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Effect of vibrational excitation of HBr on the H+HBr abstraction and exchange reactions*

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The effect of vibrational excitation of HBr on the $H+HBr \rightarrow H_2+Br$ and $H+H'Br \rightarrow H'+HBr$ reactions has been investigated on the extended LEPS surface (ELEPS) constructed on the basis of quantum chemically calculated points of PES. Together with this surface the LEPS surface of Sudhakaran and Raff [1] was used for comparison at two relative translational energies. A quasiclassical trajectory method was used to study the abstraction and exchange reaction dynamics. The reactive cross section was calculated as a function of the relative collision energy and the vibrational state of HBr. The following conclusions can be drawn from the results of the study: (i) vibrational excitation $v=0 \rightarrow v=2$ more than doubles the reaction cross section, (ii) the increase in the collision energy is most effectively channelled into the product translational energy.

Key words: Molecular collisions — Quasiclassical trajectory method — ELEPS surface — Energy transfer

Introduction

It is known from the chemistry of combustion that bromine compounds are effective flame retardants. HBr released from them interacts with active particles of the flame (H, O, OH, CH, CH_2, CH_3) via chemical reactions. One of these

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

reactions is the interaction between atomic hydrogen and HBr. The abstraction (1a) and exchange (1b) channels of this interaction are the subject of our study

$$\mathrm{H+H'Br}\begin{array}{ll} \nearrow \mathrm{HH'+Br} & \qquad (1a) \\ \searrow \mathrm{H'+HBr} & \qquad (1b) \end{array}$$

Since the reaction runs at high temperatures, one can expect that excited vibrational levels of the HBr molecule will play a significant role. Sudhakaran and Raff [1] give a summary of papers pertaining to the study of this reaction. On the basis of the known results these authors concluded that the PES of H_2Br should have a barrier of reaction (1a) not higher than 1 kcal/mol, and attractive holes deeper than 0.209 kcal/mol should not be present. For the exchange reaction barrier (1b) they indicated the value of ≈ 5 kcal/mol. The results from quantum-chemical calculations on the abstraction reaction [2] give characteristics of the PES which disagree with the experimental results and the QCT method results. For example, the values of the barrier height for reaction (1a) are at least 3 kcal/mol higher than the experimental value. As the surface constructed in this paper also shows this property, we shall use for comparison the potential energy surface constructed by Sudhakaran and Raff [1]. The QCT method was used for the study of the dynamics of the collision process of $H+HBr(v)$ system for $v = 1$, 2, 3 on these potential energy surfaces.

Potential energy surface and trajectory calculations

Reaction dynamics was calculated on the extended LEPS (ELEPS) surface, whose form was originally proposed by Wanger et al. [3a]. The analytical form of this surface involves Morse parameters and two parameters a, b for each bond instead of the original single Sato parameter Δ which was the same for all bonds, or the generalized Sato parameters [3b]; this enhances the surface flexibility. Values of the parameters a, b were determined by fitting the analytic surface to quantum chemically calculated individual points of the PES. For the quantum chemical calculation we have chosen points in the region of the reaction path, its saddle point, and the surroundings of the saddle point of reaction (1a). Additional points at other locations were also chosen. A total of 45 points was used for optimization. The energies were calculated by the linearized coupled cluster method [4] with a UHF reference function in the Huzinaga MIDI-3 basis set [5–6]. These calculations were very time consuming, and therefore the inner shell electrons were frozen in the correlation energy calculation. This technique was successfully tested for Br [7]. Introduction of this approximation leads to a rapid drop in the computer time with minimal deterioration of the quality of the PES.

The points calculated in this way formed the basis for the determination of the parameters a, b. Table 1 contains these parameters together with other parameters. In the collinear case the minimum reaction path for the surface constructed from

Table 1. Parameters for the ELEPS surface. D is in kcal/mol, β_e in Å^{-1}, R_e in Å

Bond	D_e	β_e	R_e	a	b
H—H	109.46	1.9247	0.7415	0.43477	0.64827
H—Br	90.35	1.811	1.414	0.81105	0.42276

these parameters has the barrier height 3.73 kcal/mol for reaction (1a) and 17.75 kcal/mol for reaction (1b). The barrier height of reaction (1a) increases sharply with deviation from collinearity. The geometrical parameters of the saddle point together with the data used for comparison purposes are summarized in Table 2. The value of barrier heights of the ELEPS surface is higher than that of the LEPS surface (where the symbol LEPS in our notation denotes surface III from [1]), which for reaction (1a) has a barrier fitted to the experimental value. This is due to the fact that quantum chemical calculations on the basis of which the ELEPS surface was constructed give a large barrier height. Dunning [2] calculated the barrier heights in larger basis sets and by more extended QC methods and he also obtained larger values. It seems that in order to obtain the correct value for the barrier height one must use even larger basis sets and include higher order correlations. Another way would be to apply one of the semi-empirical approaches, which was successfully used for the $F+H_2$ reaction [16]. The barrier obtained by the DIM method for the reaction (1a) [15] (1.8 kcal/mol) is between the values discussed above. Figures 1 and 2 show graphical representation of the ELEPS hypersurfaces for a collinear geometry of the atoms of the reacting systems for reactions (1a) and (1b) respectively.

In comparison with the PES of the DIM method [15] which has a barrier of markedly early character (see also Table 2), the barrier of ELEPS surface is only slightly shifted towards the entrance valley. The barrier heights of the DIM and LEPS surfaces are in better agreement with experiment for both of the reactions studied. The barrier heights of the ELEPS surface, based on our *ab initio* calculations, correspond most closely to those of Dunning's *ab initio* calculations; both of these surfaces are characterized by large values of the barrier heights compared with experiment.

Table 2. Parameters for the saddle point. Barrier height in kcal/mol, interatomic distances in Å

Surface	Abstraction reaction			Exchange reaction	
	Barrier height	R_{H-H}	R_{H-Br}	Barrier height	R_{H-Br}
ELEPS	3.73	1.00	1.54	17.75	1.65
[2]	3.8	1.26	1.49	16.2	1.64
DIM [15]	1.8	1.41[a]	1.43[a]	11.1	1.59[a]
LEPS	0.19	1.16	1.48	5.17	1.59

[a] The data were extracted from Fig. 5 of [15]

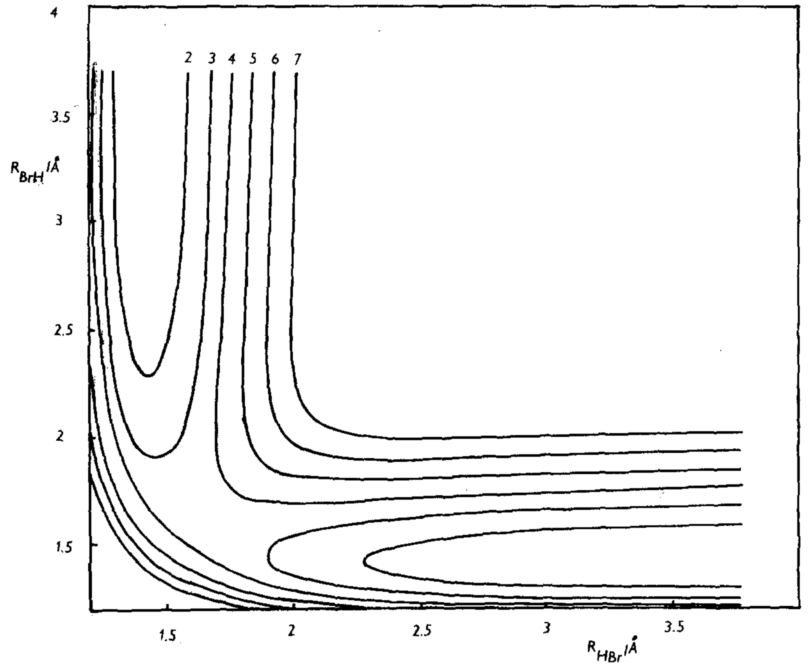

Fig. 1. ELEPS collinear potential energy surface for the abstraction reaction. Energy values of individual lines in kcal/mol are *2:* −13.1; *3:* −7.5; *4:* −2.0; *5:* 3.6; *6:* 9.2; *7:* 14.7; *8:* 20.3; *9:* 25.8; *10:* 31.4

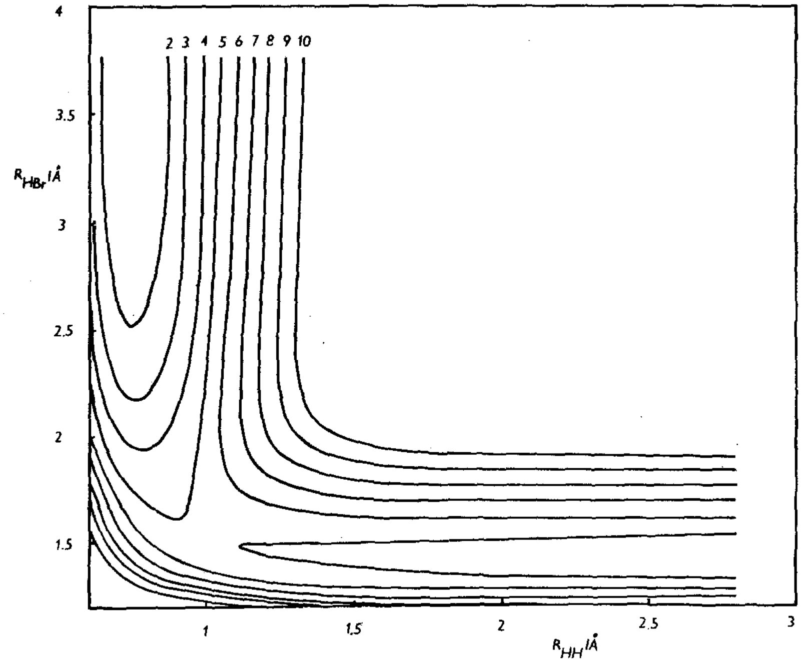

Fig. 2. ELEPS collinear potential energy surface for the exchange reaction. Energy values of individual lines in kcal/mol are *2:* 7.0; *3:* 13.6; *4:* 20.3; *5:* 26.9; *6:* 33.5; *7:* 40.1

Table 3. Cross sections results (ELEPS surface) for the abstraction reaction

E_{rel} (kcal/mole)	$\sigma(A^2)$		
	$v=0$	$v=1$	$v=2$
7.5	0.19 ± 0.04	0.42 ± 0.09	1.05 ± 0.19
15	0.53 ± 0.09	0.84 ± 0.13	1.25 ± 0.22
20	0.42 ± 0.08	0.65 ± 0.11	1.07 ± 0.20
30	0.29 ± 0.07	0.59 ± 0.10	0.85 ± 0.14

The surface constructed in this way was used for the trajectory calculations using the standard QCT method [8-9]. The initial vibrational states of HBr were states with vibrational quantum numbers $v=0$, 1, 2 and the mean rotational state was selected from a Boltzmann distribution at 800 K. Batches of 600 trajectories were run for atom-diatom relative translational energies $E_{rel}=7.5$, 10.0, 15.0, 20.0, 30.0 kcal/mol with a random selection of initial conditions. For the LEPS surface we calculated 1500 trajectories at energies 2.0 and 7.0 kcal/mol. The precision of the results of the crude Monte-Carlo technique [9] used in this paper can be judged on the basis of the standard deviation error of the reaction cross sections which are documented in Tables 3 and 4. The maximum impact parameters calculated ranged between 1.8 and 2.4 Å for the various cases. For example, at the energy $E_{rel}=7.5$ kcal/mol and with $v=0$, b_{max} equals 1.8 Å. Hamilton's equations of motion were integrated with an integration step size of 0.5×10^{-16} s, whereby the total energy and total angular momentum were conserved. QCT calculations were done using the program CTAMYM [10].

Results and discussion

Abstraction reaction

The values of the reaction cross sections for selected relative translational energies and initial vibrational states of HBr are given in Table 3. The dependence of the cross section on E_{rel} exhibits the usual behaviour. The values obtained in [1] for

Table 4. Cross sections results (LEPS surface) for the abstraction reaction; values in parentheses are taken from [1], experimental values are taken from [11]

E_{rel} (kcal/mole)	σ (Å^2)			σ_{rel}	
	$v=0$	$v=1$	$v=2$	Experimental (300 K)	Theoretical ($v=0$)
2	0.94 ± 0.02 (0.526) ± 0.05	2.04 ± 0.02	2.62 ± 0.02	1.32	0.89 (0.90)
7	1.06 ± 0.02 (0.587) ± 0.04	1.60 ± 0.02	2.24 ± 0.02	1.00	1.00

$v=0$ using the LEPS surface are given in Table 4 in parentheses. These values differ considerably from the values calculated by us even though the cross sections of the exchange reaction are numerically equal (1.30 Å^2 in both cases at $E_{\mathrm{rel}}=$ 7 kcal/mol). We found that σ_{exc} depends slightly on the value of $b_{\max}$.

In both calculations ([1] and this paper), it is found that σ_{abs} (7 kcal/mol) $>$ σ_{abs} (2 kcal/mol). This contrasts with the experimental values, where the opposite is true. In the last two columns of the table the values (our values for $v=0$) are normalized to the values at 7 kcal/mol. In the molecular beam experiment [11], however, the initial vibrational states of HBr are selected from a Boltzmann distribution at 300K.

Results from both surfaces (Tables 3, 4) show that vibrational excitation leads to an enhancement of the values of the cross sections. In both cases we can see an enhancement of a factor of 2.4 of the corresponding cross sections σ_{abs} $(v=2)$ with respect to σ_{abs} $(v=0)$. The energy value of 7.5 kcal/mol is an exception; at this energy $\sigma_{\mathrm{abs}}(v=2)/\sigma_{\mathrm{abs}}(v=0)=5.5$.

The scattering angle distributions of the product molecules indicate a rebound mechanism for the abstraction reaction for all vibrational states of HBr. A similar distribution of the products was recorded by Chapman [12] while studying the reaction $\mathrm{Be}+\mathrm{HF}\rightarrow\mathrm{BeF}+\mathrm{H}$ and by Clary and Connor [13] for the reaction $\mathrm{O}+\mathrm{H}_2\rightarrow\mathrm{OH}+\mathrm{H}$, and in many other studies as well. This distribution is shown in Fig. 3a, where the case with $E_{\mathrm{rel}}=7.5$ kcal/mol is depicted. The effect of vibrational excitation on the shape of the angular distribution is small. For the ELEPS surface vibrational excitation of HBr with $v=2$ yields a more uniform distribution around the maximum value of the scattering angle for all calculated E_{rel}. With the increasing values of E_{rel} the maximum of the products scattering angle distribution is shifted towards smaller scattering angles. For example, at $E_{\mathrm{rel}}=20.0$ kcal/mol and $v=0$, the position of the maximum ranges between 100 and 110 degrees. The QCT calculation shows that the shape of the scattering angle distribution curve is the same for all collision energies E_{rel}. Using the LEPS surface alters this shape (the position of the maximum of the curve is also changed). This is demonstrated in Fig. 3b which shows the results of QCT calculations for $E_{\mathrm{rel}}=7$ kcal/mol.

Analysis of the products provides a picture of their internal energy distribution as a function of E_{rel}. The fraction deposited in the product as vibrational energy, $f_{v'}$, decreases with increasing collision energy (Fig. 4). This is true for all vibrational states of the HBr molecule. The fraction of the rotational energy increases slightly with increasing E_{rel}. The fall of the vibrational energy is greater than the growth of the internal rotational energy; this is compensated by the growth of the translational energy of the system.

Figure 5 shows the distribution of the vibrational states of the products for different vibrational states of the HBr molecule as a function of E_{rel}. When the vibrational excitation of the HBr molecule is increased, the number of hydrogen molecules produced in the ground vibrational state $(v'=0)$ decreases. This situation dominates at $v=0$ and $v=1$. For $v=2$ and smaller values of the collision

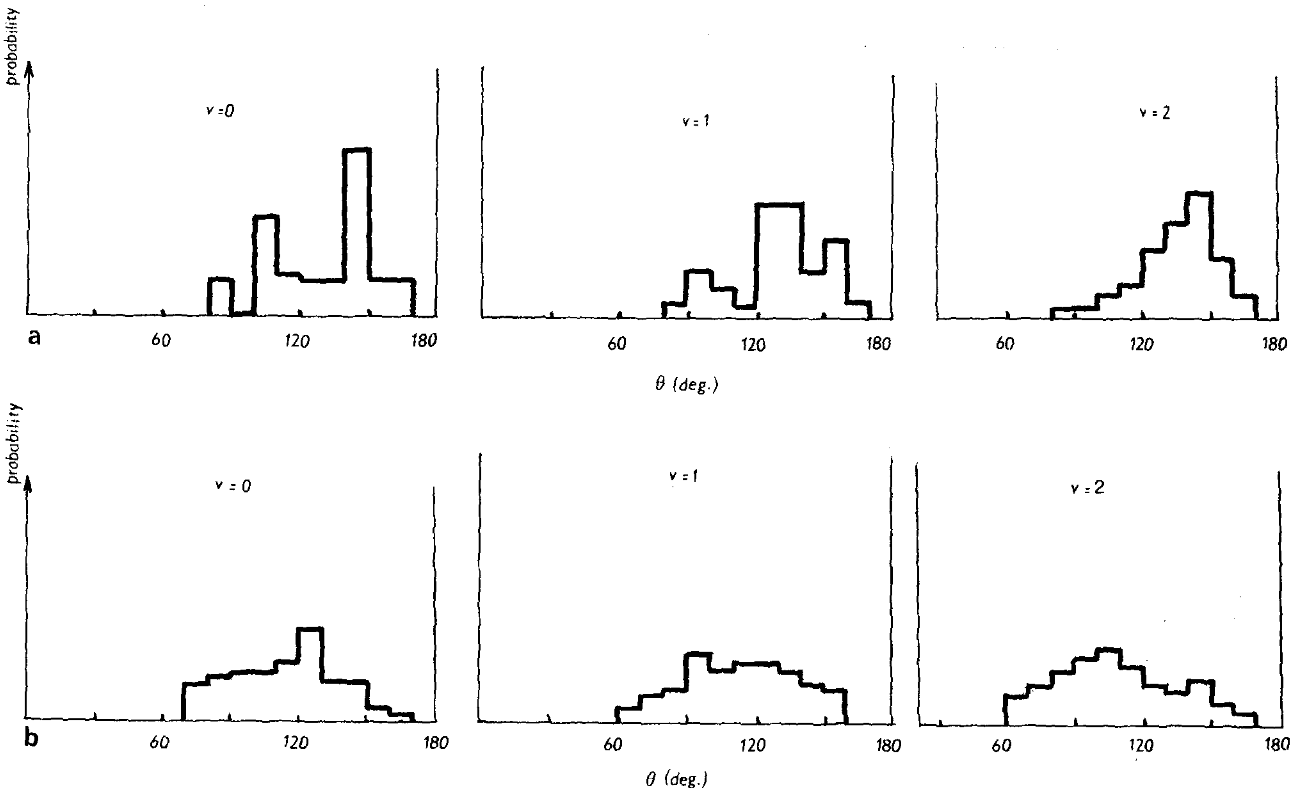

Fig. 3a. Scattering angle distribution ($\sigma(\vartheta)\sin\vartheta$) at energy $E_{rel} = 7.5$ kcal/mol (ELEPS surface). **b** Scattering angle distribution ($\sigma(\vartheta)\sin\vartheta$) at energy $E_{rel} = 7$ kcal/mol (LEPS surface)

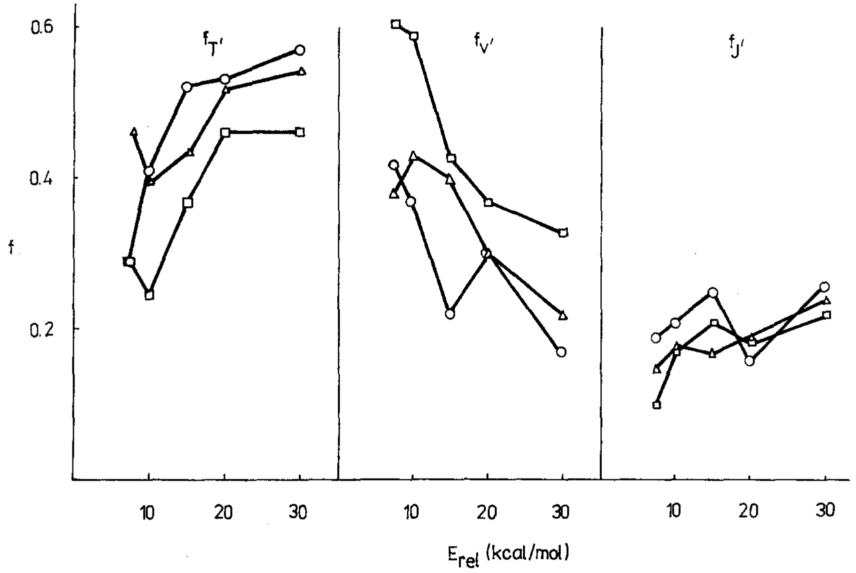

Fig. 4. Dependence of the fractions of the total available energy on $E_{\rm rel}$. ○, $v=1$; △, $v=2$; □, $v=3$.

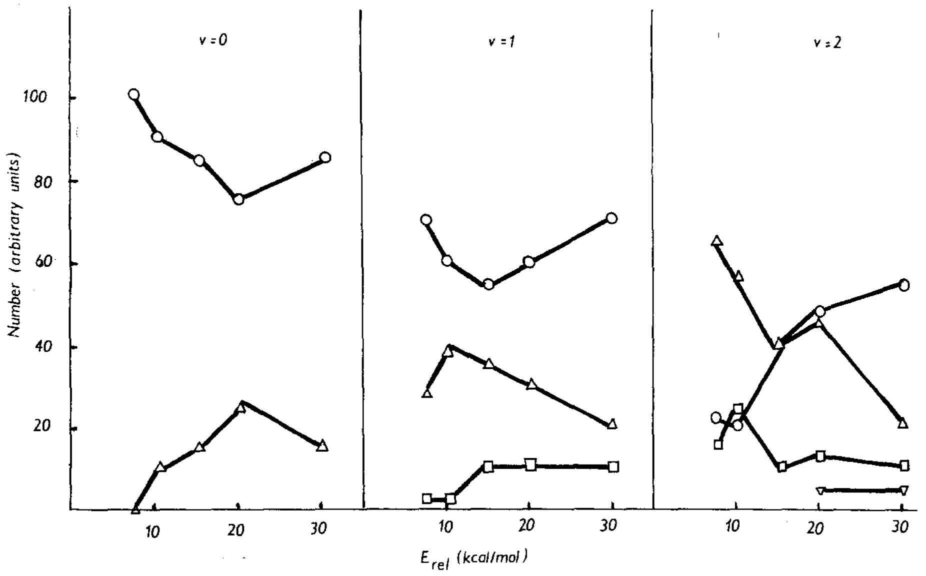

Fig. 5. Dependence of the vibrational distribution of product molecules on $E_{\rm rel}$. ○, $v'=0$; △, $v'=1$; □, $v'=2$; ▽, $v'=3$.

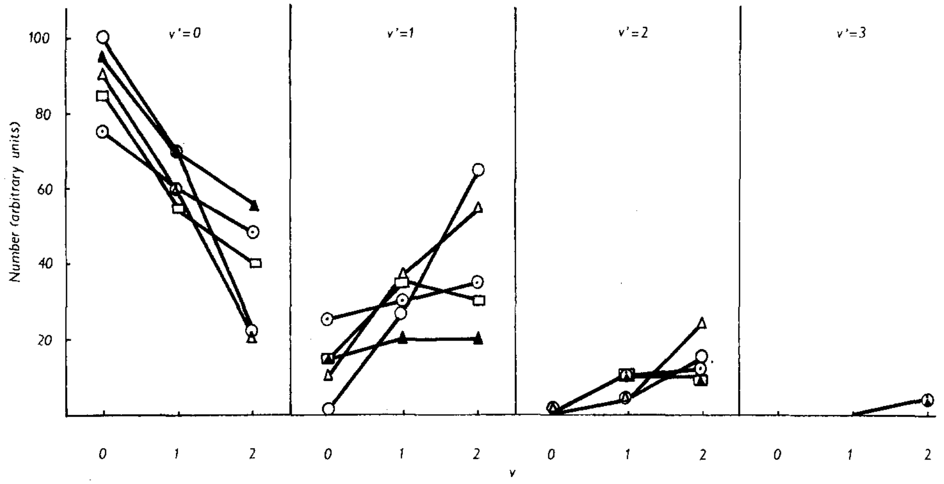

Fig. 6. Influence of vibrational excitation of HBr on the vibrational population of product molecules. Symbols ○, △, □, ⊙, ▲ stand for $E_{rel} = 7.5$ (○); 10 (△); 15 (□); 20 (⊙); 30 (▲) kcal/mol

energy, the state $v' = 1$ is most common; with higher values of the collision energy we have the $v' = 0$ most common. While the state $v' = 1$ is produced from $v = 0$, $v' = 2$ does not occur until the reactant is excited to $v = 1$. The percentage of $v' = 2$ produced is almost the same for all E_{rel} values. These conclusions are clearly demonstrated in Fig. 6. However, as can be seen from Fig. 4, the fraction of the energy released as vibrational energy in the products decreases with increasing E_{rel}.

Hodgson and Polanyi [14] studied the problem of the energy transfer in reactive collisions of three-atom systems. They have shown that the energy transfer is affected by the location of the barrier on the PES (early or late type). An early

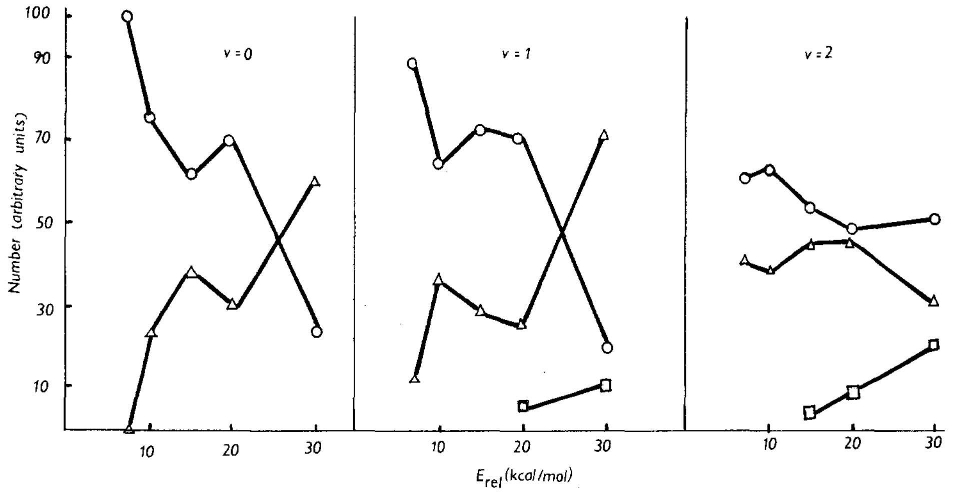

Fig. 7. Rotational distribution of product molecules. ○, $J' = 1$–5; △, $J' = 6$–10; □, $J' = 11$–15.

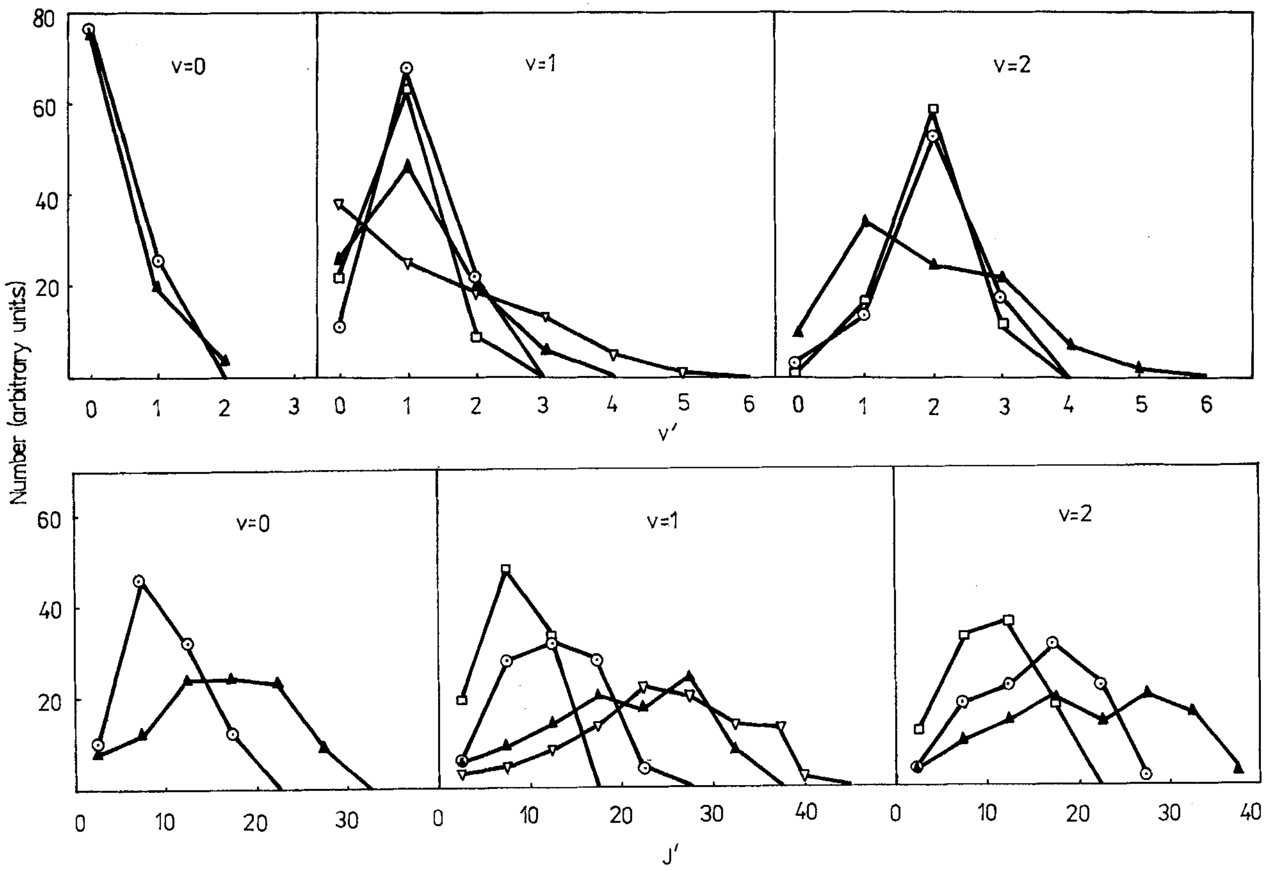

Fig. 8. Vibrational (*upper*) and rotational (*lower*) distributions of HBr molecules from the exchange reaction for various vibrational excitations of reactants (ELEPS surface). $E_{rel} = 15$ (□); 20 (⊙); 30 (▲); 40 (▽) kcal/mol

barrier favours energy transfer to product vibration while a late barrier favours energy transfer to product translation. The location of the barrier in our case is slightly early (Fig. 1). From the trajectory results (Fig. 4) it follows that at higher values of E_{rel} the transformations of the type $\Delta T \rightarrow \Delta T'$ and $\Delta V \rightarrow \Delta V'$ are most common.

The distribution of the rotational states of the products for different vibrational states of reactants as a function of the collision energy is illustrated in Fig. 7. The reactive trajectories were classified into three bins according to their rotational excitation: $J' \in [0, 5]$, $[6, 10]$, $[11, 15]$. The number of H_2 molecules in the first bin decreases with the increasing collision energy for all three types of vibrational excitation and in all three cases it is of dominant character. While excitation to the second bin occurs for all initial vibrational excitations, excitation to the third bin does not occur until $v = 1$ and it increases with increasing collision energy. Figure 4 shows that the portion of energy released as rotational energy in the products grows slightly with increasing collision energy.

Exchange reaction

The value of the barrier height is in this case much higher than in the abstraction reaction (Table 2) and that is why the energy threshold is also shifted to higher E_{rel} values. Reaction cross sections are large and increase with the increasing vibrational quantum number of the HBr molecule (Table 5). The angle distribution of the products shows for the reaction (1b) (on the ELEPS surface) a similar character as for (1a). Its maximum varies between 120° and 140°.

Greater differences between the reactions (1a) and (1b) are apparent in the vibrational and rotational excitation of the products. It is characteristic of the abstraction reaction that except for the case $v = 2$, the H_2 molecule is mostly in the ground vibrational state. The maximum of the vibrational distribution for $v = 2$ is at $v' = 1$ (Fig. 4). For the exchange reaction, the maximum of vibrational distribution is at $v' = 0$ only for $v = 0$ of reactants; otherwise (excepting the highest values of E_{rel}) it is shifted to higher values of the vibrational quantum number - to $v' = 1$ for $v = 1$ and to $v' = 2$ for $v = 2$ (Fig. 8)

The rotational distribution of the products was evaluated, in the same way as for the abstraction reaction, in bins containing 5 rotational states (Fig. 8). In

Table 5. Cross sections results (ELEPS surface) for the exchange reaction

E_{rel} (kcal/mole)	σ(Å^2)		
	$v = 0$	$v = 1$	$v = 2$
15	—	0.37 ± 0.08	1.37 ± 0.14
20	0.97 ± 0.12	1.63 ± 0.15	2.91 ± 0.19
30	2.17 ± 0.17	2.93 ± 0.19	3.63 ± 0.20
40	—	2.81 ± 0.18	—

contrast to reaction (1a), where the maximum of the rotational distribution of the products is (except for the energy $E_{rel} = 30$ kcal/mol) in the first bin, the maximum for the exchange reaction is, as expected, shifted to bins with higher values of J. In addition as E_{rel} and/or the vibrational energy of reactants increase it is shifted up to bins with $J' \in (25, 30)$ (Fig. 8).

Conclusion

We have studied the dynamics of the reactive collisions:

$$H + HBr(v) \rightarrow H_2(v', J') + Br$$

and

$$H' + HBr(v) \rightarrow H + H'Br(v', J').$$

We have found that the reaction cross section increases with increasing vibrational quantum number of the HBr molecule. The vibrational excitation energy of HBr is effectively channelled into vibrational energy of the hydrogen molecule. In the abstraction reaction the fraction of the total energy released as vibrational energy of the products decreases with increasing collision energy. At the same time the rotational energy of the products increases as a function of E_{rel} but in a less pronounced way. When E_{rel} increases the greatest increase can be seen in the translational energy of the products. In the exchange reaction, the maximum of the vibrational distribution is shifted to higher values of the vibrational quantum number. The maximum of the rotational distribution of the products with increasing E_{rel} and/or vibrational energy of the reactants is shifted to higher J' values.

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