Lyman-Alpha Emission Cross Sections for H_2^+ and D_2^+ Collisions with the Rare Gases*

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Cross sections for the emission of Lyman-alpha radiation resulting from H_2^+– and D_2^+–rare-gas collisions have been measured in the energy range from 1 to 25 keV. Excited states of the H or D atoms which decay via the $2p$-$1s$ Lyman-alpha transition result from charge transfer to antibonding states of the H_2 or D_2 molecules or from direct excitation to antibonding states of the molecular-ion projectiles. The D_2^+ cross sections are similar to those for H_2^+ when plotted at equivalent projectile velocities. The results are compared with earlier measurements of the Lyman-alpha emission cross sections resulting from H^+ and D^+ collisions with rare gases and with the total charge-transfer cross sections for the H_2^+–rare-gas systems.

INTRODUCTION

THIS paper reports measurements of absolute cross sections for the production of Lyman-alpha radiation in collisions of H_2^+ and D_2^+ with rare gases. A beam of molecular ions, ranging in energy between 1 and 25 keV, is allowed to traverse a pressure-monitored target gas cell containing rare-gas atoms. Lyman-alpha photons created during passage of the beam through the collision cell are detected with an iodine-filled, oxygen-filtered Geiger counter similar to that described by Brackmann, Fite, and Hagen.[1] The absolute values of the cross sections were obtained by comparing the measured count rates at low energies with the cross section for Lyman-alpha emission resulting from H_2^+-He collisions as reported by Dunn, Geballe, and Pretzer.[2]

Two basic processes may lead to the presence of an excited H atom among the products of an H_2^+ collision with a target gas T. These processes are

$$H_2^+ + T \rightarrow H_2^* + T^+ \rightarrow H(2p) + H + T^+ \qquad \text{(A)}$$

and

$$H_2^+ + T \rightarrow (H_2^+)^* + T \rightarrow H(2p) + H^+ + T. \qquad \text{(B)}$$

Analogous reactions occur with D_2^+ as the projectile. Reaction A will be called charge transfer plus dissociation and reaction B, projectile dissociation or breakup. Hydrogen atoms existing in the $2p$ state as a result of an encounter decay to the ground $1s$ state with the emission of a Lyman-alpha photon. Atoms formed in higher excited states may also contribute to the Lyman-alpha signal by cascade contribution through Balmer-emitting states. Essentially all of the atoms in the metastable $2s$ state pass from the observation region before radiating and escape detection. The final states of the other collision products in reactions A and B have not been determined in the experiments reported here.

TECHNIQUE

The ion-beam apparatus employed in the present measurements has been described by Dunn[3] and by Dunn, Geballe, and Pretzer.[4] Modifications of the basic apparatus include the extension of the ion-energy range to 25 keV, the addition of a pressure-monitored collision cell, and the employment of a segmented beam collector to allow study of the beam profile. These modifications have been described by Pretzer, Van Zyl, and Geballe.[5]

The relationship between the measured count rate and the cross section may be expressed as

$$\sigma(E) = \frac{[N(E) - N_b(E)]P_0 e}{(P - P_0) I L \Omega n_0 \epsilon}, \qquad (1)$$

where $\sigma(E)$ is the cross section, $N(E)$ is the measured count rate, P_0 is the atmospheric pressure, e is the electronic charge, P is the target-gas pressure, I is the ion current, L is the length of the interaction region viewed by the detector, Ω is the solid angle subtended by the detector at the interaction volume, ϵ is the efficiency of the detection system, and n_0 is Loschmidt's number. The background count rate $N_b(E)$, resulting from the impact of the ion beam with the residual target cell constituents at pressure P_b, is usually about 5% of the total signal.

Because of the inherent uncertainties associated with a calculation of the solid angle Ω, and the time dependence of the counter sensitivity ϵ, absolute cross sections are difficult to extract from Eq. (1). Using

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[1] R. F. Brackmann, W. L. Fite, and K. E. Hagen, Rev. Sci. Instr. **29**, 125 (1958).
[2] G. H. Dunn, R. Geballe, and D. Pretzer, Phys. Rev. **128**, 2200 (1962).
[3] G. H. Dunn, thesis, University of Washington, 1961 (unpublished).
[4] D. Pretzer, thesis, University of Washington, 1963 (unpublished).
[5] D. Pretzer, B. Van Zyl, and R. Geballe, *Proceedings of the Third International Conference on the Physics of Electronic and Atomic Collisions* (North-Holland Publishing Company, Amsterdam, 1964), p. 618.

instead the ratio of measured cross sections we obtain

$$\sigma(E)=\frac{[N(E)-N_b(E)](P-P_b)_1 I_1}{[N(E)-N_b(E)]_1(P-P_b)I}\sigma(E)_1, \quad (2)$$

where $\sigma(E)_1$ is an absolute cross section obtained from previous studies, i.e., the absolute values $H_2^+ + He$ reported by Dunn, Geballe, and Pretzer.[2] The shape of the measured $H_2^+ + He$ count rate versus energy curve is in good agreement with the data of these earlier investigations in the energy region where they overlap.

The ion currents employed were about 0.05 μA and the ion-energy distribution had an apparent half-width of about 100 V as measured by a retarding potential. The ion beam was mass-analyzed at 1000 eV and subsequently accelerated to the desired energy. Target gas pressures were generally about 5×10^{-5} mm Hg. The gas samples of Ne, Kr, and Xe were "spectroscopically pure" and those of He and Ar were taken from standard gas cylinders. Each was passed through a trap at dry-ice temperature. The measured count rates were found to depend linearly on ion current and target gas pressure.

The wavelength discrimination of the oxygen filter can be ascertained from the absorption cross section of oxygen reported by Watanabe.[6] In the region between 1040 and 1340 Å (the region of sensitivity of the unfiltered counter), oxygen readily absorbs ultraviolet except at seven narrow transmission "windows," one of which contains the Lyman-alpha wavelength. The counter filter combination is discussed in Ref. 2 at some length where it is shown that it is unlikely for radiations from H_2, H_2^+, He, or He^+ to contribute appreciably to the signal detected with the counter-filter combination. It remains to show whether radiation from the other rare gases is capable of penetrating the oxygen filter.

Although the spectrum of Ne exhibits no lines in this portion of the ultraviolet, potentially troublesome lines are present in the case of Ar, Kr, and Xe. In Ar and Xe the emission lines lie at wavelengths for which oxygen absorption is large. Kr has an emission line at 1165 Å, close to an oxygen-transmission window at 1167 Å. The effect of this Kr line on the data will be discussed along with the results of the measurements. Even in this case, however, there is reasonable evidence that the primary contribution to the detected signal comes from the $2p-1s$ transition of the H atom.

Although the photon detector looks at right angles to the beam trajectory, the finite dimensions of the interaction volume necessitate a small Doppler-shift correction to the data. Lyman alpha lies nearly exactly at a transmission maximum of the oxygen filter so that any Doppler shift results in greater filter absorption. This correction has been estimated both experimentally and by means of an approximate calculation and was found to be less than 10% for the measurements reported here. As the exact error introduced by Doppler effect is difficult to determine accurately because of uncertainty about the precise shape of the absorption curve, no correction has been applied to the results. The uncertainties to be listed later include an estimate of this effect.

In addition to the Doppler effect, the narrowness of the oxygen-transmission window gives rise to another effect when D_2^+ is the projectile ion. Due to the difference in reduced mass between the H and D atoms, the Lyman-alpha transition in the latter is shifted by about 0.3 Å from that of the H atom. Here again, the filter absorption at the shifted wavelength will be increased so that the measured cross sections should be smaller for D_2^+ projectiles. Auxiliary measurements with the oxygen filter evacuated indicated that, at equal velocities, the count rates were within $\pm5\%$ when H_2^+ and D_2^+ on Ne were compared.

It has been mentioned in the Introduction that some of the Lyman-alpha photons detected in the present measurements may have their origin in hydrogen atomic levels with $n\geq3$, which have decayed to the $2p$ state with the emission of Balmer-series photons. Since many of the interactions may result in highly excited atoms, the population of the $2p$ level could be influenced appreciably by this effect. Indeed, in the earlier proton–rare-gas data reported in Ref. 2, it was suggested that the second peaks appearing in the measured cross sections could be the result of such cascade effects.

An important experimental limitation must be placed on the capability of the apparatus to detect Lyman-alpha radiation resulting from a cascade population of the $2p$ level. Since the higher s and d states of the H atom are long-lived (i.e., 1.6×10^{-7} sec for the $3s$ state and 1.6×10^{-8} sec for the $3d$, with the $n>3$ levels being even longer lived), the path length available in the apparatus is insufficient for attainment of a steady-state balance between excitation and radiation. Some highly exicted atoms pass out of the region of observation before decaying to the $2p$ level. Estimates of the magnitude of this effect can be obtained from the relation

$$I/I_0=1-e^{-xP/v}, \quad (3)$$

where x is the distance from the entrance of the collision chamber to the point at which the observations are made, P is the transition probability from the upper state, and v is the beam velocity. I/I_0 represents the fraction of the steady-state intensity which can be observed as a function of x and v from each of the upper states that will eventually lead to Lyman-alpha emission detectable in our apparatus. However, since the relative populations of the upper states are unknown, we cannot calculate the percentage of detected radiation which is a consequence of Balmer-emitting channels.

[6] K. Watanabe, *Advances in Geophysics* (Academic Press Inc., New York, 1958), Vol. 5, p. 153.

It is possible, however, to determine experimentally the importance of the cascade effect. The apparatus has been modified so that the x of Eq. (3) is increased from 1.5 to 4.0 cm. With this new arrangement, regardless of the detailed population distribution among the upper states, the population of the $2p$ state via cascade must be increased because of the longer time available for radiation. On repeating the earlier measurements[2] of $H^+ + Ar$ a new relative cross section was obtained and normalized to the previous result at 6-keV proton energy. The new measurements were everywhere within 5% of the older results.

The absolute values attributed to the measurements reported in this paper carry the uncertainty of the earlier work on which they are based[2] in addition to that introduced by the present studies. The former was given as ±40%; we regard ±50% as a reasonable estimate for the present results except for the experiments involving Kr. This uncertainty is greater, perhaps as much as ±60%, because of the possibility that some radiation from Kr* is penetrating the filter. Below an incident H_2^+ energy of 1.5 keV the ion beam begins to diverge in the collision region and the data become somewhat less reliable.

The results of the present measurements have been expressed in the form of total cross sections, assuming that the radiation is emitted isotropically. The data could be corrected if the radiation were shown to be polarized and the degree of polarization were to be measured.

RESULTS

All cross sections are presented in units of 10^{-16} cm^2. H_2^+ energies are in the laboratory frame and are given in keV. D_2^+ energies are scaled by a factor of 2 to allow the cross sections to be compared at equivalent velocities of the projectile ions. The order of increasing target atomic number is not followed in this presentation because Ar and Kr exhibit irregular behavior that is best handled after the other cases have been described.

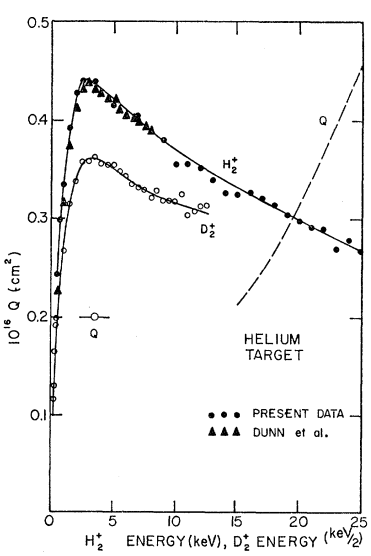

FIG. 1. Cross sections for Lyman-alpha production from H_2^+- and D_2^+-He collisions. The dashed curve is the total charge-exchange cross section for H_2^+ on He from Stedeford and Hasted (footnote 7). Present results are normalized to the data of Dunn *et al.* (footnote 2) at 6-keV H_2^+ energy.

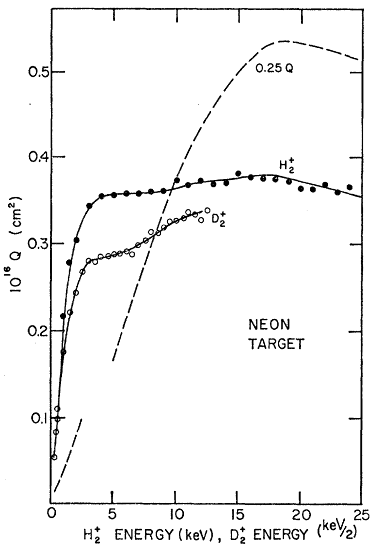

FIG. 2. Cross sections for Lyman-alpha production from H_2^+- and D_2^+-Ne collisions. The dashed curve is the total charge-exchange cross section for $H_2^+ + Ne$ from Stedeford and Hasted (footnote 7).

H_2^+, $D_2^+ + He$

The cross sections for the production of Lyman-alpha resulting from collisions of H_2^+ and D_2^+ with He are shown in Fig. 1. Also shown are the Lyman-alpha measurements of Dunn, Geballe, and Pretzer[2] and the total charge-transfer cross section for $H_2^+ + He$ as reported by Stedeford and Hasted.[7]

Note that the Lyman-alpha cross section for $H_2^+ + He$ is considerably larger than the total charge-transfer cross section in the low-energy region. Since our particular charge-transfer reaction can be no more probable than the sum of all charge-transfer reactions (represented by the total charge-transfer cross section), we interpret the low-energy peak exhibited by the Lyman-alpha data as the result of the projectile breakup process (type B) of the form

$$H_2^+ + He \rightarrow H^+ + H(2p) + He,$$
$$H(2p) \rightarrow H(1s) + L_\alpha.$$

The D_2^+ cross section exhibits a similar structure and suggests that the principal features of the cross section are determined by the velocity of the projectile ion.

The state of the target atom is assumed to be unaltered by collisions of type B. If this outcome is in fact dominant, Lyman-alpha peaks attributed to the breakup reaction will always be observed at the same projectile velocity regardless of the nature of the target atom. We find that all of the cross sections presented in this paper exhibit structure in the velocity range around 5×10^7 cm/sec (corresponding to an H_2^+ energy of 3 keV) which therefore is attributed to the projectile breakup reaction.

[7] J. B. H. Stedeford and J. B. Hasted, Proc. Roy. Soc. (London) **A227**, 466 (1955).

H_2^+, $D_2^+ + Ne$

The data for these interacting pairs are shown in Fig. 2. The shoulder at 3–4-keV H_2^+ energy is attributed to the breakup reaction discussed for He.

Figure 2 also shows the total charge-transfer cross section for $H_2^+ + Ne$ are reported by Stedeford and Hasted.[7] Note that a peak lies beneath the total charge-transfer maximum. A similar behavior was found in collisions of H^+ and D^+ with the rare gases reported by Pretzer, Van Zyl, and Geballe.[5] In these earlier measurements, charge transfer was the only mechanism by which Lyman-alpha radiation could be produced. The similarity suggests that the process responsible for the 18-keV maximum is a charge-transfer reaction of the form

$$H_2^+ + Ne \rightarrow H + H(2p) + Ne^+$$
$$H(2p) \rightarrow H(1s) + L_\alpha .$$

H_2^+, $D_2^+ + Xe$

The data obtained from studies of these reaction pairs are shown in Fig. 3. The general features of the cross sections include a large maximum at low energies, a noticeable contribution in the region of 4-keV H_2^+ energy, and an additional maximum at about 21 keV. Figure 3 also shows the total charge-transfer measurement of Stedeford and Hasted[7] which again has a maximum near the same velocity as a Lyman-alpha peak. Again, this peak is attributed to a charge transfer process of type A. The structure at 4-keV H_2^+ energy occurs at the velocity which corresponds to the breakup reaction maximum. The appearance of two peaks resulting from charge transfer would not seem unreasonable in view of the behavior exhibited by the cross sections for Lyman-alpha production in H^+– and D^+–rare-gas collisions. The maximum at 21 keV is such a manifestation. The similarities between cross sections for Lyman-alpha production resulting from molecular-ion–rare-gas collisions and those resulting from atomic-ion–rare-gas collisions will be discussed in more detail in the next section.

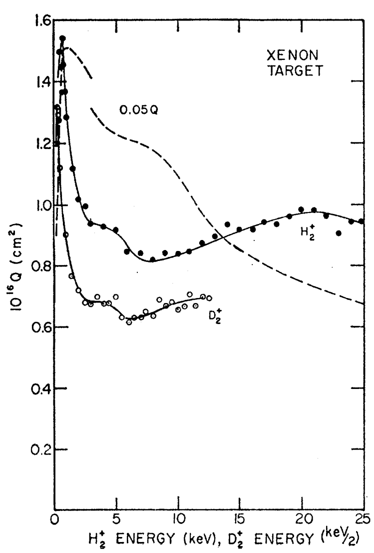

FIG. 3. Cross sections for Lyman-alpha production from H_2^+- and D_2^+-Xe collisions. The dashed curve is the total charge-exchange cross section for $H_2^+ + Xe$ from Stedeford and Hasted (footnote 7).

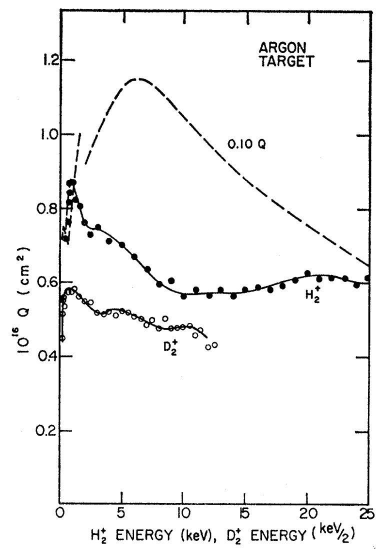

FIG. 4. Cross sections for Lyman-alpha production from H_2^+- and D_2^+-Ar collisions. The dashed curve is the total charge-exchange cross section for $H_2^+ + Ar$ from Stedeford and Hasted (footnote 7).

H_2^+, $D_2^+ + Ar$

The general appearance of the data for these reacting pairs is similar to that for ions on Xe. The results of the measurements are shown in Fig. 4. It is interesting to note, that in the case of Ar, the low-energy Lyman-alpha peak does not lie beneath the total charge-transfer maximum but does lie near the small secondary maximum in the total charge-transfer curve. Since similar behavior was observed in the Lyman-alpha cross section for H^+ on Ar, we interpret the low-energy maximum as charge transfer and the other structure in a manner similar to that for Xe.

H_2^+, $D_2^+ + Kr$

The measured cross sections for these reacting pairs are shown in Fig. 5. The Kr data are generally similar to the Xe data and the same mechanisms are proposed as responsible for the signal.

It was mentioned earlier that Kr has an emission line at 1165 Å, close to an oxygen-transmission window at 1167 Å. In order to determine whether Kr radiation was penetrating the oxygen filter to an appreciable extent, the filter was removed from in front of the counter, and the cross-section measurement was repeated. We found that, under these conditions, the cross section had the same essential features except that it was greatly enhanced in the vicinity of 6-keV H_2^+ energy. In order to test whether this enhancement was due to Kr emission, the reaction $He^+ + Kr$ was studied with the filter present. The recorded count rate exhibited a maximum at about 12 keV. Essentially no signal was observed when He^+ bombarded He. A similar result was found[5] when H^+ and D^+ were used to bombard Kr. The Kr signal in these cases reached maxima at 3 and 6 keV, respectively.

We conclude that some Kr radiation penetrates the filter in the vicinity of 6-keV H_2^+ energy to an extent that is uncertain, but is appreciably smaller than the Lyman-alpha contribution.

Ar and Xe also have emission lines within the region of response of the unfiltered counter. Again, data taken with the filter evacuated showed cross sections enhanced in the region of 6-keV H_2^+ energy. However, bombardment with He^+ showed that very little of the emission from these targets penetrated the filter, an observation consistent with the absorption properties of oxygen.

DISCUSSION

We will take up here the possibility of being able to separate (qualitatively) the contributions to the measured signal from charge transfer and projectile breakup, the similarity between the H_2^+ and D_2^+ cross sections, and the appearance of the double peak structure associated with charge-transfer interactions.

As mentioned under Results, projectile breakup can occur without any change in the state of the target atom. The interaction is then one in which the target atom merely acts as an obstacle upon which the incident H_2^+ can split into a proton and an excited H atom. In this simple model, the internal structure of the target atom may not be important and one might expect that the cross section for the breakup process is independent of the specific target system. In the case of $H_2^+ + He$ (where the signal was shown to originate primarily from processes other than charge transfer), we have an opportunity to study the features of the breakup reaction. We find a maximum at 3 keV and a smooth decay at higher energies. All other cross sections presented in this report also show the presence of structure at 3 keV. As a further check, a beam of H_2^+ was allowed to collide with N_2 and the Lyman-alpha radiation resulting from the interaction was observed.[8] Again, we found evidence of a peak at about 3 keV. All of the data are consistent with the above explanation for the structure observed at 3-keV H_2^+ energy.

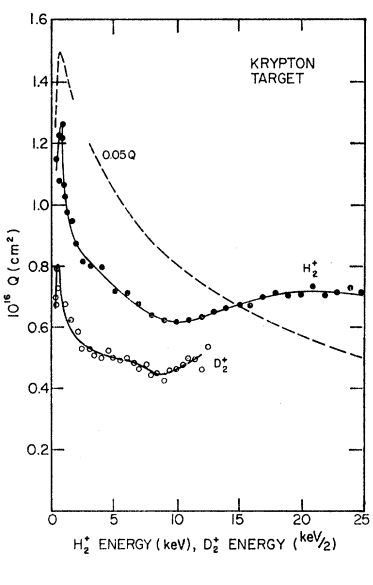

FIG. 5. Cross sections for Lyman-alpha production from H_2^+- and D_2^+-Kr collisions. The dashed curve is the total charge-exchange cross section for $H_2^+ + Kr$ from Stedeford and Hasted (footnote 7).

TABLE I. Empirical relationship between projectile mass and separation of Lyman-alpha charge-transfer cross-section maxima. E_1 and E_2 are energies in keV of first and second maxima and m is projectile mass in amu.

Target	Ion	E_1	E_2	$(E_2-E_1)/m$
He	H^+	19.0	(27.0)	8.0
	D^+	...	...	...
	H_2^+	...	...	...
	D_2^+	...	...	...
Ne	H^+	6.0	14.0	8.0
	D^+	12.0	...	...
	H_2^+	16.0	...	...
	D_2^+	...	...	...
Ar	H^+	3.0	12.0	9.0
	D^+	6.0	21.0	7.5
	H_2^+	0.8	21.0	10.1
	D_2^+	1.5	...	...
Kr	H^+	0.4	11.0	10.6
	D^+	0.8	20.0	9.6
	H_2^+	0.8	21.0	10.1
	D_2^+	1.0	...	...
Xe	H^+	0.4	10.0	9.6
	D^+	0.8	20.0	9.6
	H_2^+	0.8	20.0	9.6
	D_2^+	0.8	...	...

It is apparent from the data that all processes involved in these collisions scale with the projectile velocity, as is expected on the basis of simple theoretical considerations. The second feature of the data worthy of comment is the similarity between the H_2^+ and D_2^+ data when compared at identical projectile velocities. The smaller magnitudes of the D_2^+ data have been accounted for already by the properties of the oxygen filter.

It seems worthwhile to point out an empirical relationship among the measurements made with atomic- and molecular-ion projectiles. We exclude from this consideration the portions of the molecular-ion cross sections which have been attributed to projectile breakup and concentrate on those features of the cross section curves that apparently arise from charge-transfer processes. The quantity $(E_2-E_1)/m$, where E_1 and E_2 are the projectile energies in keV at which the first and second maxima occur and m is the mass of the incident ion in atomic mass units, is given in Table I. It appears that this quantity is approximately constant for all of the ion-target systems exhibiting two charge-exchange maxima. This observation is consistent with the conclusion that atomic and molecular ions behave here in a generally similar manner insofar as charge transfer is concerned.

[8] B. Van Zyl, thesis, University of Washington, 1963 (unpublished).