REACTIVE AND DETACHMENT PROCESSES IN HALIDE ION-H₂ COLLISIONS

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A systematic investigation of the competition between reactive and detachment channels in halide ions-H₂ collisions has been undertaken using a multicoincidence technique. Contour maps for detaching and non-detaching processes are obtained. It is found that the F^- -H₂ system behaves differently from that involving the heavier halide ions. The competition between reaction and reactive detachment processes for all systems is well accounted for by considering a non-adiabatic interaction between the two lowest ionic potential surfaces as previously discussed. From a kinematic point of view, this study suggests that at low energy (<12 eV), the various F^- -H₂ processes proceed via a scattering on the H₂ molecule as a whole, in contrast with Cl^- -H₂, Br^- -H₂ and I^- -H₂ cases for which a hard scattering on only one H atom is the dominant step. This special feature leads to a simple expression for the "isotopic effect" in total cross sections of Cl^- -H₂, Cl^- -HD and Cl^- -D₂ collision which fits well the large effect observed by Huq et al.

1. Introduction

In a series of papers [1-4] we have reported on an experimental analysis of the competition between reactive and detachment processes in halide-ion-H₂ collisions; the different channels are:

 $\begin{array}{l} X^- + H_2 \\ \rightarrow XH + H^- , \quad reaction (R) , \\ \rightarrow XH + H + e^- , \quad reactive \ detachment (RD) , \\ \rightarrow X + H_2 + e^- , \quad simple \ detachment (SD) , \\ \rightarrow X + H + H^- , \quad dissociative \ charge \\ \quad transfer (DCT) , \\ \rightarrow X + H + H + e^- , \quad dissociative \\ \quad detachment (DD) . \end{array}$

Most of the features characterizing these systems were discovered in the investigation of Cl^--H_2 collisions [1]. The latter study of Br^--H_2 and I^--H_2 collisions [2-4] reinforced the conclusions of this first analysis. The dynamics of the two reactive processes were tentatively explained by a sequential impulse model

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(SIM) [5] suggested by the observation of a strong angular peaking of both R and RD processes. On the other hand, the sharing between these two reactive channels was explained in terms of non-adiabatic electronic transitions between the two lowest potential energy surfaces (PES). Sizun et al. [6] undertook a diatomics-in-molecule (DIM) calculation of these two ionic surfaces for the Cl^--H_2 system and calculated the differential cross sections using a trajectory surface hopping method for the five channels listed above.

Total cross sections for electron production $\sigma(e^{-})$ and H⁻ production $\sigma(H^{-})$ in halide ion-H₂ systems measured by Huq et al. [7] present a completely different behaviour for Cl⁻ and F⁻ collisions. For example, in F⁻-H₂ collisions, $\sigma(e^{-})$ exhibits a large structure in the threshold region (E < 10 eV) not found in heavier halide. $\sigma(H^{-})$ is an order of magnitude larger, with F⁻ projectiles. Furthermore at low collision energy these authors found strong unexplained isotopic effects in the Cl⁻-H₂ system which are absent in the F⁻-H₂ system. This prompts us to complete our investigation by studying the F⁻-H₂ collision. Meanwhile, the data processing of our experimental results has been improved. Therefore the old Cl⁻-H₂, Br⁻-H₂ and I⁻-H₂ raw data have been

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reprocessed in order to reach a more sound comparison between the various halide ion $-H_2$ systems.

2. Experimental technique and data processing

The experiment consists of crossing a fast (≈ 100 eV) X^- halide ion beam with a slow cold H_2 beam. Products from the reaction are detected in coincidence. The H₂ beam is produced by a supersonic expansion in order to reduce the energy and angular spead inherent to heavy (halide ion)-light (H₂) collisions. The previously described [1-3] experimental setup has been modified in order to increase the ion beam intensity at the low collision energies required to study the F^--H_2 reactive processes. The $F^$ beam extracted from a discharge in a mixture of CF₄ with argon buffer gas (0.1%) is initially accelerated to 400 eV, mass selected using a Wien filter and finally decelerated just (a few centimeters) before the collision. The decelerating system is composed of two zoom lenses calculated using the formula derived by Harting and Read [8]. The F^--H_2 collisions have been investigated in the 50-300 eV lab corresponding to 4.8-28.8 eV center of mass energy E. In this new arrangement (fig. 1), fast neutral X and XH products and slow H⁻ and e⁻ are independently detected by two position-sensitive detectors based on microchannel plate assemblies. The detector of the fast neutral species is located at D=244 and 403 mm from the collision volume allowing us to intercept the entire scattering cones, $2\theta = 12^{\circ}$ for F⁻-H₂ collisions and $2\theta = 6.5^{\circ}$ for Cl⁻-H₂ collisions. The arrival position on the detector is determined with an accuracy of 0.5 mm. The charged species, H⁻ and e⁻, are extracted by a small electric field towards a similar detector assembly lying beneath the collision volume. However, only the position along the incident beam is determined (x direction in fig. 1). This latter information is only required for coincidence with H⁻, allowing to check the consistency of the correction procedure introduced to take into account the H⁻ and e⁻ extracting field and (ii) to determine the velocity of the H⁻ ions as explained below.

Let us first consider the electron-neutral coincidences. The raw data consist of the number of events $N(y, z, \Delta t)$ corresponding to neutrals detected on one elementary pixel $(\Delta_y \Delta_z = 0.25 \text{ mm}^2)$ and characterized by a difference of arrival times $\Delta t = t_n - t_e$ between the neutrals and the electrons determined with a time resolution $\delta t = 25$ ns. Therefore N is proportional to the doubly differential cross section $d\sigma/d\Omega$ where $d\Omega$ is the solid angle corresponding to the pixel $\Delta_y \Delta_z$. The laboratory angles and velocities are converted into center of mass variables to obtain the differential cross sections in the center of mass system $\sigma(\chi, v)$.

A more complicated procedure is required to ob-



Fig. 1. Scheme of the apparatus.

tain the differential cross section for coincidences with H^- ions, since only the difference of the arrival time $t_n - t_i$ is determined. However, the arrival position x of H^- on the detector correlated to the position of the neutral particle (y, z) gives an indirect determination of t_i , knowing the electric field which extracts the slow negative particles out of the collision volume [1].

For both families of coincidences the resulting cross sections $\sigma(\chi, v)$ are presented as "contour maps". The sum of $\sigma(\chi, v)$ is proportional to the total cross sections

$$\sigma_{\mathrm{T}} = \int_{0}^{\infty} \int_{0}^{\pi} \sigma(\chi, v) \, \mathrm{d}v \, \mathrm{d}\chi \, .$$

Summing $\sigma(\chi, v)$ for the different processes allows us to determine the relative probability of these processes. It should be noticed that most authors detect the reaction products scattered in a given solid angle $d\Omega$ and express their results as specific intensities $\bar{I}(\chi, v)$ [9] or cross sections $\sigma(\omega, v)$ [10] such that

$$\sigma_{\rm T} = 3\pi \int_0^{\pi} \sin \chi \, d\chi \int_0^{\infty} v^2 \bar{I}(\chi, v) \, dv \,,$$
$$\sigma_{\rm T} = 2\pi \int_0^{\pi} \sin \chi \, d\chi \int_0^{\infty} \sigma(\omega, v) \, dv \,.$$

Such $\bar{I}(\chi, v)$ and $\sigma(\omega, v)$ data give an artificially enhanced representation of the processes occurring at small angles. Furthermore, $\bar{I}(\chi, v)$ also enhances processes for small velocity v. For example, the importance of the spectator stripping process appearing at zero degrees is strongly overestimated in most of the experiments. In this respect the present $\sigma(\chi, v)$ data do not suffer this drawback.

3. Results

3.1. F^--H_2 collisions

Contour maps corresponding to coincidences with electrons are represented in fig. 2 for four relative

collision energies from 6.8 to 28.8 eV. These results correspond to the following processes.

$$F^- + H_2 \rightarrow FH + H + e^-$$
, RD, $Q_{RD} = 2 \text{ eV}$;
 $F^- + H_2 \rightarrow F + H_2 + e^-$, SD, $Q_{SD} = 3.4 \text{ eV}$;
 $F^- + H_2 \rightarrow F + H + H + e^-$, DD, $Q_{DD} = 7.5 \text{ eV}$.

In fig. 2 the velocities corresponding to the threshold of these processes are indicated as circles around the center of mass.

As a general remark, it can be seen that the contours lie roughly on circles centered at the center of mass of the system and little rovibrational excitation characterizes the RD process. This observation is consistent with the absence of dissociative detachment at higher collision energies. From E=5 eV up to 7 eV, only one RD process (hereafter referred to as RD_1) is observed as a peak around 20° which disappears above 10 eV. A second and distinct peak $(RD_2 \text{ process})$ shows up at E = 8 eV and above. Contrary to RD_1 this process is peaked at an angle which decreases with increasing energy and approximatively follows the rule $\tau = E_{c.m} \chi = \text{const.} \approx 400 \text{ eV} \text{ deg}$ up to 20 eV (fig. 3). The RD_2 peak extends towards backscattering angles showing a little rovibrational excitation. Simple detachment (SD) evolves with collision energy in a similar way as the RD₁ process up to 10 eV and is peaked at a constant angle $\chi \approx 10 \pm 5^{\circ}$.

The relative probabilities of the different processes are determined by integration of differential cross sections, the results are then normalized to the absolute total cross section for electron production measured by Huq et al. [7] (fig. 4). For E < 10 eV, both RD₁ and SD contribute to the hump in the total cross section. At higher energy the processes producing electrons are mainly due to RD₂ but both RD₂ and SD increase monotonically up to 25 eV. Above this energy the reactive detachment decreases.

Results concerning the reaction process (R)

$$F^- + H_2 \rightarrow FH + H^-$$
, $Q = 1.29 \text{ eV}$

are shown on the lower half of the contour map of fig. 2. At all energies the internal energy is constant and peaked around 2 eV. Furthermore the angle at which the cross section maximizes is located between 20° and 40° (fig. 3).



Fig. 2. Contour map for the F^--H_2 system. Electron neutral coincidences (RD and SD processes) are shown on the upper half. Coincidences with H^- ions (R process) are shown on the lower half. The threshold endothermicities and dissociative limits are indicated for each process, dotted line: SD process, dashed line: RD process, dashed-dotted line: R process. The intensity of contours varies from 1 to 7 and decreases a factor 1/8 between two successive contours. No calibration between H^- and electron intensities.



Fig. 3. F^--H_2 system. Evolution of the χ angle corresponding to the maximum intensity as a function of the collision energy for the various processes.



Fig. 4. F^--H_2 system. Total cross sections for the various channels normalized to the total cross sections for electron and H^- production of Huq et al. [7].

3.2. Cl^--H_2 collisions

3.2.1. Detachment processes

The contour maps for Cl^--H_2 and Br^--H_2 collisions are represented in figs. 5 and 6 respectively. As a striking difference with the F^--H_2 data, all maximum intensities are localized on a circle (C) centered on the center of mass of XH instead of XH₂. The radius of this circle corresponds to the elastic scattering of X^- by one H atom. The ridge corresponding to the maximum of the cross section, shown by small crosses, lies on that circle illustrating the dominant scattering of X by only one H atom. Although this location of R, RD and also SD processes on the elastic scattering circle of X⁻ on a unique H atom was already present on contour diagrams shown in our previous papers [1-4], we missed at that time this simple picture and suggested a unique χ scattering angle for X^--H_2 in R and RD processes, independently of the vibrational excitation of XH. In fact this feature leads for large scattering angles to large rovibrational excitation in contrast with the F^--H_2 case. The apparent increase of the χ angle from Cl to Br and I was therefore just apparent. At collision energies above 8 eV when the dissociative detachment channel is open, the ridge corresponding to the maximum of the cross section extends beyond the dissociation limit. Such a behaviour has previously been observed in $O^+ + D_2 \rightarrow O^+ + D + D$ at high collision energy and is related to the dissociation of OD⁺ formed by spectator process [16]. Above 8 eV the contour maps peak at a value of $35 \pm 10^\circ$ = center of mass (Cl-H₂) angle, but for a constant Q circle corresponding to the threshold of the RD process. This evolution of the behaviour of the RD process has been described in our previous paper [3] as two distinct processes called RD_1 (at low energy) and RD_2 .

Around 10 eV collision energy, in addition to the previously mentioned dissociative detachment process, a small peak appears in the forward direction, at approximately zero degree. It was previously [3] analyzed as a dissociative detachment process localized on an inelastic scattering of Cl⁻ on one H atom. This process actually contributes for at most one percent to the total detachment cross section. Again, in contrast with F^--H_2 collisions, the simple detachment



Fig. 5. Contour maps for the Cl^--H_2 collision. Same labels as in fig. 3. Also shown is the C circle (solid line) corresponding to Cl^-/H elastic scattering. Crosses indicate the ridge of the contour maps.

ment shows up only above 10 eV and its importance increases with energy. This process is characterized by a very low internal energy.

One should notice that the SD process is also



Fig. 6. Same as fig. 5 for the Br^--H_2 system.



Fig. 7. Cl⁻ $-H_2$ system. Total cross sections for the various channels normalized to the total cross sections for electron and H⁻ production of Huq et al. [7].

peaked on the same C circle indicating that the same initial kinematic is involved in the three processes.

3.2.2. Reactive process

As already discussed in our previous paper [1] the reactive process (R) is characterized by a small rovibrational excitation (<1.5 eV) and by a constant scattering angle $\chi \approx 55 \pm 5^{\circ}$. It is noteworthy that this angle corresponds to the intersection of the C and R circles (fig. 5), the R circle corresponding to the threshold of the reactive process. The total detachment cross sections determined as discussed above (F⁻-H₂ case) are shown in fig. 8. In fig. 7 is reported the angular behaviour of the maximum of cross sections as a function of the collision energy.



Fig. 8. Cl⁻-H₂ system. Total cross sections for the various channels normalized to the total cross sections for electron and H⁻ production of Huq et al. [7].

4. Discussion

The results have to be discussed on two different levels: a kinematic point of view leading to a model and a dynamic point of view involving a non-adiabatic interaction between two ionic surfaces in interaction with a neutral surface.

4.1. The nuclear rearrangement

4.1.1. Low-energy mechanisms ($E \le 10 \text{ eV}$)

As discussed above, examination of figs. 2, 5 and 6 suggests that for the F⁻-H₂ system, R and RD processes primarily involve scattering on the whole H₂ molecule whereas for Cl⁻-H₂, these processes are induced via a Cl scattering on only one H atom. This conclusion is consistent with the much higher endothermicities for reactive processes in Cl⁻-H₂ than in the F^--H_2 system, suggesting that harder collisions are required. At this point, it is interesting to compare the total cross section for "reactive processes" (R plus RD) for both systems (figs. 4 and 7) which is about one order of magnitude larger for F^--H_2 (15) a_0^2) than for Cl⁻-H₂ (1.4 a_0^2) below 10 eV relative energy. This implies that smaller impact parameters are involved in Cl^--H_2 collisions, favouring scattering by one H atom. For small impact parameters the dominant interaction between Cl- and H2 can be approximatively represented by a two-body impulsive force between Cl and H atom. During this interaction the second H atom acts as a spectator. After this first step, the rest of the reactive process leading to HCl has to be such that the velocity vector of HCl will be the same as that of Cl.

This impulsive spectator behaviour has been inferred in other channels of inelastic scattering; in AB^++C as well as in A^++BC collisional systems, vibrational excitation of a molecular ion projectile [11] or molecular target [12] or in molecular dissociation [13,14] have been predicted and observed.

In our previous papers, reactive processes were tentatively discussed in the framework of the SIM initiated by Bates et al. [15] and further developed by Mahan et al. [5].

In this model the overall thermoneutral reaction $A+BC\rightarrow AB+C$ is seen as a sequence of two binary collisions, in which the atoms interact via hard sphere potentials: A first hits B which in turn hits C, both collisions being impulsive and elastic. The only condition for reaction of A with B or C is that the energy of their relative motion is less than the dissociation of the product molecule AB or AC, the molecular product having a rovibrational energy comprised between zero and its dissociation energy. By energy conservation these limits can be expressed as values of translational excergicity Q=0 and Q=D(AB), therefore the velocity vector of AB in the center of mass frame must be inside this stability zone.

By velocity vector analysis Mahan et al. [5] have shown that the maximum velocity limit of the AB molecule resulting of a SIM is a cardioid in the c.m. frame, the cusp of which is located on the AB center of mass. The forward wings of this cardioid tangent the circle corresponding to Q=0 at a χ angle which corresponds, at high collision energy, to the χ peaking of the contour map. This angle is independent of the collision energy; it depends only of the mass ratio and tends towards the limit value of 45° for increasing projectile to target mass ratio.

This model reproduces perfectly the angular distribution of thermal reaction (or nearly) as for example in $Ar^+ + H_2 \rightarrow ArH^+ + H$ or $O^+ + D_2 \rightarrow OD^+ + D$ reactions. However, looking carefully at the $O^+ + D_2$ system [16] one can notice that the maximum of the distribution is also located on the circle corresponding to the elastic circle of O^+ on one D, on a portion limited by the two Q=0 and $Q=D(OD^+)$ circles. The only condition for an AB molecule to be formed is that the velocity of AB should be in the stability zone. Mahan et al. emphasized that this is an approximation which restricts the SIM to reactions where the potential energy surface has very simple properties: thermoneutral reactions or nearly so and no substantial wells or barriers.

The crude application of the model to endothermal reactions involves a cut of the stability zone: the circle corresponding to ΔH_0 cuts the forward wings of the cardioid. This model does not reproduce the fitting of the final AB velocity with the A velocity after the first binary elastic collision.

Armentrout and Beauchamp [17] and then Safron et al. [18] extended the SIM to include the endothermicity of the reaction. They consider two cases in which the endothermicity is taken up in the first or in the second collision. The limiting curve for production of AB(v=0) is in this case a limacon of Pascal which of course degenerates into a cardioid for $\Delta H = 0$. As an alternative process these authors also considered the complementary "knock out" reaction where after initial A and B scattering, the particle finally recombines with C. (Incidently one should be aware that stricto sensu an inelastic binary collision is impossible in the absence of electronic transitions.) Again these models do not reproduce our Cl--H₂ results nor the isotopic behaviour of the cross section. Actually the results suggest that R and RD processes involve a more restrictive sequential impulse model:

(i) The Cl⁻ ion is first *elastically* scattered by one atom of the target (H_B) with the other atom being a spectator. This is the dominant feature which determines the final velocity of the new HCl molecule.

(ii) A second "inelastic" collision between the two target atoms (H_B and H_C), involving a compression of H_2 , pushes one target atom (H_B) in the direction of the scattered Cl atom. The inelasticity of this collision will determine the endothermicity of the reaction. This second collision cannot be treated as a binary collision since such binary sequence would lead to small final relative velocity of Cl and H_B which is impossible to concile with the formation of a vibrationally excited HCl molecule. After the Cl^--H_B scattering (χ_1 angle), the presently observed inelastic processes select among all possible second collisions (depending on the H₂-Cl⁻ relative orientation impact parameters etc.) those which leave the extremity of the Cl-H_B velocity vector on the C circle corresponding to elastic scattering of Cl⁻ on one H atom.

Finally, the extremity of the Cl-H_B velocity vector should also be inside the $Q = \Delta H_0$ circle corresponding to the threshold of the considered process. Therefore the reaction can only occur if $\chi > \chi_{min}$, where χ_{min} is determined by the intersection of the C and $Q = \Delta H_0$ circles (fig. 9). χ_{min} is given by

$$\chi_{\min} = \cos^{-1} \left(\frac{\Delta^2 + v_2^2 - v_1^2}{2\Delta v_2} \right),$$

where (fig. 9)

$$A = \frac{M_{\rm C}}{M_{\rm A} + M_{\rm B}} \left(\frac{2M_{\rm A}E}{(M_{\rm B} + M_{\rm C})M}\right)^{1/2},$$

$$v_1 = \frac{M_{\rm B}}{M_{\rm A} + M_{\rm B}} \left(\frac{2ME}{(M_{\rm B} + M_{\rm C})M_{\rm A}}\right)^{1/2},$$

$$v_2 = \left(\frac{2M_{\rm C}(E - Q)}{(M_{\rm A} + M_{\rm B})M}\right)^{1/2},$$

where M_A , M_B , M_C and M are the masses of A, B, C, and A + B + C respectively. The strong dependence of χ_{\min} on the masses of the B and C atoms (here H or D) can explain the large isotopic effect observed at threshold. In a very crude calculation we assume that the total cross section is proportional to the geometric cross section $\sigma = \pi b^2$ where b is the impact parameter corresponding to the collision. In a classical approximation [19] one has $b \approx 1/E\chi$. Therefore for a given energy E the isotopic ratio is given by $R_{12} = (\chi_2/\chi_2)$ χ_1)². The ratios of the H⁻ and e⁻ production in Cl⁻- H_2 , Cl^--D_2 and Cl^--HD collisions deduced from the experiments of Huq et al. [7] are compared in fig. 10 with the prediction of this calculation. This model is seen to reproduce the experimental isotopic behaviour close to the threshold. These experimental data



Fig. 9. Newton diagram for Cl⁻-H₂ collisions showing the determination of χ_{min} .

are also compared with the Safron et al. version of the SIM [18]. If the endothermicity is included in the second collisions, Safron et al. proposed the following expression for the total cross section

$$\sigma = \pi a^2 (1 - \nu)^2$$

where

$$\nu = \left(Q \frac{(M_{\rm A} + M_{\rm B})^2 (M_{\rm B} + M_{\rm C})^2}{4EM_{\rm A}M_{\rm B}M_{\rm C} (M_{\rm A} + M_{\rm B} + M_{\rm C})} \right)^{1/2}$$

and *a* is a constant depending on the minimum approach distance of A and B. Assuming that *a* is independent of the different isotopes B and C, the isotopic ratios are just given by $R_{12} = [(1 - \nu_1)/((1 - \nu_2))]^2$. The same expression is obtained for "knock out reactions". The corresponding values for H₂, D₂ and HD targets have been reported in fig. 10. The experimental values are rather well reproduced for E > 8 eV but close to the threshold energy this model gives an R_{12} curve which shows an opposite behaviour to the experimental curve.

For F^--H_2 collisions, the absence of isotopic effects at threshold (E < 10 eV) is consistent with the fact that reactive processes are better described by a scattering of F^- on H_2 molecule as a whole.

4.1.2. High-energy mechanisms (E > 10 eV)

For Cl⁻-H₂ collisions, above 12 eV, the RD process does not remain on the C circle. In fact in this energy range, reaction and reactive detachment behave similarly as a function of energy for both Cl⁻- H_2 and F^--H_2 collisions. For example, the cross section of RD₂ process presents a maximum around E=25 eV for both systems: $\sigma_{RD_2}(F^-)=1 a_0^2$, $\sigma_{RD_2}(Cl^-) = 2 a_0^2$. Similarly cross sections for R processes in Cl^--H_2 and F^--H_2 collisions have the same values ($\approx 1 a_0^2$) in this energy range. Figs. 3 and 7 show that differential cross sections for R and RD₂ are peaked around $\chi = 35^{\circ}$ at high energy. The RD₂ process is characterized by a small rovibrational energy in both cases. This process can no longer be accounted for by the mechanism described above. At high energy, the results are better accounted for by the SIM [5] as recently discussed by Sizun and Gislason [20].

Concerning the dissociation process (DD), that becomes important above 10 eV collision energy, two



Fig. 10. Isotopic effects in Cl^--H_2 , Cl^--D_2 and Cl^--HD collisions. Solid line: the simple $R_{12} = (\chi_2/\chi_1)^2$ model. Dashed line: model of Safron et al. [18]. Circles: experimental results of Huq et al. [7].

processes of very different importance show up. (i) The dominant process is obviously related to the RD₁ mechanism discussed above, with its maximum intensity localized on the X⁻-H elastic circle (figs. 5 and 6). (ii) A minor process appears, resulting of a first inelastic binary X⁻-H encounter. The endothermicity is just the affinity of the halide ion therefore indicating that the electron detaches in the first binary collision.

4.2. Electronic transitions. Competition between R, RD and SD channels

The mechanisms responsible in Cl^--H_2 collisions for the simple detachment, reactive detachment and reaction have been discussed in detail in our previous papers [1-3]. Theoretical investigations by Sizun et al. [6] have put the description on a more quantitative basis. The main feature of this mechanism will briefly be recalled in order to discuss the case of F^--H_2 collisions.

A cut of the potential energy surfaces (PES) in the product channels is schematized in fig. 11. The two ionic PES corresponding to $HCl+H^-$ and



Fig. 11. A schematic cut of the potential energy surfaces at infinite distance in the product and reactant valley.

 $(HCl)^- + H$ channels cross along the A seam of which the A point is the apex [1]. Interaction along this seam is due to the electron exchange term. However, as is well known, the $(HCl)^-$ ion is not stable and detaches in the HCl+H continuum around the B seam. In this model, R and RD processes result from the same initial reactive process: when the system is in the product valley, the branching ratio between R and RD will depend on the vibrational character of the reactive trajectories. Trajectories with small vibrational energies will not allow the A seam to be reached, therefore only the reactive process R occurs. With larger vibrational energy, electronic transition along the A seam towards the second ionic PES becomes possible. The corresponding trajectories will, later on, reach the neutral PES along the B seam giving rise to RD₁ process. With this model it was possible to qualitatively explain the similar angular behaviour of R and RD₁, as well as the vibrational energy distribution for these processes. The new results presented here confirm this interpretation. In particular, the contour of the R process (fig. 5) lies on the C circle and appears as an extension of the RD_1 contour at smaller χ angle; this feature confirms the complementarity of these two processes.

Consider now the F^--H_2 system. the topology of the PES at infinity (fig. 12) in the product valley is similar to that of Cl^--H_2 . However, the relative position of the A seam is different due to the much lower endothermicity of the R process. This explains why the R process accomodates much more vibrational energy in the F^--H_2 system than in Cl^--H_2 . For this reason the branching ratio ρ between R and RD₁ is much larger for F^- ($\rho = 10$) than for Cl^- ($\rho \approx 1$). On the other hand, the weak vibrational excitation in the RD₁ channel (as compared with that observed in Cl^--H_2 collisions) is due to a different kinematic mechanism (see above) rather than to a specific electronic problem.

It is noteworthy that the total cross section for SD at energies below 10 eV presents the same shape as for RD₁ (fig. 4). This confirms that the same initial dynamics is responsible for both processes. In the F^- -



Fig. 12. Topology of the potential energy surfaces for XH-H infinite separation in the product valley showing that the relative position of the A seam depends on the specific endothermicity of each system.

 H_2 case, due to the lower endothermicity of the R process, the access towards the lower adiabatic surface is easier; this could explain the higher probability of getting SD process which proceeds from an interaction between this surface and the continuum [4]. Actually, at this low energy both SD and RD1 detachment processes proceed identically via transitions to the second ionic PES. Some trajectories (about 1/3) can then "come back" in the reactant valleys leading to SD processes whereas most of them (2/3) stay in the product valley (RD₁ process). At higher energy, sharing between SD and RD processes does not seem to happen (since the SD cross section is very low between 10 and 25 eV) suggesting that the R/RD_2 branching takes place at larger distance in the product valley preventing SD trajectories to "come back" in the reactant valley. This hypothesis is also consistant when comparing the characteristic scattering angle for both processes. RD1 and SD have similar scattering angles (20° and 10° respectively) whereas at high energy these characteristic angles are much more different (fig. 3). Furthermore the strong velocitydependent isotopic effect indicates that detachment processes involve a dynamical coupling.

5. Conclusion

This paper presents detailed differential cross sections concerning reactive and detachment processes for all halide ion $-H_2$ systems. This comprehensive study leads to a consistent description of all processes at energies below 12 eV which are discussed at two different levels.

The nuclear rearrangement comes first and can be described independently of the second step, which involves electronic transitions between the two lowest ionic PES (and their coupling with the continuum). It appears that the endothermicity ΔH_0 of the reactive channel should be the key parameter of the first step. In this respect, F⁻ appears to be special case with a small ΔH_0 =1.29 eV as compared with the heavier halide ions for which ΔH_0 ranges from 3 to 3.7 eV. As a consequence reactive collisions with F⁻ do not require hard collisions. Scattering with large impact parameters (on "two-atoms") can lead to processes with large cross sections and small vibrational excitation. This situation contrasts with the

three heavier systems for which the larger endothermicity results from harder collisions with smaller impact parameters. In this case the reaction is initiated by a hard binary collision. This is not only consistent with the much smaller reactive cross sections but also with the large vibrational excitation due to that large initial impulse given to only one atom. An other success of this model is its ability to account for the large isotopic effect of R and RD processes in Cl^--H_2 compared with its weakness in F^--H_2 collisions.

The second step is qualitatively the same for all systems. It involves electronic transitions between the two lowest ionic PES and their coupling with the continuum. Enough vibrational energy is required in order to reach the A seam, giving rise to RD processes and even, in F^--H_2 collisions, to SD processes.

Above 12 eV a new reactive detachment mechanism appears. Although it is present in all systems it is particularly evident in the F^--H_2 system. Since it is characterized by a scattering angle similar for all systems it is assumed that another type of sequential impulse model is reponsible for this process.

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