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 1×10^{-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 1×10^{-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 7×10^{-16} cm^2, we would expect the peak cross section of this process, at 2 eV, to be of the order of 1×10^{-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,

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

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

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

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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[1] R. F. Brackmann, W. L. Fite, and K. E. Hagen, Rev. Sci. Instr. **29**, 125 (1958).

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For molecular ions (H_2^+ or D_2^+) on molecular targets there may be contributions from

$$H_2^+ + H_2 \rightarrow H^* + [H^+ + H + H] \quad (4)$$

$$\rightarrow H^* + [H + H + H^+] \quad (5)$$

$$\rightarrow [H^+ + H + H] + H^* \quad (6)$$

$$\rightarrow [H + H + H^+] + H^*. \quad (7)$$

For He^+ projectiles on molecular targets, the possibilities are

$$He^+ + H_2 \rightarrow [He^+ + H] + H^* \quad (8)$$

$$\rightarrow [He + H^+] + H^*. \quad (9)$$

Finally, for H^+ and H_2^+ on N_2, we may have

$$H^+ + N_2 \rightarrow H^* + [N + N^+], \quad (10)$$

and

$$H_2^+ + N_2 \rightarrow H^* + [H^+ + N + N] \quad (11)$$

$$\rightarrow H^* + [H + N + N^+]. \quad (12)$$

Wherever possible, individual reactions will be suggested as the mechanism(s) responsible for the observed signal.

In each of the above cases, an excited H or D atom in the $2p$ level decays to the ground $1s$ level through emission of a Lyman-α photon. Atoms excited to higher levels during the collisions may also contribute to the measured Lyman-α signal by cascading through the $2p$ level. In reactions (2), (3), and (6)–(9), the emitters are slow and do not leave the region of detection before their decay is complete. For types (1), (4), (5), and (10)–(12), the apparatus detects only a small fraction of the total Lyman-α radiation resulting from cascade through Balmer-emitting states since the fast excited atoms move from the viewing region before reaching this point of their decay schemes.

It is to be stressed that all observed photons are emitted at or near 90° with respect to the beam axis. Cross sections presented here are total cross sections only if the radiation is emitted isotropically.

II. TECHNIQUE

The detailed properties of the apparatus employed for these measurements have been described previously.[2–4] Consequently, only a brief summary of its characteristics will be presented here.

Ions produced by electron bombardment are accelerated to 1000 eV and focused into a magnetic analyzer for selection of the ionic species to be utilized as a projectile. The desired ion energy is obtained by subsequent acceleration before the ions enter the collision cell. The collision cell incorporates several aligned entrance apertures (to maintain a 50-to-1 differential pumping ratio between the cell and the surrounding vacuum envelope), an observation region with an electrically shielded LiF window (to view the resultant ultraviolet radiation), and an exit slit (to determine a focused trajectory of the ion beam through the interaction region). The ion collector is segmented to allow a crude measure of the spatial profile of the beam. The slit and the segmented collector were employed to align the beam so that the photon signal was independent of small variations in beam trajectory.

The target gas samples (H_2, D_2, and N_2) were taken from standard gas cylinders. To reduce contamination by water vapor, each target gas sample was allowed to flow slowly through a trap at dry-ice temperature prior to its introduction into the collision cell.

Ions passing through the interaction region produce photons via one of the reactions listed in Sec. I. Some of the photons radiated at 90° to the beam direction escape through a series of LiF windows into the Geiger counter. The counter itself is sensitive only to radiation falling between 1080 and 1317 Å. Additional wavelength discrimination is obtained by insertion of an oxygen cell between the interaction region and the counter; oxygen transmits only through seven narrow windows between the above wavelength limits.[5] The blindness of the oxygen filter to other radiations within this spectral region from the projectile and target systems employed here (for example, molecular band emission) has been discussed at length in Ref. 2, where it was concluded that Lyman α represented the main contribution to the observed signal.

The cross sections were found from the relation

$$\sigma(E) = \frac{[N(E) - N_b(E)](P - P_b)_1 I_1}{[N(E) - N_b(E)]_1 (P - P_b) I} \sigma(E)_1,$$

where $\sigma(E)_1$ is an absolute cross section obtained from previous studies,[2] $N(E)$ is the measured count rate, $N_b(E)$ is the background count rate with the target gas removed from the collision cell (normally less than 10% of the total), P is the target-gas pressure, P_b is the residual background pressure, and I is the ion current. Quantities bearing the subscript 1 refer to the standard reaction.

Typical ion currents ranged about 0.1 μA and target pressures were generally of the order of 5×10^{-5} Torr. Beam currents were measured with standard microammeters and pressures with an ionization gauge (the differing gauge sensitivity for N_2 being taken into account). Photon counting rates were found to vary linearly with beam current and target-cell pressure for H^+, H_2^+, He^+ on H_2 and for H^+, H_2^+ on N_2. These

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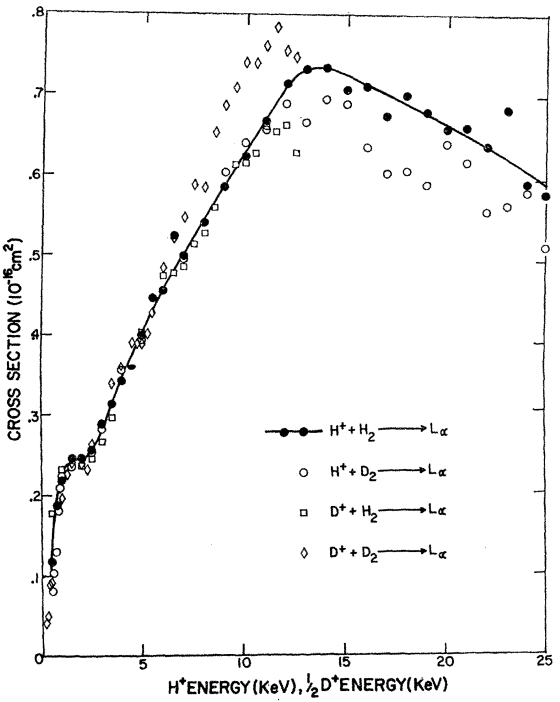

FIG. 1. Measured cross sections for Lyman-α emission from collisions of H^+ and D^+ with H_2 and D_2. The line is drawn through the data for $H^+ + H_2$, which are absolute. The other data are normalized to this curve at various energies given in the text.

checks were not repeated when deuterium was substituted for hydrogen.

The observed reproducibility of the cross-section curve relative to the signal at a fixed calibration energy is within ±15%. This figure is consistent with estimates of the errors introduced by the various readings that enter into the computation of the cross section if these are considered random. Absolute cross sections are obtained by comparison with the earlier results of Ref. 2, which quotes an uncertainty of ±40%. Thus the absolute magnitudes given here are believed to be reliable within ±55%.

III. RESULTS AND DISCUSSION

All cross sections are presented in units of 10^{-16} cm^2. Projectile energies are given in keV. D^+ and D_2^+ energies have been scaled by a factor of 2 to allow comparison of data for these ions with those of H^+ and H_2^+ at equivalent projectile velocities.

A. H^+, D^+ on H_2, D_2

The cross sections for production of Lyman-α radiation resulting from collisions between pairs of these systems are shown in Fig. 1. The H^+–D_2, and D^+–H_2 and D^+–D_2 cross sections were not calibrated absolutely and are normalized to that for H^+–H_2 at 6-keV, 4.5-keV, and 3-keV H^+ energy, respectively. Note that these results have similar features when compared at equivalent projectile velocities. These cross sections exhibit a knee in the vicinity of 1.5-keV H^+ energy followed by a large maximum at about 14 keV. Reactions 1, 2, and 3 as listed in Sec. I may all contribute to the detected signal. Although no technique was available in these experiments to distinguish among the possibilities, it is tempting to try to interpret the shape of the observed cross section. In earlier experiments on charge transfer between protons and the rare gases.[3,6,7] it was found for many cases that capture leading to population of the $n=2$ levels exhibited a large cross-section maximum at low projectile energies. The low-energy structure observed in these measurements generally reaches its maximum value at about the same energy as the maximum probability for ground-state charge capture. This fact led the authors to postulate[7] that ground- and excited-state capture may be coupled during the collision interval. In the recent experimental data of Stebbings, Young, Oxley, and Ehrhardt[8] for capture into the $n=2$ level during proton–H-atom collisions, structure also was apparent at low energy (where the total charge-transfer process is most effective). Several theoretical papers[9,10] have attempted to explain these observations in terms of a coupled-channel mechanism. The qualitative agreement between theory and experiment appears to be good, although the cross-section magnitudes are in poor agreement. It seems likely, however, that the coupling mechanism is responsible for the observed results.

In contrast to our earlier proton–rare-gas results, the knee in the present cross section does not fall where the maximum in the total (presumably mostly ground state) capture cross section lies but nevertheless is prominent at low energies where total capture probabilities are large. The discrepant feature weakens the case for interpreting the low-energy structure as a consequence of charge capture [reaction type (1) above] but nonetheless this possibility remains a reasonable one at this time.

The large maximum in the cross section at about 14 keV may then be the result of reactions (2) and (3), i.e., direct dissociative excitation to repulsive excited levels of the neutral molecule or charge capture leaving the H_2^+ ion in a dissociative excited state. This assignment is verified to some degree by the work of Hughes, Lin, and Hatfield,[11] who found the maximum in the cross sections for Balmer emissions from the target-H_2 mole-

[6] D. Pretzer, B. Van Zyl, and R. Geballe, Phys. Rev. Letters **10**, 340 (1963).
[7] D. Jaecks, B. Van Zyl, and R. Geballe, Phys. Rev. **137**, A340 (1965).
[8] R. F. Stebbings, R. A. Young, C. L. Oxley, and H. Ehrhardt, Phys. Rev. **138**, A1312 (1965).
[9] D. R. Bates and D. A. Williams, Proc. Phys. Soc. (London) **83**, 425 (1964).
[10] L. Wilets and D. F. Gallaher, Phys. Rev. **147**, 13 (1966).
[11] R. H. Hughes, S. Lin, and L. L. Hatfield, Phys. Rev. **130**, 2318 (1963).

cule following proton bombardment to lie at about 15-keV H^+ energy. The process for excitation to dissociative Balmer-emitting levels of H_2 and H_2^+ should be similar to that for excitation to dissociative Lyman-α emitting states.

B. H_2^+, D_2^+ on H_2, D_2

The results of our cross-section measurements for these collision partners are shown in Fig. 2. Any of reactions (4)–(7) may contribute here and in view of the lack of structure in these curves no interpretation in terms of mechanism will be attempted at this time. For these and all remaining data presented here, each individual cross-section curve has been calibrated absolutely.

Examination of the data reveals that cross sections in which the detected Lyman-α is radiated from a D atom appear somewhat smaller than when the emitter is an H atom. This effect can be attributed to the nature of the oxygen filter. The Lyman-α transition of the D atom is shifted from that of the H atom by about 0.3 Å because of the difference between the reduced masses of these species. Estimates of the magnitude of this effect from the published shape of the transmission window of the oxygen filter[5] show that D^+ atom-Lyman-α radiation should be absorbed about 1.25 times as much as that emanating from the lighter isotopes. The measured results indicate differences between cross sections by about this amount (see for example, He^+ on H_2 and D_2). Indeed, in comparing H^+ and D^+ collisions with Ne, for example, where no radiation other than Lyman-α can excite the unfiltered Geiger counter, no difference in signal when compared at comparable projectile velocity could be measured with an unfiltered system. Presumably, differences such as these would also exist in the cases of atomic ions (H^+ and D^+) on molecular targets (H_2 and D_2) discussed above had separate absolute calibrations been made.

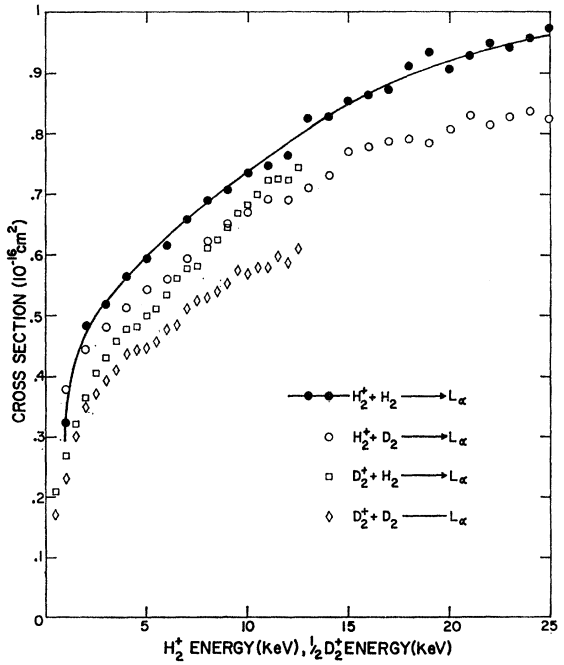

FIG. 2. Measured absolute cross sections for Lyman-α emission from collisions H_2^+ and D_2^+ with H_2 and D_2.

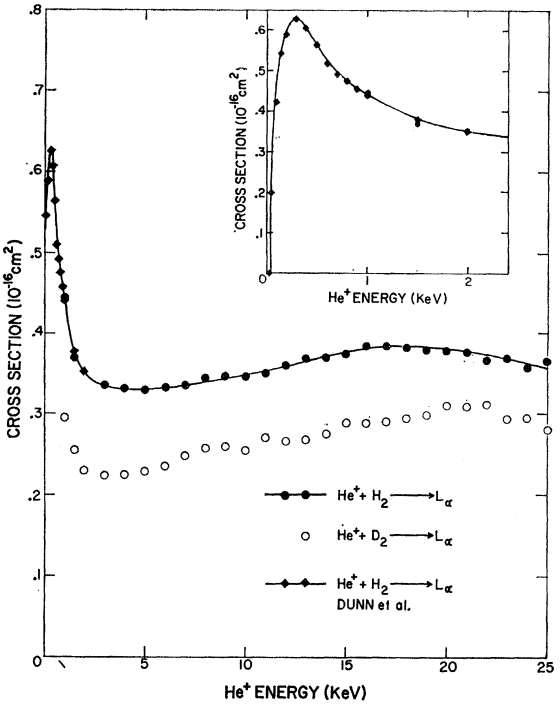

FIG. 3. Measured absolute cross sections for Lyman-α emission from collisions of He^+ with H_2 and D_2.

C. He^+ on H_2, D_2

For these pairs the source of detected radiation is the target member of the collision. The form of the curves of Fig. 3 suggests that they result from two distinct processes. The large low-energy maximum is attributed to process 9. For this process, the difference between the internal energies of the system at infinite separation in their initial and final configurations is only 3.5 eV. The cross sections of reactions characterized by such small ΔE's generally reach maxima at low projectile energies. Here, the possibilities for a more intimate reaction, i.e., a potential curve pseudocrossing, are larger. This assignment has been investigated in some detail in Ref. 2, the data from which are included here for projectile energies below 2000 eV. The high-energy contribution is then probably the result of the dissociative excitation of H_2, i.e., reaction-type (8). The effect of the filter absorption of the deuterium Lyman-α line is most evident here.

One might ask whether by comparing Figs. 1–3 from the collisions of H^+ and D^+, H_2^+ and D_2^+, and He^+,

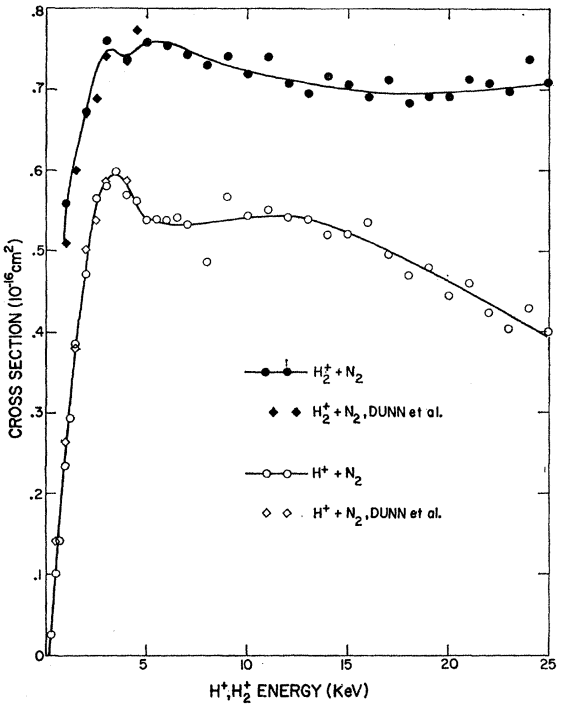

FIG. 4. Measured absolute cross sections for Lyman-α emission from collisions of H^+ and H_2^+ with N_2.

respectively, on H_2, one can gain information about the dissociative excitation processes, i.e., reactions (2), (6), and (8). The data suggest that neither the laboratory projectile energy nor the energy available for interaction in the center-of-mass system provides a proper scale for comparison of similar features in the cross sections. That the cross sections scale according to projectile velocity when systems of such dissimilar structure are involved remains a possibility but the multiplicity of emitters when H^+ and H_2^+ are employed prohibits us from reaching a conclusion on this point. It is unlikely that, in this energy range, the details of the collision can be completely ignored; intermediate states ought to be different for each of the three reaction groups considered above. From an experimental standpoint, additional information could be obtained by studying the dissociative excitation process with a wider variety of projectile systems.

D. H^+, H_2^+ on N_2

Figure 4 shows results of our investigation for ions on N_2 and includes for comparison the low-energy data of Ref. 2. These results must be considered less reliable than the others due to the possibility that molecular nitrogen radiations have penetrated the oxygen filter. For the reactions discussed in previous sections, signal-counting rates with the oxygen-filter cell evacuated are approximately twice as large as those obtained under normal conditions (about 1-cm path length of oxygen at atmospheric pressure). This ratio is consistent with the calculated attenuation of the Lyman-α photon flux by the filter. In addition, the experimental cross section was similar in shape with and without oxygen in the filter, suggesting that most of the radiation viewed by the detector was Lyman-α. In the case of N_2, however, the situation was different. The shape of the cross-section curve with an evacuated filter was of completely different character and roughly one order of magnitude larger than that observed with oxygen in the filter. This observation suggests that one or more of the excited states of the nitrogen systems (N^+, N, N_2^+ or N_2) which are known to radiate in the region of sensitivity of the unfiltered counter are populated by these collisions. What fraction of this radiation penetrates the oxygen filter at or near one of its transmission maxima is unknown.

Despite this uncertainty, results for these systems are presented here to bring out some interesting aspects of the structure apparent in these curves. Observe, for example, the definite double maximum present in the H^+–N_2 data. This result bears striking similarity to measurements by the authors[6] of the Lyman-α emission cross sections for proton–rare-gas collisions, most closely resembling those for protons on argon. The low-energy Lyman-α peak occurs at about the same energy as the total charge-transfer maximum, as has been the case for proton–rare-gas collisions. Here with a molecular target is experimental evidence that excited-state capture appears to be coupled to ground-state capture. Similar structure has been observed by Murray, Young, and Sheridan[12] in the Balmer-α radiation emitted following H^+–N_2 collisions.

The results for H_2^+ on N_2 resemble those for molecular ions on the rare gases, particularly Ar. The interpretation of this curve follows closely that given in Ref. 4.

ACKNOWLEDGMENTS

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