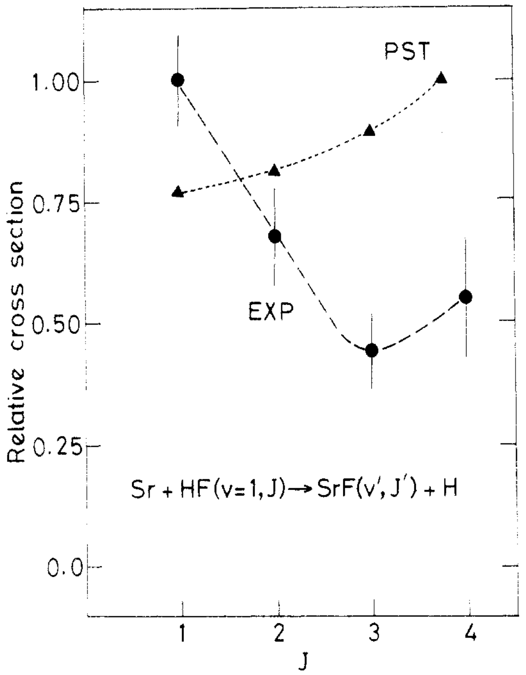

Figure 12. Comparison of experimental results with the PST predictions. The error bars are 2σ statistical uncertainties. Lines connecting data points have been added to aid visualization. Reproduced with permission from ref 20. Copyright 1981, American Institute of Physics.

the latter is more efficient than the former, in agreement with the only available experimental result, for reaction R8.

(iii) for direct as well as indirect collisions the angular momentum factors also have a role to play in deciding the collisional outcome.

The effect of J on σ for a reaction arises from two factors: (1) statistical and (2) dynamical. For a fixed v and T, increase in J means increase in the total energy of the system and therefore increase in the available number of product states. In the absence of any angular momentum constraints, this would result in an increase in σ and such an increase can be predicted from a knowledge of the vibrotational levels for the reactant and product molecules. This is the PST approach.[8] If the increase in σ calculated by PST is the same as that observed experimentally or computed by QCT or QM approach on an assumed PES, the effect is purely statistical. Any difference is due to the *dynamical* factor, i.e., dependent on the PES. Predictions from PST are compared with the experimental findings for reaction R4 in Figure 12. The decline in $\sigma(J)$ for this reaction as well as others (see above) is in contradiction to the PST expectations and therefore is a *dynamical* effect. Any increase in the "observed" σ, larger than what is expected from PST is also a dynamical effect. Similarly, at a given E, if repartitioning of energy between R and V or T results in a change (increase as well as decrease) in σ that is not predicted by PST, it is also a dynamical effect. In the case of the indirect reaction (R7) the observed rotational enhancement is predicted by the RRKM–Herschbach[65] statistical theory. In addition, the observed inefficiency of R in comparison to T was identified to originate from the centrifugal barrier effect and *not* incomplete energy randomization.

A quantification of the difference between the "expected" (or "prior") and "observed" σ or k is achieved through a *surprisal analysis*. The "surprisal" (I) is defined as $I = -\ln(\sigma/\sigma^\circ)$ or $-\ln(k/k^\circ)$, where the superscript (°) refers to the "prior" based on a (reasonable) model. The shape of the surprisal plot would enable us to discover the number and nature of the constraints (energy, angular momentum, etc.) that determine the effect of J on σ or k. Surprisal analysis of the QCT results on the effect of reagent rotation on σ and k for a variety of systems has been carried out by Levine and Manz.[5a] They conclude, "Rotational Energy consumption appears to be strongly correlated with the steric requirements of the reaction." They demonstrate that the effect is different on the two branches of the F + HD ((R23), (R24)) as well as the H + HBr ((R30), (R31)) reaction. They point out further that the effect is different for the even and odd J states in reaction R12. This is difficult to understand as classical mechanics cannot distinguish between ortho and para hydrogen.

We must caution that there is no unique "prior" to compare with the "observation". Often, the prior does not include the angular momentum constraint. But there are prescriptions available that incorporate the angular momentum conservation, for example, the statistical adiabatic channel model of Quack and Troe.[8e] We have used the term PST in a general sense. Similarly, we must add, the fact that statistical predictions *do* depend upon the initial state means that the "memory" is not completely lost. A discussion on the "memory" and statistical theories may be found elsewhere.[8e]

So far the clearest dynamical effect observed is the decline in $\sigma(J)$ near threshold and this has been attributed to the disruption of the preferred orientation, due to rotation. If this were the sole factor, we could predict certain qualitative behaviors based on the mass combination of the reagents:

(i) H + LL. The heavy atom would be slow in moving toward the light diatom which in turn can move away from the preferred alignment. Therefore there should be a sharp decline in σ with increasing J.

(ii) L + HH. The light atom would move in so fast that for low J, the heavy diatom would not have sufficient time to move out of alignment. Therefore σ should be nearly independent of J.

(iii) H + LH → HL + H. The heavy atom is moving in slowly while the light end of the diatom can move out of alignment easily with increasing J. Therefore $\sigma(J)$ should be a decaying function.

(iv) H + HL → HH + L. It is the heavy end of the diatom that is reactive and it would remain stationary while the light end rotates. But the latter can come in between the two reacting atoms and make the collision nonreactive. $\sigma(J)$ should be a decaying function.

(v) L + HL → LH + L. A flat $\sigma(J)$ should obtain, but a decline should not be surprising.

(vi) L + LH → LL + H. A declining $\sigma(J)$ should obtain at low T.

(vii) L + LL. A declining $\sigma(J)$ should obtain at low T. We must add that just as rotation can get the atoms out of alignment, increased rotation can bring them back to alignment. Therefore, a decline in $\sigma(J)$ would invariably be followed by an increase in $\sigma(J)$. In Table III, we compare our predictions with the "observed" results for a variety of systems at low J values. We see that the concept of "orientation alignment" is of rea-

TABLE III. Comparison of Kinematic Expectations and Experimental/QCT Results on the Effect of J on σ or k

mass combination	system	expected	obsd[a]
H + LL → HL + L	F + H_2 → FH + H	decline	decline
	Cl + H_2 → ClH + H		
	O + H_2 → OH + H		enhancement
L + HH → LH + H	H + Cl_2 → HCl + Cl	flat	v = 0, little effect; higher v, enhancement
	H + Br_2 → HBr + Br		v = 0, little effect
	H + O_2 → HO + O		enhancement
H + LH → HL + H	Br + HBr → BrH + Br	decline	enhancement
	F + HCl → FH + Cl		decline[b] in k
H + HL → HH + L	K + ClH → KCl + H	decline	decline[b]
	Sr + FH → SrF + H		decline[b]
	Na + FH → NaF + H		decline[b] in k
	Na + ClH → NaCl + H		decline[b] in k
	Li + FH → LiF + H		decline
L + HL → LH + H	H + BrH → HBr + H	flat	v = 0, no effect; v = 2, enhancement
L + LH → LL + H	H + HBr → H_2 + Br	decline for low T	little effect
L + LL → LL + L	H + HH → H_2 + H	decline for low T	decline for low T on PK surface

[a] Unless otherwise stated effect on σ is quoted. [b] Experimental result.

sonable validity. At energies well above threshold it is not of much use. Even near threshold for a reaction like $O(^3P) + H_2$, a direct reaction, despite the sharp increase in E_b with change in θ, rotational excitation was found to enhance the reaction. The reasons for such an exceptional behavior are not clear yet.

What is the correlation between the features of the PES and the effect of J on σ and k? Alternatively, based on the observed $\sigma(J)$ and $k(J)$, what can we infer about the details of the PES? This is a difficult question and satisfactory answers are yet to come forth. For understanding the effect of reagent vibration, sample trajectories on the scaled and skewed[42] PES contours for the collinear configuration have served as a diagnostic tool and generalizations such as reagent vibration enhances the reaction cross section if the saddle point is in the exit channel and more so if the surface is of *sudden* category have emerged in the last few years.[4,6] Unfortunately, for the effect of reagent rotation, no such clear-cut picture has emerged so far. Based on the model studies of Hodgson and Polanyi,[63] one is tempted to conclude that rotational enhancement and inhibition would be observed on I and II type surfaces, respectively. Unfortunately, this conclusion is too simple to be of general validity and a large number of exceptions are already known (see above). Elsewhere,[12c] Polanyi argues that on a surface with an early barrier (type I), R would behave like T (i.e., enhance the reaction) if the reagent interaction is highly anisotropic as this would facilitate $R \rightarrow T$ conversion. Similarly, if the vibration–rotation coupling is large, R would behave like V and enhance the reaction on a II type PES; for the same reason it would inhibit the reaction on a I type PES.

A detailed understanding of the role of R on different types of PES is hampered by the fact that analyzing the trajectories with rotation is difficult. Three dimensions are required to represent the PE contours as a function of two interatomic distances and one approach angle. As a result, visual representation of trajectories on the PES becomes impractical. Bond-force plots[40] and daisy plots[66] particularly for the planar collisions have been used to represent the course of the collision. For example, Polanyi and Schreiber[40] have illustrated how H_2 (J = 1) is more reactive than H_2 (J = 0) on the SE1 surface by maintaining the collinearity of the system over a long time, with the help of a bond-force plot as reproduced in Figure 13. The anisotropy of the potential as would be evident from PE contours for fixed bond distances of the reactant molecule would be an important factor. A series of such plots for different fixed-bond distances would provide a reasonable picture of the forces that would affect the course of the collision. Unfortunately, such plots do not convey the full picture of the PES as in "real" collisions, bond length is not constrained.[67] Also, they do not contain information on the transition and the product regions. A plot of E_b vs. θ should indicate the magnitude of the torque that would force the incoming atom to align with the diatom. In particular, a comparison of such a plot for two different surfaces should enable us to judge the differences in the effect of J on σ on the two surfaces. Unfortunately, such plots also are of limited value only as "true" collisions do not maintain the same angle throughout the collision. Also, we have pointed out earlier in the discussion that for the reaction $O(^3P) + H_2$ while the E_b vs. θ plot (Figure 10) would make us expect a decline in $\sigma(J)$, a substantial enhancement has been noticed.

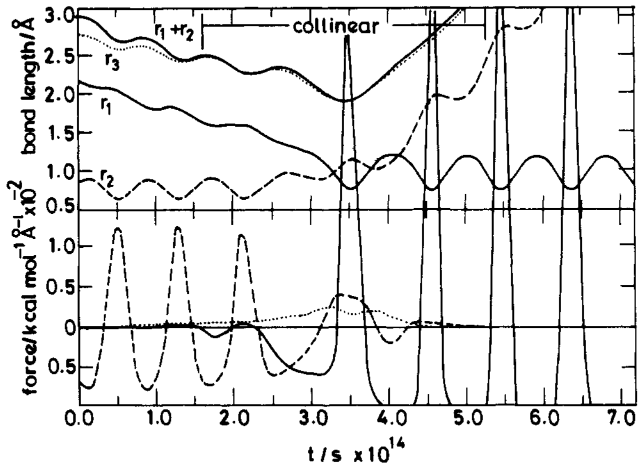

Figure 13. Example of a bond-force plot illustrating the orientation alignment for the reaction F + H_2 (v = 0, J = 1) at $T_{trans}°$ = 300 K on SE1 surface. Reproduced with permission from ref 40. Copyright 1977, Chemical Society, London.

In spite of the above remarks about the understanding of the correlation between the features of the PES and the effect of J on σ and k, it is clear that $\sigma(J)$ is sensitive to the changes in PES and would therefore serve as a valuable probe in judging the quality and *reliability* of a proposed (ab initio or other model) PES of a reactive system—much more than reaction attributes like PVD.[40]

III. Product Energy Distribution

So far we have been discussing the effect of rotational excitation on σ and k and the factors responsible for the same. But this concerns only the first half of a collision. A study of the product vibrotational (and therefore translational) energy distribution provides a clue to the nature of the PES governing the second half of the collision. While a large volume of data, experimental as well as theoretical, are available (see ref 7c for an extensive list of references) on the effect of V and T, very little is known on the effect of R on PED.

A. Experimental

Historically, detailed PED studies became possible because of the infrared chemiluminescence technique of Polanyi and co-workers[68] and the results were reported in the form of triangular plots. But, varying J to study its effect on PED was a problem. Ding et al.[7d] studied the variation in the PED by heating the reagent source and thereby altering $T_{\text{rot}}°$ for reactions R4 and R40

$$\mathrm{F} + \mathrm{D_2} \rightarrow \mathrm{FD} + \mathrm{D} \qquad \text{(R40)}$$

Although in principle, $\langle R \rangle$ could be calculated at different $T_{\text{rot}}°$ and correlated with the changing $\langle V' \rangle$, $\langle R' \rangle$, and $\langle T' \rangle$ no clear-cut picture emerged. However, it was found clearly that

$$\langle \Delta V \rangle \rightarrow \langle \Delta V' \rangle \text{ and } \langle \Delta T \rangle \rightarrow \langle \Delta T' \rangle + \langle \Delta R' \rangle$$

Therefore, one could infer that for the reverse reactions

$$\langle \Delta R' \rangle \rightarrow \langle \Delta T \rangle + \langle \Delta R \rangle$$

was to be expected.

Soon afterwards, Coombe and Pimentel[69] reported on the PVD in reaction R10 by the chemical laser method. By comparing the PVD arising from para enriched and normal hydrogen over the temperature range 235–450 K, they concluded that para hydrogen (even J) produced greater vibrational excitation.

In a more elaborate study involving para and normal hydrogen at 77 K and 290 K, and using the infrared chemiluminescence technique, Douglas and Polanyi[70] could explicitly study the effect of increasing J from 0 to 1 and 2 on PVD. Although there was no significant difference in the product rotational distribution with changing J, product vibrational excitation for $J = 1$ was less than that for $J = 0$ or 2 in agreement with the results of Coombe and Pimentel.[69]

In an interesting combination of chemiluminescence depletion and infrared chemiluminescence studies, Blackwell et al.[7a] showed that despite a range of J states being populated, vibrational adiabaticity, $\Delta V \rightarrow \Delta V'$, is mostly maintained for the reaction

$$\mathrm{Cl} + \mathrm{HO} \rightarrow \mathrm{ClH} + \mathrm{O} \qquad \text{(R41)}$$

They also observed that product rotational excitation is slightly *larger* than reagent rotational excitation at high v.

The only other technique used to measure the PED is the laser-induced fluorescence (LIF) of Zare and co-workers.[71] By laser-exciting HF under single collision conditions and monitoring the excitation spectra of SrF, Karny, Estler, and Zare[21] showed that increasing J from 1 to 3 for $v = 1$ populates the $v' = 2$ level for the product molecule in reaction R11. In this particular experiment, polarized light source was used such that the excited HF molecule was oriented perpendicular to the metal beam. These workers also showed that this broadside attack preferentially populates the $v' = 2$ level of SrF in comparison to the HF molecule being oriented parallel to the approach direction of the metal atom. By extending this study, Man and Estler[20] have established that the PVD for this reaction is nearly *statistical* and that increase in J from 1 to 2 to 3 (for HF, $v = 1$) increases the population in the higher vibrational states ($v' = 0$–5).

Recently, Zare and co-workers[72] have developed a new three-photon ionization technique to study the vibrotational distribution for H_2. This opens up new avenues for studying the PED in reactions involving H_2 as a product.

B. Theoretical

Reaction R12 is the only system for which the J dependence of the PED has been studied theoretically—by using the QCT technique on different (semiempirical) surfaces. All other studies can be called model studies, an exception being the study of reaction R13 for which an accurate ab initio surface is available. Details of the various studies and their conclusions are summarized below.

The first model study to investigate the influence of the rotational excitation on the PED was by Hodgson and Polanyi[63] for an equal mass combination (1 amu). On their +I surface, they found that at $T = 9$ kcal mol^{-1} and $V = 0.0$ kcal mol^{-1}, increase in R from 0 to 2 kcal mol^{-1} changed the $\langle V' \rangle$, $\langle R' \rangle$, and $\langle T' \rangle$ from 5.4, 0.2, and 3.4 to 5.3, 0.7, and 5.0 kcal mol^{-1}, respectively. That is $\langle V' \rangle$ remains unchanged and $\langle \Delta R \rangle \rightarrow \langle \Delta R' \rangle + \langle \Delta T' \rangle$. On the +II surface, change in V, R, and T from 14.5, 0.0, and 1.5 to 16.5, 2.0, and 1.5 kcal mol^{-1}, respectively, results in PED changing from 5.1, 1.06, and 9.84 to 7.02, 4.18, and 8.8 kcal mol^{-1}, respectively. In this case, the analysis is a little difficult as V also has changed by 2 kcal mol^{-1}. Since, in general $\Delta V \rightarrow \Delta V'$, one could assume that the additional V' in this case has come from the additional V. Therefore, the conversion rule seems to be $\Delta R \rightarrow \Delta R'$ at the expense of T'. Symbolically $\Delta R \rightarrow \Delta R' - \Delta T'$.

$H + H_2$. Recently, Barg et al.[38b] have investigated the influence of J on PED for reaction R13 on PK and SLTH surfaces by the QCT technique. Since all the product molecules are in $v' = 0$, J' states, the analysis is simple and instead of reporting $P(J')$ they report $\langle J' \rangle$ as a function of J as reproduced in Figure 14. Qualitatively, PK and SLTH surfaces lead to the same steep dependence of $\langle J' \rangle$ on J at $T = 9.844$ kcal mol^{-1}. But at a higher T (14.72 kcal mol^{-1}), there is a noticeable difference in $\langle J' \rangle$ between the two surfaces. The only available QM results show only a *weak* dependence of $\langle J' \rangle$ on J on the PK surface at the lower energy raising serious doubts on the validity of the QCT technique in describing PED. Yet, the rest of the discussion in this review pertains only to the QCT results as there is no other tool available for such an investigation in three dimensions.

In a more elaborate ($0 \leqslant v \leqslant 12$, $2 \leqslant J \leqslant 30$, $T_{\text{trans}}° = 300$ K) study of the dependence of the $\langle v' \rangle$ and $\langle J' \rangle$ on v and J, Blais and Truhlar[39] find that while the $\langle v' \rangle \sim v$, supporting the often-quoted vibrational adiabat-

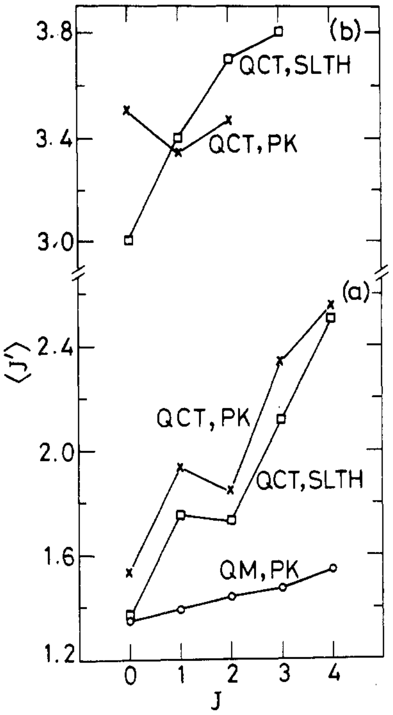

Figure 14. Variation of $\langle J' \rangle$ with J for the reaction H + H_2 ($v = 0$), at (a) $T = 9.844$ kcal mol^{-1}; (b) $T = 14.72$ kcal mol^{-1}. Abbreviations are defined in Figure 5. Reproduced with permission from ref 38b. Copyright 1981, American Institute of Physics.

TABLE IV. Comparison of the Experimental Mean Fraction of the Total Available Energy Entering Product Vibration, $\langle f_{v'} \rangle$ with the Corresponding Quantity Obtained from QCT Studies

J	expt[70]	Muckerman[73]	Jaffe-Anderson[74]	Schreiber[75]
0	0.70	0.80	0.64	0.69
1	0.67	0.79	0.62	0.67
2	0.69	0.74	0.59	0.62

icity rule, $\langle J' \rangle \not\approx J$. However, it remains a fact that both $\langle v' \rangle$ and $\langle J' \rangle$ are dependent on J.

F + H_2. The J dependence of the product vibrational excitation for reaction R10 has been studied on different LEPS surfaces by different workers;[40,41,73-75] but all of them show a much larger change than what has been observed experimentally by two different approaches as illustrated in Table IV. The much favored Muckerman-5 surface also does not yield satisfactory results. While $\langle f_{v'} \rangle$ has been found to be the least for $J = 1$ experimentally, all the QCT studies predict a monotonic decrease with increase in J not only for reaction R12 but also for reaction R40, R23, and R24. This reiterates our earlier view that prediction of PVD alone cannot be relied upon, in judging the accuracy (or adequacy) of a model PES. Its J dependence provides a much more stringent criterion for the validity of the surface.

Polanyi and Schreiber[40] find that on their SE1 surface, enhanced reagent rotation $\Delta R = 3.39$ kcal mol^{-1} corresponding to $J = 0 \rightarrow J = 4$ increases $\langle R' \rangle$ by 4.18 kcal mol^{-1}. This cannot be explained on the basis of conservation of angular momentum alone, although detailed studies of Hijazi and Polanyi[76] suggest a significant correlation between J' and J for such a H + LL mass combination. The strong repulsion between the products (HL.L) when released in a bent configuration exerts a torque on HL making it rotationally excited. It is reasonable to expect that increased reagent rotation increases the chances of a bent intermediate and therefore product rotation.

Cl + H_2. In an analogous study for reaction R25 on an LEPS surface, for $v = 0$, in the range $T = 4$–12 kcal mol^{-1}, Persky[44] finds that PRD is nearly statistical. While ΔT ends up mostly as $\Delta T'$ and to a lesser extent in $\Delta V'$ and $\Delta R'$, ΔR ends up mostly as $\Delta R'$ and $\Delta V'$ and only to a small extent as $\Delta T'$. Similarly, for the deuterium analogue (R26) also, at lower T, reagent → product conversion is $\Delta R \rightarrow \Delta R' + \Delta V' + \Delta T'$ while at higher T, it is *largely* $\Delta R \rightarrow \Delta R'$. For (R27), ΔR leads mostly to $\Delta R'$ and very little $\Delta T'$ while for (R28), the opposite behavior is found. For both processes, part of ΔR appears as $\Delta V'$.

Li + FH. From our own laboratory,[61] we have examined the PVD as a function of J at $v = 2$, $T = 8.7$ kcal mol^{-1}. Decrease of σ with increasing J is associated with a shift in the histogram peak towards higher v' while the increase in σ with increase in J is associated with a shift in the histogram peak towards a lower v'. The PVD appears nearly bimodal for $J = 9$ and becomes so spread out for $J = 15$ that it is difficult to say whether it remains bimodal or not. Values of $\langle V' \rangle$, $\langle R' \rangle$, and $\langle T' \rangle$ are found to vary erratically as a function of R such that no clear-cut picture could emerge. The only striking feature of these results is that when J changes from 5 to 7 ($R = 1.81$ kcal mol$^{-1} \rightarrow 3.38$ kcal mol^{-1}), $\langle R' \rangle$ changes from 10.21 to 13.81 kcal mol^{-1}. In this particular case, $\Delta R \rightarrow \Delta R'$; in addition, part of V and T have been converted to R'.

We have also investigated the orientation dependence of PVD for this reaction. We find PVD to be broader for $\theta = 90°$ than for $\theta = 0°$. Specifically, while all $v' =$ 0–7 are populated at $\theta = 90°$, $v' = 0, 1, 6$, and 7 are *not* at $\theta = 0°$, within the statistical error limits of our calculation. Although these results are not directly comparable to the only experimental result available on this subject for $v = 1$, $J = 1$ for reaction R11, we can say that, there is a qualitative agreement between the two in that *a broadside attack favors higher vibrational excitation.* Origin of this effect and its general applicability to other (v,J) states are presently being investigated in our laboratory.

What can we infer about the PES from the J dependence of the PED? If we could say that calculating/measuring the J dependence of σ or k probes the nature of the PES during the first half of the collision, we can add that calculating/measuring the PED provides clues on the features of the PES during the second half of the collision; its J dependence in particular links the features of the PES in the product configuration space to that in the reactant configuration space. Reagent rotational excitation makes the trajectories sample a larger portion of the reactant space of the PES and particularly the anisotropy of the reagent rotor while PRD contains information on the anisotropy of the product rotor. We could cite an example here for the reagent rotational excitation taking the trajectory to an unexplored region of the PES. In reaction R41 at low v the channel

$$\text{Cl} + \text{OH} \rightarrow \text{ClO} + \text{H} \qquad \text{(R42)}$$

is forbidden. However, at high v, this channel becomes allowed. In the absence of rotation, the formation of [ClOH] would not be common while rotational excitation can make this configuration possible and hence enhance the reaction cross section for the formation of ClO. This could be considered as a macroscopic branching. We could cite an example of a microscopic branching. In the case of the reaction

$$\mathrm{H + ClI \rightarrow HCl + I} \qquad \text{(R43)}$$

a bimodal vibrational energy distribution is observed for the product HCl molecules. One of them is attributed to the direct encounter between H and Cl while the other corresponds to the H attacking the I end; but because of the heavy mass of Cl and I atoms, there is enough time for the H to come in between and result in the formation of HCl. This would mean that the bimodal distribution for the product HCl would be sensitive to change in J of the ClI reactant. To the best of our knowledge such a J-dependence has not been studied as of this date.

IV. Product Angular Distribution

To the best of our knowledge, the only product angular distribution available for different J values is for reaction R9 and has been reported by Dispert et al.[12d] With increase in J from 1 to 3, the angular distribution broadens.

The model study of Hodgson and Polanyi[63] showed that for an increase of 2 kcal mol^{-1} in R, $\langle\theta_{\mathrm{mol}}\rangle$ remained approximately the same on the +I surface, but it increased appreciably on the +II surface. The angular distribution also became broader on the latter surface.

While Barg et al.[38b] do not report any noticeable change in the differential cross section for reaction R13, Blais and Truhlar[39] report a substantial decrease in $\langle\theta_{\mathrm{mol}}\rangle$ with vibrational and rotational excitation; more so with the latter. For reaction R12, Polanyi and Schreiber[40] found no change in $\langle\theta_{\mathrm{mol}}\rangle$ with reagent rotational excitation, beyond the statistical error estimates. The same conclusion was reached by Persky[44] for the reaction of Cl with H_2, D_2, and HD. However, Jaffe and Anderson,[74] Blais and Truhlar,[77] and Polanyi and Schreiber[78] have noted that the $\langle\theta_{\mathrm{mol}}\rangle$ shifts backwards with increasing rotational excitation of the reactant molecule in the reaction of F with H_2, D_2, and HD, respectively.

In the Li + FH reaction, changes in $\langle\theta_{\mathrm{mol}}\rangle$ are within the statistical error estimates for J = 0–9; but a further increase in J from 9 to 15 results in a change in $\langle\theta_{\mathrm{mol}}\rangle$ from 88 ± 4.6° to 73 ± 7.2°. That is, a *large* rotational excitation results in a larger forward scattering of LiF. Clearly, more elaborate studies are required to investigate the role of J in deciding PAD.

V. Interconversion of $\vec{J}$, $\vec{L}$ and $\vec{J}'$, $\vec{L}'$

Except for a brief mention on the angular momentum factors, our discussion so far has been restricted to mostly energy considerations. In recent years, considerable insight has been gained into the role of $\vec{J}$ and $\vec{L}$ in deciding the same in the products.

For example, from kinematic considerations, it was expected[79] that in H + HL → HH + L collisions, $\vec{L}$ will be converted into $\vec{J}'$ and this has been subsequently verified by trajectory studies[76] on model surfaces. In such a case, we expect an increase in J to have little effect on the magnitude of J'. Similarly, in the reverse reaction, L + HH → LH + H one expects $\vec{J} \rightarrow \vec{L}'$. In such a case enhancement of J would have little effect on J'. However, at small b (and therefore $|\vec{L}|$) in order to conserve angular momentum, enhancement of J would result in increased T'. This means that the reagent → product conversion would be $\Delta R \rightarrow \Delta T'$. For the H + LL → HL + L mass combination, if the repulsive energy release takes place at a bent configuration, one expects a large J'. In such a case, enhancement in reagent rotation would enhance the chances of a bent configuration and hence enhanced J'. Energy conversion would be expected to be mostly $\Delta R \rightarrow \Delta T'$. A corollary to the above arguments would be that $\vec{L}\cdot\vec{J}'$ ~ 180° and that the collision is planar.

So, one sees that a clear understanding of the interconversion between $\vec{L}$, $\vec{J}$ and $\vec{L}'$, $\vec{J}'$ would enhance our understanding of the role of reagent rotation in bimolecular exchange reactions.

A related question is the preferred alignment of products relative to the reactant approach. Observation of preferred alignment of products in specific states in an experiment involving oriented reactants in selected states would be the limit of state-selected chemistry. It looks like we are heading for the same. A summary of the experimental results obtained as of this date on product alignment can be found elsewhere.[80]

VI. Conclusions

By reviewing most of the available experimental and theoretical results, we have tried to highlight the major findings on the effect of reagent rotation on reaction cross section/rate coefficient, and product energy and angular distributions. For most of the *direct* reactions, there is an *initial decline* in $\sigma(J)$ *followed by an increase* and possibly a leveling off. At very high values of J, there is bound to be an increase in σ due to a large number of product states becoming available. The initial decline in $\sigma(J)$ is marked near threshold and is attributed to the disruption of the preferred orientation for a reaction. There are clear indications that the *angular momentum* factors play an important role in governing the collisional outcome. In most of the situations, where results are available on the repartitioning of the total energy, *reagent rotation* is found to be *less efficient than vibration* and sometimes comparable in efficiency to translation in causing the reaction. The differences in exo(endo)thermicity between reactions do not seem to be crucial in deciding the role of R. Very little is known on the correlation between the features of PES and the various reaction attributes. Variation in E_b with θ has been identified to be the source of the "orientation alignment" and the consequent decline in $\sigma(J)$. But there are exceptions like (R38) for which $E_b(\theta)$ varies steeply and yet there is a clear rotational enhancement of the reaction. QCT studies for many reactions illustrate that $\sigma(J)$ is sensitive to the changes in PES and would serve as a valuable probe in deciding the validity of a PES or similarity (or lack thereof) between two surfaces, much more than reaction attributes like product vibrational energy distribution.

For reactions involving *long-lived complexes* (due to the presence of a potential well or H + LH mass combination), the available (although limited) experimental and theoretical results suggest a general *rotational enhancement*. There are exceptions like reaction R8! Detailed studies show the centrifugal barrier effect to be more important than incomplete energy randomization. The fact that the reaction attributes for a complex reaction also depend on the initial state of the reagents demonstrates the "memory" of the system despite its "statistical" behavior.

In the various parts of the review, we have tried to point out the (many) exceptions to the (few) generalizations that have been made. We hope that this "stock-taking" serves to induce many more studies on the effect of reagent rotation on bimolecular exchange reactions in the near future.

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VII. Appendix

At an impact parameter b, orbital angular velocity

$$\omega_{\mathrm{orb}} = |\vec{L}|/I = \mu_{\mathrm{A,BC}} v_{\mathrm{rel}} b / \mu_{\mathrm{A,BC}} b^2 = (2T/\mu_{\mathrm{A,BC}} b^2)^{1/2}$$

Approximating the rotational angular momentum $|\vec{J}| = J\hbar$

$$\omega_{\mathrm{rot}} = J\hbar / \mu_{\mathrm{BC}} r_{\mathrm{BC}}^2$$

For maintaining the "alignment", $\omega_{\mathrm{orb}} = \omega_{\mathrm{rot}}$. Therefore, the alignment would be regained at a value of

$$J = (2T/\mu_{\mathrm{A,BC}})^{1/2} (\mu_{\mathrm{BC}}/\hbar)(r_{\mathrm{BC}}^2/b)$$

Integrating over b

$$\langle J \rangle = \int_0^{b_{\mathrm{max}}} 2\pi b J \mathrm{d}b \Big/ \int_0^{b_{\mathrm{max}}} 2\pi b \mathrm{d}b = 4\pi(2T/\mu_{\mathrm{A,BC}})^{1/2}(\mu_{\mathrm{BC}}/\hbar)(r_{\mathrm{BC}}^2/b_{\mathrm{max}})$$

VIII. Glossary of Symbols and Abbreviations

T, V, R	*reagent* translational, vibrational, and rotational *energies*, respectively
v, J	*reagent* vibrational and rotational *quantum numbers*
T', V', R'	*product* translational, vibrational, and rotational *energies*
v', J'	*product* vibrational and rotational *quantum numbers*
E	total energy $= T + V + R = T' + V' + R'$
T_{th}	threshold (translational) energy
E_{b}	barrier height
$T_{\mathrm{trans}}{}^{\circ}$, $T_{\mathrm{vib}}{}^{\circ}$, $T_{\mathrm{rot}}{}^{\circ}$	translational, vibrational, and rotational *temperatures*
θ	approach angle
θ_{mol}	product molecular scattering angle
b	impact parameter
σ	reaction cross section
$\bar{\sigma}$	thermally averaged σ
k	rate coefficient
$\sigma(T)$	σ as a function of T
$\sigma(J)$	σ as a function of J
$k(J)$	k as a function of J
$\langle\ \rangle$	average
$\langle\ \rangle_{\mathrm{r}}$	average for reactive collisions
$\vec{J}, \vec{L}, \vec{J}', \vec{L}'$	rotational and orbital angular momentum *vectors* for the reactants and products, respectively
Γ	branching ratio
LEPS	London–Eyring–Polanyi–Sato
PAD	product angular distribution
PED	product energy distribution
PES	potential-energy surface
PK	Porter–Karplus
PST	phase space theory
PVD	product vibrational energy distribution
PRD	product rotational energy distribution
QCT	quasiclassical trajectory
QM	quantum mechanical
SLTH	Siegbahn–Liu–Truhlar–Horowitz

IX. References and Notes

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