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Associative ionization in collisions of H_2^+, D_2^+ with H^- and D^-

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Abstract. This paper reports on the measurement of the absolute cross sections of the following associative ionization processes:

$$H_2^+ + H^- \longrightarrow H_3^+ + e$$
$$H_2^+ + D^- \longrightarrow H_2D^+ + e$$
$$D_2^+ + H^- \longrightarrow D_2H^+ + e$$
$$D_2^+ + D^- \longrightarrow D_3^+ + e.$$

Measurements were carried out using merged beams and chopping the negative beam to evaluate the background. The measurements cover the barycentric energy range from 0.07 to 10 eV. The four cross sections were, within experimental error, equal both in magnitude and energy dependence.

In a recent paper [1], we presented an experimental study of associative ionization in the collision of He^+ with H^- and D^-. In this paper, a new set of measurements is reported dealing with the associative ionization of H_2^+ and D_2^+ with H^- and D^-.

Associative ionization, which is of great interest in several fields of physics and chemistry, is especially important for understanding the formation of molecules in interstellar clouds. The H_3^+ ion, for instance, is as pointed out by Datz *et al* [2], the forefather of nearly 100 interstellar molecules.

The dissociative recombination of H_3^+ and isotopic varieties has been intensively studied both theoretically [3, 4] and experimentally [2, 4–9]. But the processes leading to the formation of H_3^+ are less well documented. In a discharge, the principal mode of formation is the reaction

$$H_2^+ + H_2 \longrightarrow H_3^+ + e \tag{1}$$

which has a very large cross section as was shown in 1958 by Stevenson and Schissler [10]. But as pointed out by Dalgarno [11], other processes exist that might be efficient in other conditions. One of them is associative ionization in the collision of H_2^+ with H^- and is dealt with in this paper. The cross sections of the following reactions have been measured:

$$H_2^+ + H^- \longrightarrow H_3^+ + e \tag{2}$$
$$H_2^+ + D^- \longrightarrow H_2D^+ + e \tag{3}$$
$$D_2^+ + D^- \longrightarrow D_3^+ + e \tag{4}$$
$$D_2^+ + H^- \longrightarrow D_2H^+ + e. \tag{5}$$

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Table 1. Experimental associative ionization cross sections in $H_2^+ + H^-$ collisions.

v_r (10^6 cm s^{-1})	E_{cm} (eV)	σ (10^{-16} cm^2)	$\pm\Delta\sigma$ (10^{-16} cm^2)
0.45	0.071	3.13	0.25
0.477	0.080	2.75	0.28
0.504	0.089	2.35	0.28
0.544	0.104	2.23	0.17
0.570	0.114	2.10	0.17
0.610	0.131	1.96	0.20
0.704	0.174	1.54	0.15
0.757	0.201	1.37	0.14
0.838	0.246	1.15	0.09
0.931	0.304	0.972	0.078
1.065	0.398	0.804	0.048
1.198	0.503	0.648	0.051
1.305	0.597	0.596	0.048
1.411	0.699	0.533	0.043
1.558	0.851	0.439	0.035
1.851	1.201	0.293	0.023
1.998	1.399	0.240	0.024
2.197	1.693	0.199	0.020
2.397	2.015	0.152	0.015
2.676	2.511	0.102	0.010
2.915	2.980	0.094	0.009
3.379	4.005	0.052	0.005
3.776	5.002	0.0355	0.0036
4.279	6.423	0.0199	0.0036
4.623	7.496	0.0125	0.0013
4.927	8.513	0.0077	0.0012
5.349	10.034	0.0028	0.0007

The experimental set-up used for the measurements was the same as that described in [1]. A beam of H_2^+ (or D_2^+) produced by an ECR source, was merged with a beam of H^- (or D^-) and the reaction products formed in a region delimited by a bias voltage were separated by a magnetic analyser and detected by a channel electron multiplier. The kinetic energy of the triatomic ions arriving on the channel electron multiplier was between 15 and 18 keV so that the detection efficiency was as high as 0.95 ± 0.02. The resolution of the collision energy (barycentric energy) was better than 0.013 eV, being mainly limited by the angular dispersion of the ions in the beams.

In tables 1–4 we present the experimental results for reactions (2)–(5) respectively. As the molecular ions were produced in a low-pressure ion source, there is no doubt (see for instance von Busch and Dunn [12]) that their vibrational population was very close to a Franck–Condon distribution: that is, with 90% of the ions with a vibrational quantum number $v < 6$ and a maximum at $v = 1$–2 in the case of H_2^+ and 90% with $v < 9$ and a maximum at $v = 3$ in the case of D_2^+. No attempt was made to modify this distribution in this work.

The cross sections for associative ionization in the collision of H_2^+ with H^- and D^- are shown in figure 1 as a function of the barycentric energy and in figure 2 as a function of the relative velocity. The cross sections for D_2^+ with H^- and D^- are shown in figures 3 and 4. Figure 5 summarizes all the results shown as a function of the barycentric energy. It should be noticed that the four cross sections are almost identical

Table 2. Experimental associative ionization cross sections in $H_2^+ + D^-$ collisions.

v_r (10^6 cm s^{-1})	E_{cm} (eV)	σ (10^{-16} cm^2)	$\pm\Delta\sigma$ (10^{-16} cm^2)
0.362	0.069	3.29	0.33
0.394	0.082	2.72	0.27
0.416	0.091	2.55	0.0.26
0.437	0.100	2.351	0.26
0.500	0.132	1.844	0.22
0.564	0.167	1.546	0.17
0.617	0.200	1.283	0.13
0.691	0.251	1.034	0.10
0.755	0.299	0.93	0.08
0.872	0.399	0.747	0.082
0.978	0.503	0.597	0.065
1.074	0.606	0.554	0.061
1.158	0.706	0.46	0.046
1.265	0.841	0.387	0.043
1.381	1.003	0.334	0.040
1.572	1.300	0.234	0.030
1.742	1.596	0.178	0.028
1.954	2.008	0.146	0.020
2.146	2.420	0.115	0.017
2.390	3.003	0.089	0.015
2.761	4.009	0.047	0.009
3.080	4.987	0.0313	0.0068
3.515	6.496	0.0188	0.0041
3.780	7.515	0.0115	0.0035
4.248	9.487	0.0056	0.0032

and that their dependence on the collision energy E approximately obeys an E^{-1} law at low energy.

That the cross section is, at low energy, inversely proportional to the collision energy E, can be understood as a result of the Coulomb attraction between the reactants. This attraction makes it possible for them to reach those small internuclear distances where associative ionization can occur up to larger impact parameters when the energy is smaller. For the closest approach to be smaller than a given value R^*, the impact parameter must be less than a critical value b^* given by:

$$(b^*)^2 = \frac{R^*}{E} + (R^*)^2. \tag{6}$$

Taking $R^* = 3a_o$, one gets, when $E \longrightarrow 0$

$$(b^*)^2 = \frac{3}{E}. \tag{7}$$

The cross section can then be written as

$$\sigma = \pi (b^*)^2 P. \tag{8}$$

where P is the probability that the reaction (autoionization) takes place, averaged over all the trajectories with an impact parameter smaller than b^*. At low energy, this probability does not depend on the asymptotic kinetic energy because the relative velocity of the reactants, in the region $R < R^*$, is determined by the Coulomb attraction. The cross section is thus inversely proportional to E.

Table 3. Experimental associative ionization cross sections in $D_2^+ + D^-$ collisions.

v_r (10^6 cm s^{-1})	E_{cm} (eV)	σ (10^{-16} cm^2)	$\pm\Delta\sigma$ (10^{-16} cm^2)
0.363	0.092	3.56	0.47
0.409	0.118	2.56	0.38
0.457	0.147	2.16	0.35
0.505	0.178	1.86	0.17
0.552	0.213	1.63	0.15
0.599	0.252	1.32	0.16
0.646	0.293	1.19	0.11
0.741	0.385	0.97	0.16
0.835	0.489	0.79	0.10
0.930	0.606	0.65	0.08
1.018	0.735	0.53	0.06
1.166	0.952	0.42	0.05
1.307	1.197	0.31	0.05
1.402	1.375	0.29	0.04
1.637	1.876	0.22	0.04
1.871	2.454	0.14	0.02
2.107	3.11	0.10	0.02
2.341	3.84	0.06	0.01
2.810	5.53	0.024	0.005
3.277	7.53	0.01	0.003
3.744	9.827	0.005	0.003

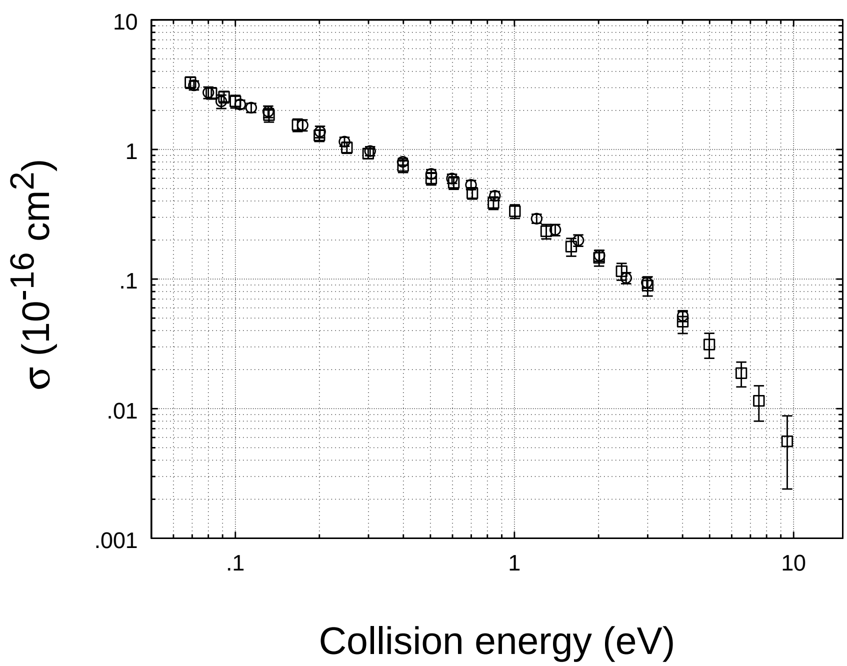

Figure 1. Associative ionization cross sections for reactions involving H_2^+ as a function of the barycentric energy. Open circles $\equiv H_2^+ + H^- \longrightarrow H_3^+ + e$; open squares $\equiv H_2^+ + D^- \longrightarrow H_2D^+ + e$.

But there is another condition to be fulfilled for associative ionization to be possible, namely that the rotational energy of H_3^+ does not exceed its binding energy D. The rotational

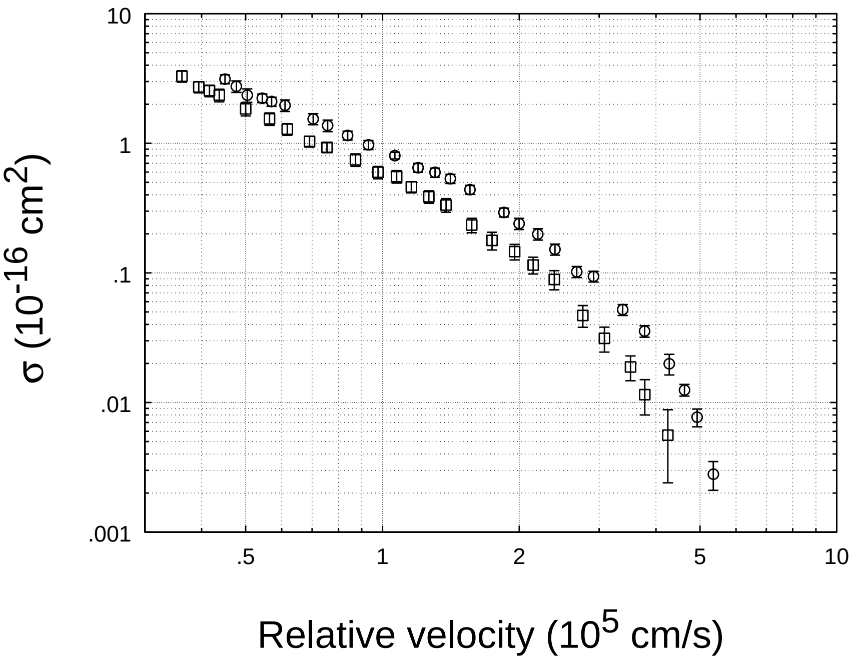

Figure 2. Associative ionization cross sections for reactions involving H_2^+ as a function of the relative velocity. Open circles $\equiv H_2^+ + H^- \longrightarrow H_3^+ + e$; open squares $\equiv H_2^+ + D^- \longrightarrow H_2D^+ + e$.

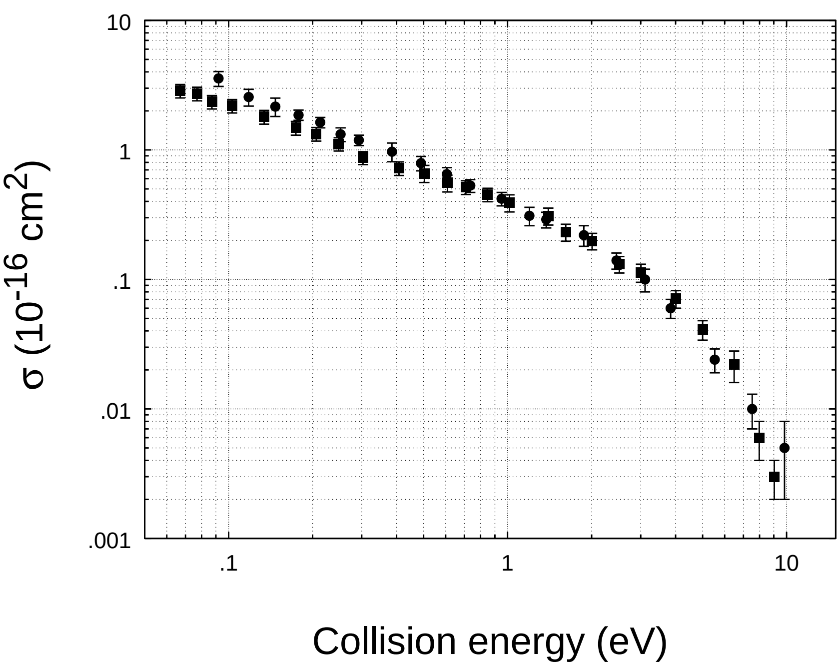

Figure 3. Associative ionization cross sections for reactions involving D_2^+ as a function of the barycentric energy. Full circles $\equiv D_2^+ + D^- \longrightarrow D_3^+ + e$; Full squares $\equiv D_2^+ + H^- \longrightarrow D_2H^+ + e$.

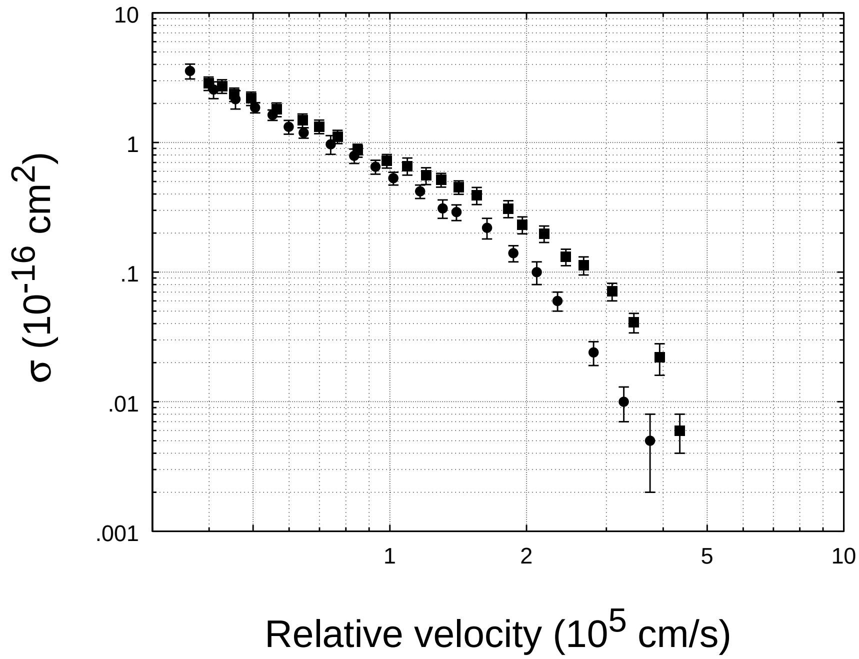

Figure 4. Associative ionization cross sections for reactions involving D_2^+ as a function of the relative velocity. Full circles ≡ $D_2^+ + D^- \longrightarrow D_3^+ + e$; Full squares ≡ $D_2^+ + H^- \longrightarrow D_2H^+ + e$.

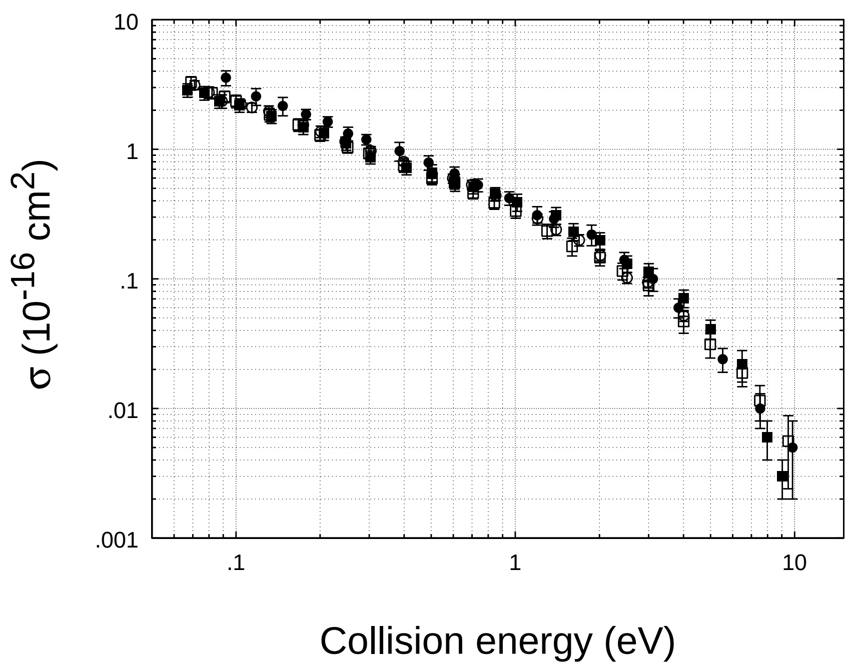

Figure 5. The four cross sections as a function of the barycentric energy. Symbols as in the others figures.

Table 4. Experimental associative ionization cross sections in $D_2^+ + H^-$ collisions.

v_r (10^6 cm s^{-1})	E_{cm} (eV)	σ (10^{-16} cm^2)	$\pm\Delta\sigma$ (10^{-16} cm^2)
0.399	0.067	2.86	0.34
0.427	0.077	2.72	0.33
0.454	0.087	2.35	0.28
0.495	0.103	2.19	0.26
0.563	0.134	1.80	0.22
0.642	0.174	1.48	0.18
0.699	0.206	1.33	0.16
0.767	0.248	1.11	0.13
0.849	0.303	0.87	0.10
0.985	0.408	0.721	0.086
1.093	0.503	0.659	0.099
1.202	0.608	0.556	0.083
1.297	0.708	0.515	0.062
1.418	0.847	0.452	0.054
1.554	1.016	0.391	0.059
1.824	1.4	0.309	0.046
1.959	1.615	0.232	0.035
2.188	2.01	0.198	0.029
2.443	2.513	0.131	0.019
2.672	3.004	0.113	0.018
3.087	4.011	0.071	0.011
3.448	5.004	0.041	0.007
3.928	6.49	0.022	0.006
4.353	7.98	0.006	0.002
4.632	9.03	0.003	0.001

energy E_r is determined by the angular momentum L associated with the relative motion of the reactants

$$E_r = \frac{L^2}{2I} \tag{9}$$

$$L = \mu v_0 b \tag{10}$$

$$I = \alpha r^2 \tag{11}$$

where μ is the reduced mass of the collision partners and v_0 their relative velocity. I is the moment of inertia of H_3^+, supposed to be in its triangular configuration D_{3h} with the nuclei at a distance r from each other. The condition $E_r < D$ thus becomes

$$\frac{\mu}{\alpha} E \frac{b^2}{r^2} < D. \tag{12}$$

This gives an upper limit b^* to the impact parameter, where

$$(b^*)^2 = \frac{\alpha}{\mu}\frac{D}{E} r^2 \tag{13}$$

or, with $r = 1.65a_0$, $D = 0.158$ Hartree and $\alpha/\mu = \frac{3}{2}$

$$(b^*)^2 = \frac{0.65}{E}. \tag{14}$$

This limit is smaller than that given by (7) and is the one to be used in formula (8). The cross section can then be expressed as

$$\sigma = \frac{2.0P}{E} \tag{15}$$

and is therefore inversely proportional to the collision energy.

It can easily be verified that the value $\alpha/\mu = \frac{3}{2}$ is valid for all four reactions (2)–(5). Thus no isotopic effect can be expected from there. Isotopic effects can only arise through the probablity P. On initial consideration it might seem that this probability should be larger with heavier masses, at a fixed collision energy, as the velocity is then smaller and a longer time is available for autoionization. However, the ionic state along which the collision proceeds towards the autoionizing configuration crosses many covalent states where mutual neutralization is possible. The resulting loss of flux could be higher with heavier masses because of their lower velocity at the crossings. Unfortunately, the size of this effect is difficult to evaluate (see, for instance, the paper by Eerden *et al* [13]). Nevertheless, this could at least qualitatively explain why the cross sections measured for reactions (2)–(5) are almost identical at the same energy.

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