L_α Emission from Low-Energy Collisions $H^+ + Ar$, $H_2^+ + Ar$, $H^+ + H_2$

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Absolute integral cross sections for L_α emission from the title collision systems are reported for energies from threshold to several hundred eV_{CM}. They are discussed in comparison with the systems $Ar^+ + H$, H_2.

We have recently reported on L_α measurements from low-energy $Ar^+ + H$ [1] and $Ar^+ + H_2$ [2] collisions. In this note we communicate results on the "mirror systems" $H^+ + Ar$ and $H_2^+ + Ar$, as well as on the related $H^+ + H_2$ system. The apparatus, a mass analyzed ion beam/gas target chemiluminescence arrangement, is the same as in [1, 2]. The processes studied here are endothermic as follows:

$$H^+ + Ar \rightarrow H^* + Ar^+ - 12.356\ eV, \quad (1)$$

$$H_2^+ + Ar \rightarrow H^+ + H^* + Ar \quad - 12.844\ eV, \quad (2a)$$

$$\rightarrow H \quad + H^* + Ar^+ - 15.004\ eV, \quad (2b)$$

$$H^+ + H_2 \rightarrow H^* + H_2^+ - 12.028\ eV, \quad (3a)$$

$$\rightarrow H^+ + H + H^* - 14.673\ eV. \quad (3b)$$

H* designates excitation to H(2p).

Figure 1 shows the results on reactions (1) and (2). Suchannek and Sheridan [3] have measured carefully calibrated absolute cross sections for (1) down to 507 eV_{CM}, while all other studies of this luminescent charge transfer were done in the keV region (for further references, see [1]). The relative cross sections measured by us are in excellent agreement with the results of [3] at their four lowest energies (see Fig. 1). By normalization to these points, our measurements for reactions (1)–(3) were put on an absolute scale.

The very gradual rise from threshold of the $H^+ + Ar$ cross section is striking, especially if compared to $Ar^+ + H$, Fig. 5 in [1]. In the latter case, 10^{-17} cm^2 is reached as early as 5 eV above threshold, against a corresponding 500 eV for (1), Figure 1. A consideration of the $(Ar-H)^+$ potential energy curves (e.g. Fig. 6 in [1]) shows that H(2p) is accessible from $Ar^+ + H$ via repulsive curves, while for $H^+ + Ar$ a transition from the attractive ArH^+ ground state curve is required. This appears to greatly impede the reaction, an interesting case for a quantum mechanical study.

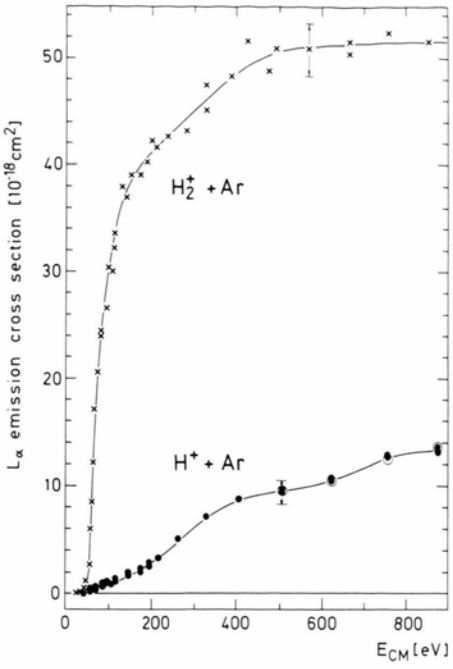

Fig. 1. Integral cross sections for L_α production in the two collision systems indicated. For $H^+ + Ar$, results from [3] are also shown (open circles), to which the present data were normalized.

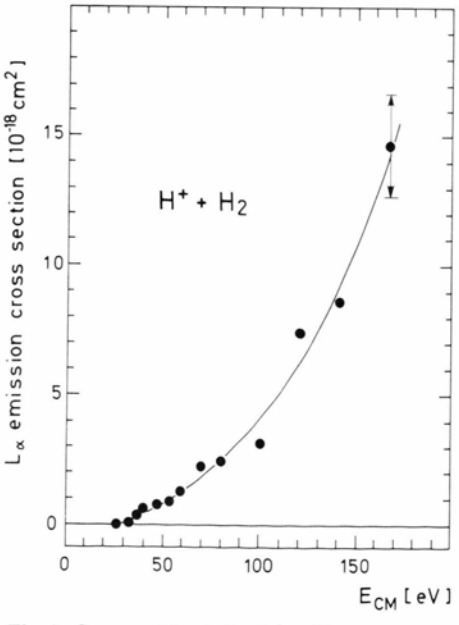

Fig. 2. Same as Fig. 1, for $H^+ + H_2$.

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In stark contrast to $H^+ + Ar$ is the steeply rising cross section for $H_2^+ + Ar$, Figure 1. Charge transfer and exchange reactions in this system have been studied many times (e.g. [4] and references therein), and L_α production has been reported at energies > 1 keV [5]. Among the two mechanisms (2a, b), collisional dissociation, (2a), appears much more likely than the dissociative charge transfer, (2b). This was shown conclusively for the system $H_2^+ + He$ in [5], and these authors favoured an analogous situation for $H_2^+ + Ar$. Also, a consideration of the ArH_2^+ potential energy surfaces (e.g. Fig. 8 in [2]) shows that the final state of (2a) will be more accessible than that of (2b), not only because it lies lower in energy and is encountered first, via a repulsive surface, but also because it does not require a charge transfer. Finally, as explained in [2], $Ar^+ + H + H^*$ would have to compete with $Ar^* + H^+ + H$ formation. On the other hand, an exchange reaction

$$H_2^+ + Ar \rightarrow HAr^+ + H^* - 8.988\ eV \qquad (2c)$$

might have been expected to contribute at the lowest energies, but was not found.

The initial slope of the cross section for (2), Fig. 1, is similar to that for L_α from $Ar^+ + H_2$, Fig. 4 in [2]. However, the threshold energies are very different. For $H_2^+ + Ar$, L_α is not observed until the collision energy exceeds ~ 50 eV, corresponding to an activation energy of reaction (2) of at least 35 eV. For the mirror system $Ar^+ + H_2$, on the other hand, the L_α onset is at 15 eV, near the thermochemically expected value. The shape of the cross section curve for $H_2^+ + Ar$ indicates that this reaction occurs at a well-defined avoided intersection of potential energy surfaces. This point must be located high above the product energy level. An explanation for such a high activation energy might be that in the course of the $H_2^+ + Ar$ reaction the H–H internuclear distance does not change much until the partners come very close. By contrast, with $Ar^+ + H_2$ an H–H bond stretch accompanies the initial transition to the $Ar + H_2^+$ surface (see potential energy contours and discussion in [6]). The impuls tending to separate the H atoms as a result of this $Ar^+ + H_2 \rightarrow Ar + H_2^+$ charge transfer may then carry the system to a point where the $Ar + H^+ + H^*$ surface is accessible at the lowest possible energy. The schematic ArH_2^+ surfaces shown in [2], Fig. 8, are suggestive of this.

Cross sections for (3) have been measured by several groups ([7]–[9], and references therein), but mostly in the keV region. Only the experiment of Dunn et al. [7] extended from 3 keV down to 0.5 keV. Here the cross section was found to decrease from 0.3 to 0.07 Å^2. Our points, Fig. 2, lie somewhat above an extrapolation of Dunn's measurements (by factors of 2 and 4 at 100 and 160 eV_{CM}, respectively). In some of the earlier $H^+ + H_2$ experiments, processes (3a) and (3b) could be differentiated, using a Doppler shift technique. A data compilation in [9] shows that around 5 keV the cross section for dissociative excitation of H(2p), reaction (3b), is only 1/3 of that for electron capture, (3a), and dropping steeply towards lower energies, while that for (3a) exhibits only a slight decrease. This indicates that in our experiments only (3a) should have contributed. Figure 2 shows that the onset occurs just slightly above the nominal threshold. The overall curve shape is similar to that for (1). This is reasonable because in the two cases electrons are captured from species with very similar ionization potentials (15.76 and 15.43 eV) and proton affinities (3.9 and 4.4 eV, for Ar and H_2, respectively). However, the absolute magnitude of the cross section for (3a) is about 10 times greater than for (1).

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