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# Isotope Effect in the Dissociative Attachment in $H_2$ at Low Energy*

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The dissociative attachment cross section for formation of $H^-$ and $D^-$ from $H_2$, HD, and $D_2$ has been measured in the threshold range from 3.75 to 5 eV using a mass spectrometer for ion identification. A pronounced isotope effect is observed. The cross section of $H^-$ from $H_2$ has a peak value of $1.6\times10^{-21}$ cm$^2$; $D^-$ from HD, $1\times10^{-22}$ cm$^2$; and $D^-$ from $D_2$, $8\times10^{-24}$ cm$^2$; all peaks occurring at 3.75 eV. Negative-ion formation in this energy range proceeds via the compound state $^2\Sigma_u{}^+$ whose lifetime against autodetachment is calculated from the above cross sections to be about $1\times10^{-15}$ sec. Because of this short lifetime and the relatively long time needed for the atoms to separate, the probability of survival of the negative ion, and therefore the dissociative-attachment cross section in $H_2$ at 3.75 eV, is small. For the heavier isotopes, the separation time is even longer and therefore the dissociative-attachment cross section is minute. The same compound state is also responsible for vibrational excitation of the hydrogen molecule.

It is now well established that electron collisions with atoms and molecules proceed, in certain energy regions, via an intermediate compound state in which the electron attaches itself temporarily to the atom or molecule. Although these compound states have lifetimes as short as $10^{-15}$–$10^{-14}$ sec, their existence must be taken into account because they produce effects which otherwise would not be present. Examples are the vibrational excitation of molecules,[1,2] resonances in the elastic scattering on atoms and molecules,[3–5] and certain aspects of negative-ion formation. This paper is concerned with the role of compound states of molecules in the negative-ion formation by dissociative attachment.

In a recent paper,[6] we reported that negative-atomic-hydrogen ions $H^-$ are formed by electron impact on $H_2$ with a very sharp onset at an electron energy of 3.75±0.07 eV. We postulate that this process, $e+H_2\rightarrow H^-+H$, proceeds via a compound state of $H_2{}^-$ with a short lifetime. The physics of the reaction can be best understood with the aid of the potential-energy diagram for $H_2$ and $H_2{}^-$ shown in Fig. 1. At electron energies between about 1 to 4 eV, the compound state $^2\Sigma_u{}^+$ can be formed[7,8] by the temporary attachment of an electron to the $H_2$ molecule. At incident-electron energies below 3.75 eV, the compound-system decays by the emission of an electron to the ground or a higher vibrational state of $H_2$ ($^1\Sigma_g{}^+$). The peak of the vibrational cross section, which probably coincides with the peak of the formation cross section of the compound state, occurs at about 2 eV. This vibrational excitation has been studied experimentally[1,9] as well as theoretically.[8] When formation of $H^-$ becomes energetically possible at 3.75 eV, a new channel of decay is opened and the system can decay into $H^-+H$ with the atoms having very low kinetic energy. This decay mechanism of the compound state of $H_2$ and its isotopes HD and $D_2$ is the subject of this paper.

## I. DECAY OF COMPOUND STATES

Holstein[10] has pointed out that a compound state which lies above the dissociation limit for the negative ion can lead to dissociative attachment, but that such a state is unstable towards autodetachment. Thus the cross section for dissociative attachment is the product of the cross section for formation of the compound state $Q_0$ and the probability that in fact the system survives to a "stabilization" point $R'$. These considerations have been further discussed by Demkov[11] and by Bardsley, Herzenberg, and Mandl.[12] The latter authors give an expression for the negative-ion-formation cross section $Q_-$:

$$Q_-=Q_0\exp\left[-\int_{R_0}^{R'}\frac{\Gamma(R)}{\hbar}\frac{dR}{v(R)}\right]. \qquad (1)$$

Here, $\Gamma$ is the width (and $\hbar/\Gamma$ is the lifetime) of the compound state with respect to autodetachment. This

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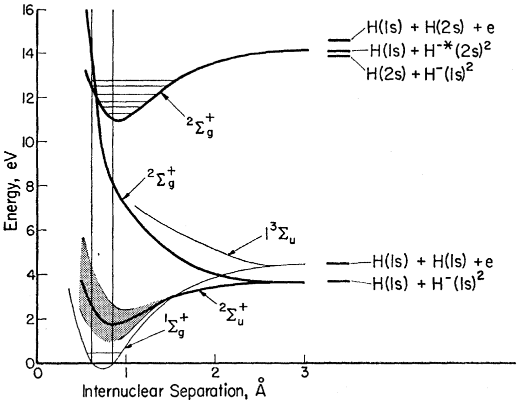

FIG. 1. Schematic potential-energy curves for $H_2$ and $H_2^-$. The heavy lines represent the $H_2^-$ system and the light lines represent the neutral $H_2$ system. The ${}^2\Sigma_u{}^+$ state is unstable toward autodetachment, causing a broadening of the potential-energy curve. The stippled area is a schematic representation of the short lifetime of this state. This state is the intermediate for dissociative attachment at low energies and for vibrational excitation. The higher negative-ion states have a much longer lifetime and thus have a small energy width.

width is a function of the internuclear separation $R$. The integration extends from the formation point $R_0$ to the stabilization distance $R'$ and $v(R)$ is the relative velocity of separation of the nuclei. We can replace the exponent of (1) by the appropriate average width $\bar{\Gamma}$ and by the time $\tau$, which is needed for the products to reach the stabilization point. We then write

$$Q_- = Q_0 \exp(-\bar{\Gamma}\tau/\hbar); \qquad (2)$$

Eqs. (1) and (2) are not exact,[8,12] but in view of the many uncertainties in the theory and interpretation of the data we shall use Eq. (2) as the basis for further discussion. It should be noted that the total width is the sum of the partial widths for decaying into the various vibrational states of the $(H_2+e)$ system. Separation into three particles, $(H+H+e)$ is energetically possible at energies above 4.46 eV.

The potential-energy diagram of Fig. 1 shows the ground state of $H_2$, ${}^1\Sigma_g{}^+$, and the compound state ${}^2\Sigma_u{}^+$. The finite width of the latter state is shown schematically by the stippled area surrounding the solid curve. This width must be a function of internuclear separation, decreasing at large internuclear separations.[8] For completeness, the higher states of the $H_2^-$ system are also included. At energies above about 8 eV the ${}^2\Sigma_g{}^+$ repulsive state is responsible for dissociative attachment[13,14] and leads to the formation of $H^-+H$, both having kinetic energy. The "bound" state ${}^2\Sigma_g{}^+$, drawn after Taylor and Williams,[15] leads to resonances in the elastic[5] and vibrational[9] cross sections of $H_2$ and is probably responsible for the structure observed in the formation[13] of $H^-$ at an electron energy about 12 eV. Above 13.8 eV, formation of $H^-(1s)^2+H(2s)$ has been observed[13,14] and leads to negative ions having very low kinetic energy and having a peak cross section at about 14.2 eV.

## II. RESULTS

The experimental arrangement has been described previously[16] and will therefore be discussed only briefly. It consists of a differentially pumped collision chamber in which the gas under study is introduced. An electron beam from a thoria-coated iridium filament is aligned by a magnetic field of about 150 G and passes through the collision chamber. The energy distribution of the electron beam can be effectively reduced by using the retarding potential-difference method.[17] The retarding potential-difference (RPD) method reduces the signal-to-noise ratio of the measured currents, and it is not used when the cross sections are very small, as is the case for the formation of $D^-$ ions from HD and $D_2$. The ions produced are expelled out of the chamber by a small electric field (~2 volt/cm) and are analyzed in a magnetic mass spectrometer. Since the collision

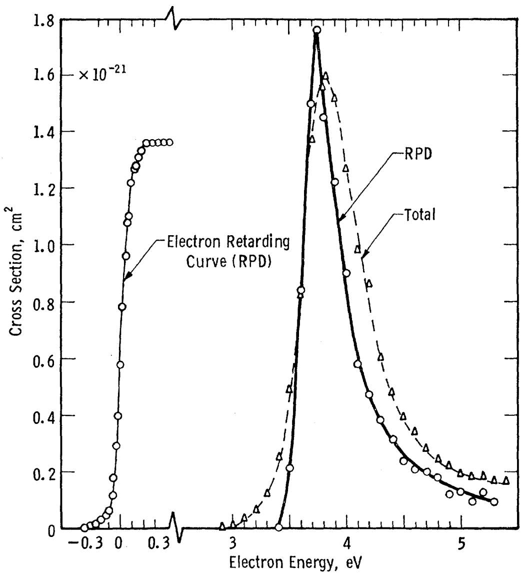

FIG. 2. Cross section for $H^-$ formation from $H_2$ at low energies. The solid curve is the dissociative attachment curve obtained using the retarding-potential-difference technique (width of electron-energy distribution at half-maximum about 0.1 eV) and the dashed curve is obtained using the total electron-energy distribution (0.45 eV). The electron-retarding curve, shown on the left side of the figure, is obtained using the retarding potential-difference method. The energy scale calibration refers to the maximum of the electron-energy distribution and thus is correct for the peak of the cross section at 3.75 eV. The $H^-$ signal is linearly proportional to the $H_2$ pressure.

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chamber is differentially pumped, pressures up to $10^{-1}$ Torr can be used for the measurement of very small cross sections. However, linearity of ion currents with collision-chamber pressure is preserved only up to $5\times10^{-2}$ Torr.

The pressure in the collision chamber is determined from a measurement of the positive-ion current collected on the ion repeller. For this measurement, the "repeller" electrode is biased so as to collect all the positive ions produced in the chamber at an electron energy of 90 eV. Usually, the high-pressure ionization gauge mounted in the volume of the first pumping stage is calibrated in terms of the pressure in the collision chamber and subsequently this gauge is used for monitoring the pressure in the collision chamber.

Figure 2 shows a plot of the $H^-$ cross section from $H_2$, both with and without use of the retarding potential-difference method. Also, an electron retarding curve obtained with the use of the RPD method is shown; Figs. 3 and 4 show the $D^-$ ion signal from HD and $D_2$ in the low electron-energy region (3 to 6 eV). The negative ions formed near the peak have nearly zero kinetic energy; they are formed in a primary process, as evidenced by the linear pressure dependence of the ion currents.[6] The electron-energy scale for these processes has been determined from electron-retarding curves and is referred to the peak of the electron-energy distribution, thus placing the peak of the cross section at the proper position on the electron-energy scale. A qualitative comparison (see Fig. 2) of the electron-retarding curve and the rising portion of the $H^-$ cross section obtained using the retarding potential-difference method shows that the shapes of these curves look very similar. This would seem to indicate, as pointed out in Ref. 6, that the true energy dependence of the cross section is much sharper than observed experimentally. However, a least-squares method for solving the integral equation which connects the true energy dependence of the cross section with the observed ion current[18] shows that this may not be so, and that in fact the rising portion of the true cross section resembles closely the experimental curve obtained with the RPD

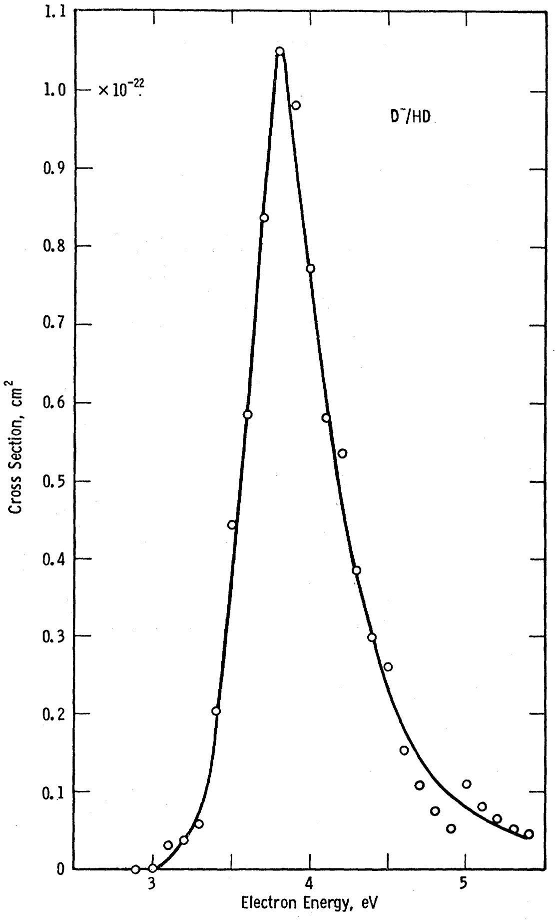

FIG. 3. Cross section for $D^-$ formation from HD at low energies. The entire energy width of the electron-energy distribution (0.45 eV at half-maximum) is used in this experiment, causing a broadening of the threshold region.

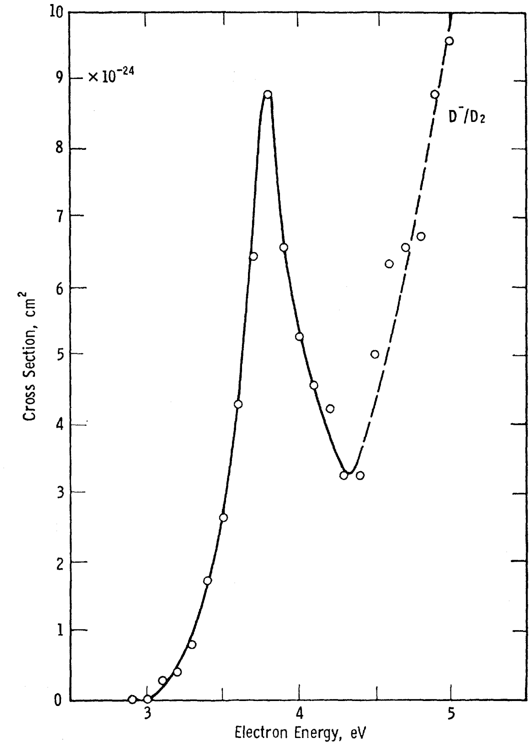

FIG. 4. Cross section for $D^-$ formation from $D_2$ at low energies. The curve is obtained using the entire energy width of the electron beam. The process responsible for the formation of $D^-$ above 4.4 eV (dashed curve) is not understood. This signal is unaffected by a liquid-nitrogen trap in the gas-inlet line and is linearly dependent on the gas pressure.

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[18] C. W. Helstrom [J. Opt. Soc. Am. **57**, 297 (1967)] discusses image restoration by the method of least squares. The authors are indebted to C. W. Helstrom for performing the calculations discussed in the text.

method. The latter conclusion was confirmed by folding the measured electron-energy distribution into a sharply rising cross section, which led to a more steeply rising curve than observed experimentally. However, only limited tests were performed regarding the sensitivity of the analysis to the measured electron-energy distribution, which is necessarily afflicted by noise and by systematic errors. Thus, at the present time, our confidence in the conclusions of the computer analysis is limited.

The low-energy dissociative-attachment peak in the hydrogen molecule and its isotopes is found to occur at 3.75±0.07 eV. Since these ions as well as the ions at 14.2 eV are formed with low kinetic energy, we evaluate attachment cross sections for the low-energy process by comparing the negative-ion current near 3.75 eV to the negative-ion current at 14.2 eV and use the cross sections for the 14.2 eV process reported in the literature.[14] This procedure overcomes the problem of kinetic energy discrimination, usually found in mass spectrometers. The normalization is performed in a pressure region in which both the 3.75 and 14.2 eV signals depend linearly on gas pressure. Serious errors can result if this condition is not fulfilled.[19]

In Fig. 3 the attachment process leading to the formation of only $D^-$ ions in HD is shown; $H^-$ formation with a cross section within a factor of 2 of the $D^-$ cross section is also observed. In evaluating the cross section for the formation of $D^-$ alone at low energy (Fig. 3) we have used the value of the cross section at 14.2 eV that would be due to $D^-$ alone,[20] i.e., $1.23\times10^{-20}$ cm$^2$, which is half the value reported by Rapp, Sharp, and Briglia.

The peak cross sections obtained are $1.6\times10^{-21}$ cm$^2$ for $H^-$ from $H_2$, $2.1\times10^{-22}$ cm$^2$ for $(H^-+D^-)$ from HD, and $8\times10^{-24}$ cm$^2$ for $D^-$ from $D_2$.[21] All quoted cross sections are obtained without use of the retarding potential-difference method to make them self-consistent and are considered accurate, relative to each other within 20%. The absolute values are less certain (within a factor of 2).[22]

We wish to stress that the low-energy dissociative-attachment process, resulting from the ${}^2\Sigma_u{}^+$ state shows a pronounced isotope effect, as evidenced by a decrease of the $D^-$ cross section from $D_2$ by more than two orders of magnitude compared to $H^-$ from $H_2$. This is in striking contrast to the relatively small isotope effects (factor of 2) observed for the dissociative-attachment process above about 8 eV (resulting in fragments having kinetic energy) and for the process $H_2+e\rightarrow H(2s)+H^-(1s)^2$, around 14 eV. This implies that the mean width of the ${}^2\Sigma_u{}^+$ state is considerably larger than either the repulsive or the bound ${}^2\Sigma_g{}^+$ states of the $H_2^-$ system, as can be seen by examining Eq. (2).

We can calculate $\bar{\Gamma}\tau$, the product of the mean width of the ${}^2\Sigma_u{}^+$ compound state and the separation time $\tau$ for $H+H^-$ from the three measured cross sections, using Eq. (2). Assuming that $\bar{\Gamma}$ has the same value for $H_2$, HD, and $D_2$ and realizing that the separation time for $D_2$ and HD are $\sqrt{2}\tau$ and $(\sqrt{1.33})\tau$, respectively, we obtain

$$\frac{Q_-(H_2)}{Q_-(HD)}=\frac{1.6\times10^{-21}}{2.1\times10^{-22}}=\exp\left[\frac{\bar{\Gamma}\tau}{\hbar}[(\sqrt{1.33})-1]\right] \tag{3}$$

and

$$\frac{Q_-(H_2)}{Q_-(D_2)}=\frac{1.6\times10^{-21}}{8\times10^{-24}}=\exp\left[\frac{\bar{\Gamma}\tau}{\hbar}(\sqrt{2}-1)\right], \tag{4}$$

and arrive at values of $\bar{\Gamma}\tau=8.7\times10^{-15}$, from Eq. (3) and $\bar{\Gamma}\tau=8.5\times10^{-15}$ eV sec, from Eq. (4). Thus we conclude that Eq. (2) describes fairly accurately the observed isotope effect.[23] If we assume $\tau$ to be of the order of a vibration time, $\tau\sim10^{-14}$ sec, then the mean width of the state $\bar{\Gamma}$ will be about 1 eV. The large width obtained for the compound state agrees with theoretical calculations.[8]

If the value obtained for $\bar{\Gamma}\tau$ and the experimentally determined peak-attachment cross section $Q_-$ for $H_2$ at 3.75 eV are substituted into Eq. (2), we obtain a value for the capture cross section for the formation of the compound state in hydrogen and its isotopes, $Q_0=7\times10^{-16}$ cm$^2$. Using the shape of the vibrational

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[19] P. J. Chantry, A. V. Phelps, and G. J. Schulz [Phys. Rev. **152**, 81 (1966)] discuss the behavior of electron beams traversing a collision chamber at pressures at which the mean free path of the electrons is equal to or smaller than the length of the collision chamber.

[20] Rapp, Sharp, and Briglia (Ref. 14) use a total-ionization tube to determine the cross-section values at 14.2 eV. The cross section quoted by these authors for the 14.2-eV peak therefore refers to the sum of the $H^-$ and $D^-$ formation from HD.

[21] In Fig. 4 a rapidly rising $D^-$ signal at electron energies greater than 4.4 eV is observed. In order to estimate the contribution of $D^-$ formed by this process to the resonant peak, it is necessary to extrapolate the rising portion of the curve obtained at higher electron energies. Two forms of the extrapolation have been adopted, one in which the signal reaches zero at 3 eV contributing some signal at the energy corresponding to the peak, and the other in which there is no contribution to the peak. These two determinations differ by about 20%. The value quoted in the text is a mean of these two values. The cause for the difference in shape in the energy dependence of the cross sections of $D^-/D_2$ compared to $D^-/HD$ and $H^-/H_2$ is not understood.

[22] In the case of $H^-$ formation from $H_2$, two values, namely, $2.08\times10^{-20}$ cm$^2$ (Ref. 14) and $3.5\times10^{-20}$ cm$^2$ (Ref. 13) are reported for the peak-attachment cross section at 14 eV. The cross-section value for the 3.75 eV peak will be $1.6\times10^{-21}$ cm$^2$ or $2.8\times10^{-21}$ cm$^2$, depending on the cross-section value chosen for the 14-eV peak. The cross-section values quoted in the text for the low-energy peak in $H_2$ and its isotopes have all been obtained by referring to the cross sections reported in Ref. 14 for the 14 eV peak for $H_2$, HD, and $D_2$. By so doing we remove any systematic errors in the relative magnitudes of the cross sections for the three molecules.

[23] In arriving at a value of $\bar{\Gamma}\tau$ we have neglected the differences in spatial extent of the three isotopes. Although the shape and magnitude of the vibrational cross section for $D_2$ is essentially the same as that for $H_2$ (see Ref. 1), it is possible that the narrower width of the Franck-Condon region of $D_2$ and HD compared to $H_2$ also contribute to the observed isotope effect.

excitation in $H_2$, this cross section can be extrapolated to the peak of the compound-state cross section at about 2 eV, where we estimate the value to be about $1\times10^{-15}$ cm$^2$. This value is in good agreement with the theoretical maximum expected at that energy, and is of the order of magnitude expected of the contribution of the compound state to the elastic cross section.

## III. CONCLUSIONS

We have observed a large isotope effect in dissociative attachment of the hydrogen molecule and its isotopes, resulting from the short lifetime of the compound state $^2\Sigma_u{}^+$. Using the measured cross sections for $H^-/H_2$, $D^-/D_2$, and $D^-/HD$, we arrive at a mean width for the compound state of 1 eV which corresponds to a mean lifetime of about $1\times10^{-15}$ sec. Bardsley, Herzenberg, and Mandl[8] arrived at almost the same conclusion from a theoretical interpretation of the vibrational cross section in $H_2$. Thus we reach a rather simple explanation of low-energy inelastic processes in $H_2$: low-energy incident electrons form the compound state $H_2{}^-$ which decays either by the emission of an electron to the ground and vibrational states of $H_2$ or to $H^-+H$, when the latter process is energetically possible. Since the peak cross section for the compound state occurs at about 2 eV, and since dissociative attachment is not possible below 3.75 eV, the latter process proceeds in the high-energy wing of the compound state. Since the cross section $Q_0$ for forming the compound state at 3.75 eV is $7\times10^{-16}$ cm$^2$, we would expect the peak cross section of this process, at 2 eV, to be of the order of $1\times10^{-15}$ cm$^2$.

## ACKNOWLEDGMENTS

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# Lyman-α Radiation Resulting From Ion Collisions with Molecular Gases*

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Cross sections for the emission of Lyman-α radiation resulting from ion–target-gas collisions have been measured for projectile energies between 1 and 25 keV. All combinations of $H^+$, $D^+$, $H_2{}^+$, $D_2{}^+$, and $He^+$ projectiles on $H_2$ and $D_2$ targets as well as $H^+$ and $H_2{}^+$ on $N_2$ have been studied. Although product excited H or D atoms which decay via the $2p$-$1s$ Lyman-α-emitting transition may result from a variety of collision mechanisms, some interpretation has been possible using data from earlier experiments.

## I. INTRODUCTION

THIS paper reports measurements of absolute cross sections for production of Lyman-α radiation resulting from impacts of ions on gaseous targets. An ion beam of selected energy between 1 and 25 keV is allowed to traverse a pressure-monitored, target gas cell containing the target species. Lyman-α photons emitted at 90° to the beam trajectory are observed with an iodine-filled, oxygen-filtered Geiger counter as developed by Brackmann, Fite, and Hagen.[1] The existing low-energy data of Dunn, Geballe, and Pretzer[2] were used as a standard of normalization to make the present measurements absolute.

Numerous mechanisms exist through which an excited H atom may be produced during an ion-target encounter. For atomic ions ($H^+$ or $D^+$) on molecular targets ($H_2$ or $D_2$) we may have as sources for Lyman-α radiation,

$$H^++H_2\rightarrow H^*+[H^++H]\,, \qquad (1)$$

$$\rightarrow [H^++H]+H^*\,, \qquad (2)$$

$$\rightarrow [H+H^+]+H^*\,, \qquad (3)$$

where the order of the participants on the left has been preserved. Collision products appearing in brackets have not been detected here and their states, whether bound or free, ground state or excited, are not specified.

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