# Production of Excited Atoms by Impact of Fast Electrons on Molecular Hydrogen and Deuterium

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Absolute emission cross sections for production of atoms in the $n=2$–6 excited states have been determined for dissociative excitation of molecular hydrogen and deuterium by electrons having energies in the range from 0.05 to 6 keV. The excited atoms have been observed by optical detection of their fluorescence, Lyman-$\alpha$ radiation in the case of $n=2$ and Balmer-$\alpha$, $\beta$, $\gamma$, and $\delta$ radiation in the case of the higher states. In general there is more than one possible molecular transition which can lead to dissociation into a particular atomic state. In the case of the $n=2$ level, however, it has been possible with the aid of previous investigations to identify some transitions which may lead to both the $2s$ and $2p$ atomic states. For the formation of the higher excited states the systematics of the processes has been determined by means of analysis of the data in the Bethe–Born approximation. A strong isotope effect was found for the production of excited atoms from molecular hydrogen and deuterium. Approximately 20% fewer excited atoms are formed in the case of the heavier isotope. This difference arises due to a competition between dissociation and other processes, in particular autoionization.

## I. INTRODUCTION

Electron-impact cross sections for molecular processes find use in many fields of physics and chemistry, in particular collision and astrophysics and radiation and photochemistry. In this paper the radiation from excited hydrogen atoms produced via dissociative excitation of molecular hydrogen and deuterium by electron impact is studied.

Dissociative processes in molecular hydrogen were recognized as early as 1925 by Blackett and Franck,[1] who observed Balmer radiation in electron-impact excitation. More recently other electron-impact experiments have been carried out on dissociation leading to the $n=2$ excited atomic state. In these studies the excited species were detected by observation of Lyman-$\alpha$ radiation. Cross-section measurements have been carried out by Fite and Brackmann,[2] Dunn *et al.*,[3] and de Heer *et al.*[4] The mechanism for H($2s$) formation has been studied by Leventhal *et al.*[5] The cross-section measurements were restricted to the H($2p$) atomic state and, with the exception of Ref. 4, to relatively low energies ($<500$ eV).

In the present work the preceding cross-section measurements for dissociative excitation of $H_2$ by electrons are extended to the H($2s$) level and to higher atomic states ($n=3$, 4, 5, and 6). The latter processes are investigated by observation of Balmer radiation. The electron energy range extends from 0.05 to 6 keV.

Some recent theoretical information on excitation of

molecular hydrogen,[6] dissociation of $H_2{}^+$,[7] and on polarization of radiation resulting from dissociation[8] are used in the interpretation of our results.

Information from experiments of photon impact, ion impact, and other types of electron-impact experiments are considered in the discussion and explanation of our results.

## II. EXPERIMENTAL

### A. General

A complete description of the apparatus, shown here in Fig. 1, has been given in Ref. 9. It consists of a stainless-steel cylindrical vessel divided in two parts. The first contains the electron source and the second the electrode system and a connection to the monochromator allowing observation of the radiation. The electron beam (0–6 keV) is directed into the collision chamber and the current measured in a Faraday cage. An axial magnetic field is produced around both chambers in order to confine the electron beam. Variation of the field strength did not influence the radiation of the processes studied here. Use of a particular potential configuration of the electrode system avoided the effects of secondary electrons.

To study the excitation processes over the total energy range, two different potential configurations of the electrodes in the collision chamber were used (see Ref. 9). From threshold to 500 eV a configuration was used that favored accurate energy definition and a narrow energy distribution in the beam ($\sim 1.5$ eV) while from 200 eV to 6 keV the potentials were such as to ensure maximum suppression of secondary elec-

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[1] P. M. S. Blackett and J. Franck, Z. Physik **34**, 389 (1925).

[2] W. L. Fite and R. T. Brackmann, Phys. Rev. **112**, 1151 (1958).

[3] G. H. Dunn, R. Geballe, and D. Pretzer, Phys. Rev. **128**, 2200 (1962).

[4] F. J. de Heer, H. R. Moustafa Moussa, and M. Inokuti, Chem. Phys. Letters **1**, 484 (1967).

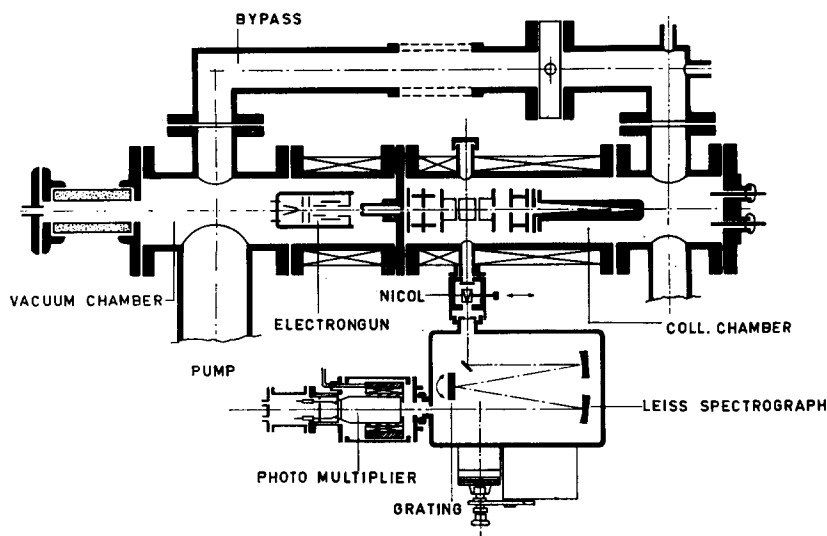[5] M. Leventhal, R. J. Robiscoe, and K. R. Lea, Phys. Rev. **158**, 49 (1967).

[6] S. P. Khare, Phys. Rev. **152**, 74 (1966).

[7] R. N. Zare, J. Chem. Phys. **47**, 204 (1967).

[8] R. J. van Brunt and R. N. Zare, J. Chem. Phys. **48**, 4304 (1968).

[9] H. R. Moustafa Moussa, F. J. de Heer, and J. Schutten, Physica **40**, 517 (1969).

FIG. 1. Schematic view of the apparatus for excitation measurements.

trons. The cross sections determined in the overlapping energy region of the two configurations agreed to within 3%.

In the investigation of formation of metastable H($2s$) atoms a so-called quenching electric field has been used. This field was produced by a potential placed between electrodes above and below the observation region. This is discussed in Sec. II.B.

In order to keep the energy spread in the electron beam relatively small ($\sim$1.5 eV), the magnitude of the beam was kept as low as was consistent with accurately measurable light signals. Beams of about 25 $\mu$A were used near threshold while over 200 $\mu$A was sometimes necessary at high electron energies.

The pressure in the collision chamber was determined with a McLeod gauge modified to overcome the effects of diffusion of mercury vapor.[10] Pressures of between 2.0 and 2.5 $\mu$ were used. Care was taken to ensure that this pressure range was in the region where absorption of radiation by the target gas and secondary processes could be neglected.

Fluorescence from the sample gas was observed at 90° to the electron beam axis. In the case of Lyman $\alpha$ the radiation was detected by a 1-m normal incidence vacuum-ultraviolet monochromator. This instrument, which is described in Ref. 11, is fitted with a MgF₂-coated 1200-lines/mm Bausch & Lomb grating (dispersion 8.3 Å/mm). The Balmer radiation was measured using a Leiss monochromator equipped with an 1800-lines/mm Bausch & Lomb replica grating blazed at 5000 Å (see Ref. 9). Both monochromators were fitted with E.M.I. 6256S photomultipliers, the one used in the vacuum monochromator having a sodium salicylate screen before the photosensitive layer. Because

of the low sensitivity of this multiplier at wavelengths longer than 6500 Å an interference filter (40-Å bandwidth of Baird Atomic) was used in the monochromator for measurement of the Balmer-$\alpha$ radiation (6563 Å). The filter suppressed the effects of stray light.

## B. Measurement of H($2s$) Atoms

The metastable H($2s$) atoms were caused to radiate by application of an electrostatic field across the observation region and measuring the increase in Lyman-$\alpha$ radiation. This method of electric field quenching has been used in previous investigations on atomic[12] and molecular hydrogen.[5]

An electric field of 120 V/cm was found to be sufficient to obtain a saturation in the Lyman-$\alpha$ radiation. This field was applied in such a manner that the potential was not changed along the axis of the electron beam by putting the electrodes (6 and 7 of Ref. 9) above and below the observation region at equal positive and negative voltages.

In order to check whether this change in the potential of the electrodes affected any emission measurement, the He II transition at 1215 Å produced by electrons in helium was investigated. The cross field had no influence on the cross section. Furthermore, the increase of the Lyman-$\alpha$ signal with the quenching voltage was independent of reversal of the field across the observation region. This showed that the electron beam was not being removed from its path by the quenching field.

## C. Evaluation of the Emission Cross Sections

Our relative emission cross sections for Lyman-$\alpha$ radiation were normalized on the absolute cross sec-

[10] F. J. de Heer, J. Schutten, and H. R. Moustafa Moussa, Physica **32**, 1766 (1966).
[11] H. R. Moustafa Moussa and F. J. de Heer, Physica **36**, 646 (1967).

[12] See for example, R. F. Stebbings, W. L. Fite, D. G. Hummer, and R. J. Brackmann, Phys. Rev. **119**, 1939 (1960); I. A. Sellin, *ibid.* **136**, A1245 (1964).
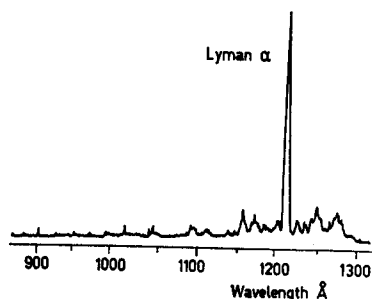
FIG. 2. Reproduction of molecular hydrogen emission spectrum between 900 and 1300 Å, scanned with a monochromator resolution of 2 Å. Electron energy, 50 eV.

tions of Fite and Brackmann.[2] The normalization was done at 250 eV.

The detector used by Fite and Brackmann was an oxygen-filtered iodine-filled Geiger counter. This detector has been described in detail previously.[13] Such a detector plus filter is sensitive not only to Lyman-$\alpha$ radiation but also to other specific wavelengths between 1100 and 1250 A. Therefore Fite and Brackmann quote their cross sections as those for countable ultraviolet. In Fig. 2 we reproduce a scanning of the emission spectrum of molecular hydrogen excited by electrons between 900 and 1300 Å. Except for Lyman $\alpha$, no strong emissions are present so that we may consider the cross sections of Fite and Brackmann as those for Lyman-$\alpha$ radiation.

Comparison of our cross sections with the combined values of Fite and Brackmann[2] and Dunn et al. given in Ref. 3, gave agreement to within 4% over an energy range of 200–400 eV indicating that our cross-section values are independent of the normalization energy.

No polarization measurements were possible with the equipment used in the vacuum ultraviolet so that no corrections for polarization could be made.

For the Balmer radiation, emission cross sections $\sigma_{ij}$ were determined using the following equation:

$$\sigma_{ij} = \frac{4\pi}{\omega} \frac{S(\omega)}{(I/e)NLk(\lambda)}, \quad (1)$$

where $S(\omega)$ represents the light intensity in the space angle $\omega$, $(I/e)$ is the number of incident particles passing per second through the collision chamber, $N$ is the number of target particles per cubic centimeter, $L$ is the emission path length observed by the monochromator, and $k(\lambda)$ is the quantum yield (efficiency) of the optical system at the required wavelength as determined using a standard tungsten ribbon lamp.[14]

In Eq. (1) it is assumed that the radiation produced by the collisions is distributed isotropically. Checks using a Polaroid filter indicated that the atomic Balmer

radiation produced by the molecules had only small polarization and no corrections for this effect were therefore made.

The emission cross sections have not been corrected for cascade from higher levels.

### D. Error Discussion

The errors in the Lyman-$\alpha$ cross sections arise mainly from day-to-day variations in the quantum yield of the monochromator, the gas-pressure measurements, and the normalization procedure. The possible error arising from the first two sources is about 10%. The error resulting from the normalization procedure is estimated to be about 30%, as indicated by Fite and Brackmann.[2]

The cross sections for the process H(2s)→H(1s) were determined by measuring the change in the Lyman-$\alpha$ radiation when the electrostatic field was applied. The possible errors are therefore of the same magnitude as for Lyman-$\alpha$ radiation. Fite et al.[15] have found that radiation from a field-quenched H(2s) atom is partially polarized due to mixing of the (2s) level with the higher of the two H(2p) states ($2^2P_{3/2}$). Corrections for this effect have not been made here.

In the determination of the Balmer radiation the variations of the quantum yield (efficiency) of the monochromator could be controlled and the major errors in the Balmer $\beta$, $\gamma$, and $\delta$ emission cross sections therefore arise only from the calibration of the optical system and the pressure measurement. The absolute errors are estimated to be 7% for these lines. For Balmer $\alpha$, an additional error arises due to the relatively low sensitivity of the photomultiplier for this radiation. The error here is estimated to be 12%. For all the spectral lines investigated the relative energy dependence could be reproduced to within an accuracy of 4%.

Even though great care has been taken in obtaining the absolute quantum yield of the optical system in the visible region, the possibility of a systematic error still

TABLE I. Cross sections of excitation of helium in $10^{-19}$ cm²/atom (corrected for polarization and cascade).

| Energy (eV) | Level | | | | | |
|---|---|---|---|---|---|---|
| | $4^1S$ | $5^1S$ | $6^1S$ | $4^1D$ | $5^1D$ | $6^1D$ |
| 35[a] | 2.24 | | | | | |
| 40 | | | | 1.83 | | |
| 100 | 1.08 | 0.528 | 0.296 | 0.998 | 0.557 | 0.322 |
| 200 | 0.703 | | | 0.500 | 0.285 | 0.165 |
| 500 | 0.356 | 0.173 | 0.100 | 0.194 | 0.112 | 0.0644 |
| 1000 | 0.190 | 0.0940 | 0.0514 | 0.0918 | 0.0528 | 0.0316 |
| 2000 | 0.103 | 0.0505 | 0.0284 | 0.0524 | | |
| 5000 | 0.0433 | | | 0.0210 | | |

[a] Energy at which the maximum is reached.

[13] R. T. Brackmann, W. L. Fite, and K. E. Hagen, Rev. Sci. Instr. 26, 493 (1955).
[14] J. van den Bos, G. J. Winter, and F. J. de Heer, Physica 40, 357 (1968).
[15] W. L. Fite, W. E. Kauppila, and W. R. Ott, Phys. Rev. Letters 20, 409 (1968).

TABLE II. H, D$(2p)$ and H, D$(2s)$ cross sections for electrons in $H_2$, $D_2$.[a]

| Electron energy (eV) | Hydrogen | | Deuterium | |
|---|---|---|---|---|
| | $\dfrac{\text{Lyman } \alpha}{\text{H}(2p)}$ | $\dfrac{\text{H}(2s)-\text{H}(1s)}{\text{H}(2s)}$ | $\dfrac{\text{Lyman } \alpha}{\text{D}(2p)}$ | $\dfrac{\text{D}(2s)-\text{D}(1s)}{\text{D}(2s)}$ |
| 50 | 15.9 | 7.71 | 12.9 | 6.32 |
| 60 | 15.3 | 7.42 | 12.6 | 6.17 |
| 80 | 14.2 | 6.88 | 11.6 | 5.68 |
| 100 | 13.1 | 6.35 | 10.7 | 5.25 |
| 150 | 10.8 | 5.24 | 9.09 | 4.45 |
| 200 | 9.32 | 4.52 | 7.68 | 3.76 |
| 250 | 7.98 | 3.87 | 6.53 | 3.20 |
| 300 | 6.94 | 3.36 | 5.68 | 2.78 |
| 350 | 6.25 | 3.03 | 5.11 | 2.50 |
| 400 | 5.81 | 2.82 | 4.59 | 2.20 |
| 500 | 4.82 | 2.34 | 3.76 | 1.84 |
| 600 | 4.08 | 1.98 | 3.16 | 1.55 |
| 800 | 3.22 | 1.56 | 2.59 | 1.27 |
| 1000 | 2.70 | 1.31 | 2.12 | 1.04 |
| 1500 | 1.96 | 0.950 | 1.55 | 0.759 |
| 2000 | 1.59 | 0.771 | 1.26 | 0.617 |
| 2500 | 1.32 | 0.664 | 1.05 | 0.515 |
| 3000 | 1.14 | 0.553 | 0.868 | 0.425 |
| 4000 | 0.878 | 0.426 | 0.655 | 0.321 |
| 5000 | 0.756 | 0.367 | 0.585 | 0.286 |
| 6000 | 0.630 | 0.306 | 0.497 | 0.243 |
| 50 | H$(3p) \leq 0.357$ | | D$(3p) \leq 0.292$ | |

[a] Upper limits for H, D$(3p)$ cross sections at 50 eV. Units are $10^{-18}$ cm$^2$/molecule (uncorrected for polarization and cascade).

exists. In order to allow a means of evaluating such errors, the absolute excitation cross sections, corrected for cascade and polarization, of several helium lines are given in Table I. Since reliable calculations of these cross sections will be available soon, the inclusion of the helium values allows the Balmer cross sections to be adjusted appropriately.

## III. RESULTS

When the atomic hydrogen $2p$ state is formed it decays completely via Lyman-$\alpha$ radiation. Therefore, neglecting cascade effects, the cross section for emission of Lyman-$\alpha$ radiation is the same as the cross section for production of the excited state. The same can be said with respect to formation of the hydrogen atomic $2s$ state when it is caused to radiate by a quenching field. Absolute excitation cross sections can therefore be obtained directly for the $n=2$ state of the hydrogen atom.

Table II gives the cross sections for formation of H, D$(2p)$, and H, D$(2s)$ resulting from dissociative excitation of molecular hydrogen and deuterium. Assuming that almost all the Balmer radiation is from $ns$ and $nd$ states to $2p$, cascade contributes about 10% to our $2p$ formation cross sections at 50 eV. This cascade effect decreases at higher energy, being about 5% at 1000 eV. For $2s$ formation the cascade effect is very small (see below). Our H$(2p)$ results are essentially the same as those obtained by de Heer et al.[4] although the energy range has been extended from 3 to 6 keV.

Careful scannings of the wavelength region where the Lyman-$\alpha$ and Lyman-$\beta$ emission lines lie allowed us to obtain an upper limit for the emission cross section of the H, D$(3p) \rightarrow$ H, D$(1s)$ radiation at 1026 Å (allowance was made for the changing quantum yield of the vacuum spectrograph). This upper limit was obtained for the electron-impact energy at which Lyman $\alpha$ reaches a maximum (50 eV).

An upper limit of the absolute cross section for formation of the $(3p)$ atomic state could be obtained by taking into account that 88% of the $(3p)$ states decay via $3p$-$1s$ (1026-Å) radiation. This decay ratio was derived from the transition probability given by Bethe and Salpeter.[16] The upper limits of the cross section are given in Table II.

Tables III and IV contain the absolute emission cross sections for Balmer-$\alpha$, $\beta$, $\gamma$, and $\delta$ radiation from molecular hydrogen and deuterium, respectively.

It is interesting to compare the cross section for formation of H, D$(3p)$ with the emission cross section for Balmer $\alpha$ at the same impact energy. Both cross sections are of the same order of magnitude, the first being about two times smaller than the second. Two conclusions can be drawn from this result. The first is that the number of atoms formed in the $3s$-plus-$3d$ states is of the same order of magnitude as the number formed in the $3p$ level. The other conclusion is that the Balmer-$\alpha$ emission cross section $(n=3 \rightarrow n=2)$ is approximately the sum of the cross sections for forma-

[16] H. A. Bethe and E. E. Salpeter, in *Handbuch der Physik*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1957), Vol. 35, p. 352.

TABLE III. Balmer emission cross sections for hydrogen.[a]

| Electron energy (eV) | $\alpha$ $n=3\rightarrow2$ | $\beta$ $n=4\rightarrow2$ | $\gamma$ $n=5\rightarrow2$ | $\delta$ $n=6\rightarrow2$ |
|---|---|---|---|---|
| 50 | 9.37 | 1.76 | 0.530 | 0.223 |
| 60 | 9.58 | 1.86 | 0.555 | 0.234 |
| 80 | 9.40 | 1.86 | 0.545 | 0.226 |
| 100 | 8.88 | 1.68 | 0.530 | 0.202 |
| 150 | 7.16 | 1.40 | 0.405 | 0.164 |
| 200 | 6.06 | 1.10 | 0.347 | 0.133 |
| 250 | 5.09 | 0.930 | 0.290 | 0.110 |
| 300 | 4.36 | 0.807 | 0.254 | 0.0939 |
| 350 | 4.15 | 0.692 | 0.214 | 0.0800 |
| 400 | 3.50 | 0.610 | 0.183 | 0.0717 |
| 500 | 3.12 | 0.487 | 0.152 | 0.0579 |
| 600 | 2.66 | 0.405 | 0.124 | 0.0466 |
| 800 | 2.02 | 0.306 | 0.0936 | 0.0355 |
| 1000 | 1.47 | 0.238 | 0.0736 | 0.0279 |
| 1500 | 1.11 | 0.167 | 0.0498 | 0.0191 |
| 2000 | 0.833 | 0.130 | 0.0382 | 0.0146 |
| 2500 | 0.690 | 0.102 | 0.0308 | 0.0118 |
| 3000 | 0.583 | 0.0841 | 0.0256 | 0.00981 |
| 4000 | 0.476 | 0.0655 | 0.0200 | 0.00805 |
| 5000 | 0.399 | 0.0523 | 0.0159 | 0.00625 |
| 6000 | 0.324 | 0.0449 | 0.0136 | 0.00503 |

[a] Units are $10^{-19}$ cm²/molecule (uncorrected for polarization and cascade).

tion of the 3s and 3d states. To understand this, it is necessary to consider the $[(3p-2s)/(3p-1s)]$ branching ratio which shows that 88% of the $3p$ atoms radiate to the ground state. This makes the $3p-2s$ transition a small contribution to the total Balmer-$\alpha$ radiation. On the contrary the $(3s)$ and $(3d)$ states can only radiate to the $2p$ and therefore give essentially all the Balmer radiation. For example, the contribution of $(3p)$ to the Balmer $\alpha$ at 50 eV is about 4%.

Similar considerations can be given for the higher Balmer emission processes. It is reasonable to assume that the $np$ level is not formed predominantly. From known[16] transition probabilities it follows that the $(np)$ atoms predominantly radiate to the ground state while an important part of the $(ns)$ and $(nd)$ atoms decay with Balmer emission to the $(2p)$ state. Therefore, the Balmer emission cross sections are chiefly determined by the formation of the $(ns)$ and $(nd)$ atomic states.

Most of the Balmer radiation will therefore give cascade contributions to the Lyman-$\alpha$ radiation (H, D $2p-1s$) whereas the cascade effects in the Balmer series will be negligible.

Examination of the emission cross sections for all the atomic lines considered shows that the number of D atoms formed in any excited state is always about 20% less than the number of H atoms formed at the same electron-impact energy. This strong isotope effect, which has also been observed in the production of Lyman and Balmer radiation in $CH_4$ and $CD_4$[17] is direct evidence for the existence of a competition be-

[17] D. A. Vroom and F. J. de Heer, J. Chem. Phys. 50, 573 (1969), preceding article.

tween dissociation and other molecular processes in these molecules. This point will be discussed fully in the next section.

## IV. DISCUSSION

### A. General

Excitations to the dissociative parts of both neutral and ionic molecular potential-energy curves will give rise to atomic species. There are three molecular processes which must be considered as possible sources of these atomic states. The first of these is direct excitation from the ground molecular state to a repulsive state or to a bound state above its dissociation limit. These curves may be molecular or ionic. Another process which can lead to production of atoms is excitation to a bound state followed by predissociation. The third process leading to dissociation is cascade from an excited bound molecular level to a lower repulsive curve.

If the products of these dissociative processes include excited atoms, then atomic radiation will result. Because of the possibility of having more than one dissociation process leading to production of a particular atomic state, the cross section for formation of that state must be the sum of the cross sections of the individual excitation and ionization processes leading to production of that state.

In excitation of atoms by electrons, both initial and final states are generally known in the collision process. It is then possible to decide whether the transition in the atom is optically allowed, or optically forbidden, or that exchange of electrons is occurring involving change of multiplicity. In molecules, however, the

TABLE IV. Balmer emission cross sections for deuterium.[a]

| Electron energy (eV) | $\alpha$ $n=3\rightarrow2$ | $\beta$ $n=4\rightarrow2$ | $\gamma$ $n=5\rightarrow2$ | $\delta$ $n=6\rightarrow2$ |
|---|---|---|---|---|
| 50 | 7.55 | 1.41 | 0.450 | 0.196 |
| 60 | 7.88 | 1.51 | 0.485 | 0.216 |
| 80 | 7.96 | 1.53 | 0.484 | 0.213 |
| 100 | 7.36 | 1.45 | 0.448 | 0.200 |
| 150 | 6.42 | 1.16 | 0.366 | 0.150 |
| 200 | 5.19 | 0.963 | 0.290 | 0.116 |
| 250 | 4.65 | 0.804 | 0.237 | 0.0919 |
| 300 | 3.78 | 0.683 | 0.196 | 0.0787 |
| 350 | 3.44 | 0.595 | 0.173 | 0.0660 |
| 400 | 3.06 | 0.520 | 0.145 | 0.0595 |
| 500 | 2.33 | 0.411 | 0.115 | 0.0445 |
| 600 | 1.90 | 0.323 | 0.0946 | 0.0360 |
| 800 | 1.51 | 0.247 | 0.0676 | 0.0271 |
| 1000 | 1.27 | 0.196 | 0.0557 | 0.0215 |
| 1500 | 0.858 | 0.136 | 0.0370 | 0.0141 |
| 2000 | 0.668 | 0.0945 | 0.0273 | 0.0102 |
| 2500 | 0.514 | 0.0770 | 0.0224 | 0.00786 |
| 3000 | 0.454 | 0.0653 | 0.0182 | 0.00640 |
| 4000 | 0.352 | 0.0513 | 0.0137 | 0.00494 |
| 5000 | 0.279 | 0.0412 | 0.0109 | 0.00403 |
| 6000 | 0.244 | 0.0338 | 0.00953 | 0.00359 |

[a] Units are $10^{-19}$ cm²/molecule (uncorrected for polarization and cascade).

possibility of more than one molecular transition lead-
ing to production of some excited atomic state makes
the situation more complex. Some of these transitions
may be optically allowed, others optically forbidden and
some may only result from electron exchange processes.
The type of transition produced in the molecule deter-
mines the energy dependence of the corresponding cross
section. By studying this energy dependence for disso-
ciative formation of excited hydrogen, it is possible to
determine the relative importance of optically allowed,
forbidden, and exchange transitions in the collision
process.

## B. Theory

At sufficiently high electron energy, the excitation
cross section $\sigma$ for an optically allowed (dipole) transi-
tion is, in the Bethe–Born approximation,[18,19] expressed
by

$$\sigma = (4\pi a_0^2 R/E_{el}) M_n^2 \ln c_n E_{el}, \tag{2}$$

where $E_{el}$ is the electron energy corrected above 1 keV
for relativistic effects, $a_0$ is the first Bohr radius, $R$
is the Rydberg energy, and $c_n$ is a constant which
depends on the final state $n$. (In the case of formation
of excited hydrogen atoms by dissociation of molecules,
$n$ refers to the final state of the excited atom.)

For dissociative excitation of a molecule, the term
$M_n^2$ is related to the optical oscillator strengths for all
dipole transitions to molecular states which dissociate
to a particular atomic level $n$. This term may be
expressed as[4]

$$M_n^2 = \int_{E_n}^{\infty} \eta_n(E) \frac{df(E)}{dE} \frac{R}{E} dE, \tag{3}$$

where $E$ is the excitation energy transfered to the
molecule and $[df(E)/dE]$ is the differential optical
oscillator strength which is related to the photoabsorp-
tion cross section, $\sigma_{ph\ abs}(E)$, by

$$df(E)/dE = (mc/\pi e^2 h)\sigma_{ph\ abs}(E). \tag{4}$$

$E_n$, in Eq. (3), is the threshold energy for dissociation
into state $n$, and $\eta_n(E)$ is the efficiency factor indicat-
ing what fraction of excited molecular states give rise
to the dissociation product in state $n$ $(0 \leq \eta_n(E) \leq 1)$.

For optically forbidden transitions it can be shown
that, at high energies, the cross section varies as[18,20,21]

$$\sigma = B_n/E_{el}, \tag{5}$$

where $B_n$ is a constant depending on the sum of all
optically forbidden processes leading to formation of
atoms in state $n$.

For electron exchange processes, the Ochkur approxi-
mation[22] gives the variation of the cross section with
electron-impact energy as

$$\sigma \propto E_{el}^{-3}. \tag{6}$$

Examination of Eqs. (3), (5), and (6) shows that
allowed, forbidden, and exchange processes may read-
ily be distinguished by examination of the energy
behavior of the cross sections in the high-energy region.
This can be done by plotting the cross sections in the
form $\sigma E_{el}/4\pi a_0^2 R$ vs $\ln E$. In this "Bethe plot," optically
allowed transitions give lines with positive slope $M_n^2$,
optically forbidden transitions give curves with zero
slope, and exchange processes give lines with negative
slope. For the optically allowed transitions the positive
slope $M_n^2$ is related to the optical oscillator strength
for the process.

Investigation of the various possible mechanisms
leading to direct production of excited atoms from
molecular hydrogen by electron impact enables the
possible processes to be partially classified. The first
mechanism, excitation followed by dissociation, can be
represented as

$$e + H_2 \rightarrow e + H_2{}^*,$$
$$H_2{}^* \rightarrow H + H^*. \tag{7}$$
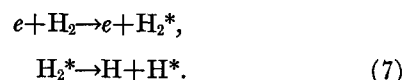
Such processes may proceed by allowed, forbidden,
or exchange transitions. At high energies only the first
two of these will be important as the cross sections for
exchange processes decrease rapidly with energy. Cas-
cade from upper bound levels to dissociative curves
falls into this class of reactions.

Ionization followed by dissociation is the other
possible mechanism,

$$e + H_2 \rightarrow e + H_2{}^{+*} + e,$$
$$H_2{}^{+*} \rightarrow H^+ + H^*. \tag{8}$$
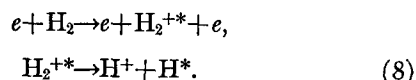
For molecular hydrogen this must be a two-electron
transition as there are no inner-shell electrons. For
such two-electron transitions it has been found before
in He that $\sigma E_{el}$ becomes almost constant at high ener-
gies,[11] as in optically forbidden transitions. This will
also be the case for dissociative ionization of hydrogen.[23]

The results obtained for the formation of the various
atomic levels considered here can now be discussed in
terms of the general remarks given above.

## C. H, D(2p) (Lyman-α Radiation)

Figure 3 gives the $\sigma E_{el}/4\pi a_0^2 R$-vs-$\ln E_{el}$ plot of the
H, D(2p) and H, D(2s) cross sections for molecular
hydrogen and deuterium (see also Table II). A least-
squares fit of the linear part of the H, D(2p) curves in

[18] H. A. Bethe, Ann. Physik **5**, 325 (1930).
[19] W. F. Miller and R. L. Platzman, Proc. Phys. Soc. (London) **70**, 299 (1957).
[20] B. L. Schram and L. Vriens, Physica **31**, 1431 (1965).
[21] B. L. Schram, thesis, University of Amsterdam, 1966.

[22] V. I. Ochkur, Zh. Eksp. Teor. Fiz. **45**, 734 (1963) [Sov. Phys.—JETP **18**, 503 (1964)].
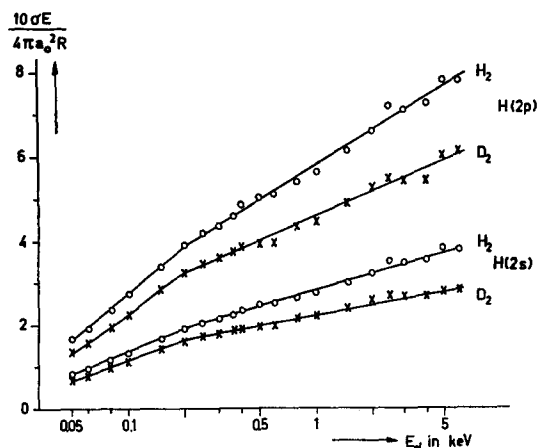[23] F. Fiquet-Fayard and J. Chiau, Phys. Letters **A26**, 512 (1968).

FIG. 3. Cross sections for H, D(2$p$) and (2$s$) formation in the case of electron impact on $H_2$, $D_2$, plotted as $\sigma E_{el}/4\pi a_0^2 R$ versus $E_{el}$.

Fig. 3 yields $M_{2p}^2$ for formation of (2$p$) atoms in dissociation. The values are given in Table V.

The result obtained for $M_{2p}^2$(H) is essentially the same as that determined previously by de Heer et al.[4] who, with the aid of Eq. (4), compared their value with the photoabsorption and photoionization data of Cook and Metzger.[24] They[4] obtained an upper limit of 0.11 for $M_{2p}^2$(H) from the optical data but point out that this result is likely to be an underestimate as photoabsorption data tend to yield $df/dE$ values which are too small in regions of sharp band structure.[25] The agreement between the upper limit of the $M_{2p}^2$(H) value from photon impact and the value determined in this work is good.

In the absorption spectrum of $H_2$ it is known that predissociation of the $D\,^1\Pi_u$ molecular state above the second vibrational level occurs leading to production of atoms in the 2$p$ state.[26,27,24] Cook and Metzger[24] show that the absorption bands to the $D\,^1\Pi_u$ state above the energy at which predissociation can occur are strong, indicating that this process may be one of the major contributors to the production of Lyman-$\alpha$ radiation. This mechanism for production of the 2$p$ state is in agreement with the electron-impact measurements of Fite and Brackmann[2] who measured the threshold for Lyman-$\alpha$ radiation to be 14.5 eV in very good agreement with the value of 14.46 eV found by Cook and Metzger[24] for the onset of predissociation. Furthermore the $X\,^1\Sigma_g^+ \rightarrow D\,^1\Pi_u$ transition is optically allowed, in agreement with the strong slope obtained in our Bethe plot of the H, D(2$p$) data.

The extent to which the $D\,^1\Pi_u$ state contributes to the formation of H(2$p$) can be estimated using the generalized oscillator strength calculated by Khare.[6]

The value given in this publication for the total excitation to the $D\,^1\Pi_u$ state is 0.052. This value can be compared with our $M_{2p}^2$. Using $f(D\,^1\Pi_u) = 0.052$, and an average excitation energy of 15 eV, one obtains

$$M_{D\,^1\Pi_u}^2 \cong \frac{0.052}{(15/13.6)} = 0.047,$$

where 13.6 is the Rydberg energy. The value of 0.047 is about 40% of our measured $M_{2p}^2$(H) of 0.120. Since predissociation occurs above the $v=2$ vibrational level a considerable number of the excited atoms could arise from predissociation. The remaining H(2$p$) atoms must arise from other excitation processes, probably from unknown states embedded in the ionization continua.

Apart from the measurements of de Heer et al.[4] the only other measurements[2,3] on the production of Lyman-$\alpha$ radiation by electron impact on molecular hydrogen have concentrated on energies from threshold to 500 eV. The energy dependence of these results[2,3] is in agreement with our results. There have been no previous determinations of Lyman-$\alpha$ radiation arising from electron-impact excitation of molecular deuterium.

Production of Lyman-$\alpha$ radiation by ion impact has been reported by Dunn et al.[3] and Van Zyl et al.[28] and by photon impact by Beyer and Welge.[29] In the case of the ion impact, the energies of the particles were in a range which does not allow comparison with the results obtained here, while the photon results, although not directly comparable, do point out the importance of the predissociation process. Further evidence for the production of excited atoms due to predissociation is found in the photoionization study of Chupka et al.[30]

### D. H, D(2$s$) (Quenched Lyman-$\alpha$ Radiation)

The cross sections for H, D(2$s$) formation are given in Fig. 3 in a "Bethe plot." As in the case of H(2$p$),

TABLE V. $M_n^2$ values for the Balmer and Lyman emission from $H_2$ and $D_2$.

|            | Hydrogen  | Deuterium |
|------------|-----------|-----------|
| $M_{B\alpha}^2$ | 0.00344   | 0.00222   |
| $M_{B\beta}^2$  | 0.000184  | 0.0000267 |
| $M_{B\gamma}^2$ | 0.0000432 | $\cdots$  |
| $M_{B\delta}^2$ | 0.0000223 | $\cdots$  |
| $M_{2p}^2$      | 0.120     | 0.0839    |
| $M_{2s}^2$      | 0.0572    | 0.0411    |

[24] J. R. Cook and P. H. Metzger, J. Opt. Soc. Am. **54**, 968 (1964).

[25] See, for example, V. D. Meyer, A. Skerbele, and E. N. Lassettre, J. Chem. Phys. **43**, 3769 (1965).

[26] H. Beutler, Z. Physik. Chem. **B29**, 315 (1935).

[27] G. Herzberg and A. Monfils, J. Mol. Spectry. **5**, 482 (1960).

[28] B. van Zyl, D. Jaecks, D. Pretzer, and R. Geballe, Phys. Rev. **158**, 29 (1967).

[29] K. D. Beyer and K. H. Welge, Z. Naturforsch. **22a**, 1161 (1967).

[30] W. A. Chupka, M. E. Russell, and K. Refaey, J. Chem. Phys. **48**, 1518 (1968).

the curve has a strong positive slope indicating that optically allowed transitions in the molecule are again dominant. The $M_{2s}^2(H)$ and $M_{2s}^2(D)$ values were determined by a least-squares fit to the asymptotic region of the curve. The values are given in Table V.

Since optically allowed processes are present, our $M_{2s}^2$ value must be comparable with photon absorption data. The upper limit calculated for $M_{2p}^2(H)$ from the data of Cook and Metzger[24] must include the contributions to $M_{2s}^2(H)$. It is therefore the sum of the measured $M_{2p}^2(H)$ and $M_{2s}^2(H)$ values which must be compared to the calculated upper limit of 0.11. The total $M_2^2$ obtained here $(0.120+0.057=0.177)$ is larger than the calculated upper limit but this value is probably an underestimate (see preceding section). Similar results can be obtained for deuterium.

Unlike the case for formation of $H(2p)$, there is no known optical process leading to formation of $H(2s)$. There have, however, been recent measurements by Leventhal et al.[5] on the energy of metastable atoms produced by dissociative excitation of $H_2$. These results can be used to give additional information in that they show two processes existing for production of metastables. The first of these, which is the least important, results in the production of slow atoms and can be explained as the results of transitions to bound curves above their dissociation limit. These transitions have, in the quantum-mechanical formulation of the Franck–Condon principle, a small probability and therefore are not the major contributors to formation of $H(2s)$. Processes which may occur here have been shown by Leventhal et al.[5] to be direct excitation to $B\,^1\Sigma_u^+$, $B'\,^1\Sigma_u^+$, $e\,^3\Sigma_u^+$, $E\,^1\Sigma_g^+$, and $a\,^3\Sigma_g^+$.

The second and major path leading to metastables results in atoms with considerable kinetic energy being formed (average $\sim$5 eV). The shape of the energy distribution[5] of these particles indicates that transi-
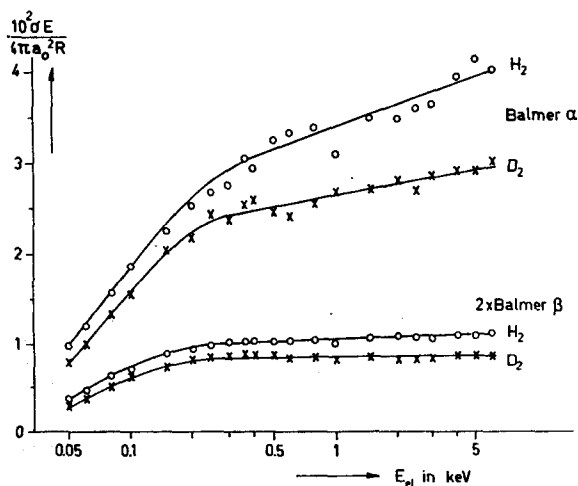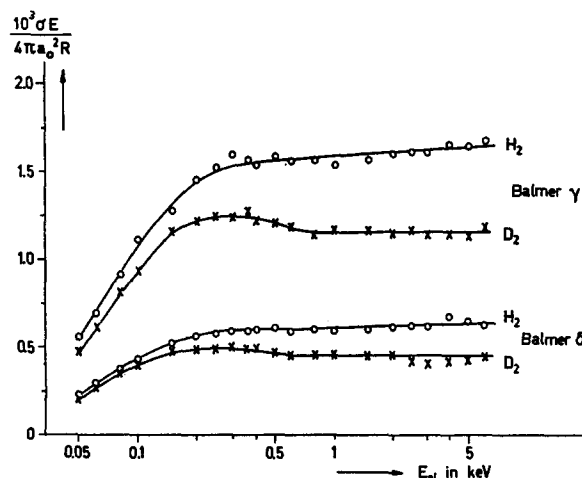


FIG. 5. Cross sections for Balmer-$\gamma$ and $\delta$ production in the case of electron impact on $H_2$, $D_2$, plotted as $\sigma E_{el}/4\pi a_0^2 R$ versus $E_{el}$.

tions to one or several closely spaced steeply repulsive curves are the main processes. The strong dipole character of the cross-section results (see Fig. 3) indicates that the upper states must be such as to allow optical processes. These states must be embedded in the ionization continuum.

Chupka et al.[30] have suggested that $H(2s)$ atoms might be formed by predissociation of the $D\,^1\Pi_u$ state. However, results of Leventhal et al.[5] and Beyer and Welge[29] indicate that all the predissociation leads to formation of $H(2p)$.

## E. Balmer Radiation

The interpretation of the results of the Balmer radiation is much more difficult than for Lyman $\alpha$, the major problem being that the various $l$ sublevels of a particular formed level $n(3-6)$ cannot be separated. However, an analysis of our cross sections for $H(n=3)$, as given in Sec. III, suggests that the population of $ns$, $np$, and $nd$ states for $n\geq 3$ may be of the same order of magnitude. A second problem is that not much is known about the higher excited states in the molecular hydrogen molecule.

The Bethe plots of the Balmer emission cross sections are given in Figs. 4 and 5. Above 500 eV the slope of the curves becomes a constant. For the hydrogen lines a small positive slope exists for all the processes indicating that some optically allowed transitions contribute to formation of the excited atoms. An estimate of the strength of these processes can be obtained from the calculated $M_n^2(H)$ values. The results obtained are given in Table V. For deuterium the positive slope was measurable only in the case of the Balmer-$\alpha$ and $\beta$ lines. The $M_n^2$ values are also given in Table V. Examination of the results shows that as the principal quantum number of the states increases the relative importance of optically allowed transitions becomes less.
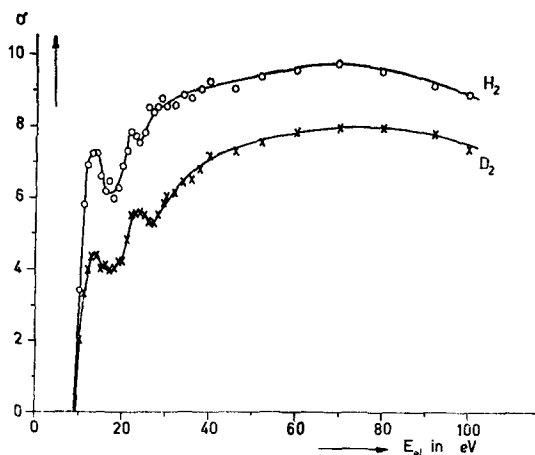


FIG. 4. Cross sections for Balmer-$\alpha$ and $\beta$ production in the case of electron impact on $H_2$, $D_2$, plotted as $\sigma E_{el}/4\pi a_0^2 R$ versus $E_{el}$.

FIG. 6. Cross sections for Balmer-$\alpha$ production in the case of electron impact on $H_2$, from threshold up to 100 eV (uncorrected energy scale), $\sigma$( $10^{-19}$ cm²/molecule).

The small maxima seen in the Balmer-$\gamma$ and $\delta$ Bethe plots for deuterium may be due to singlet–triplet transitions in the molecule (electron exchange).

The small slope in the Bethe plots for all Balmer lines indicates the relatively small importance of optically allowed processes. As pointed out previously simultaneous excitation and ionization processes which leave the ion in an excited state may occur by optically forbidden processes. The fact that all excited ion states of molecular hydrogen are dissociative[31,32] suggests that dissociative ionization resulting in excited atoms may be important.

Other evidence that transitions to excited ionic states of molecular hydrogen are not negligible exists. Rapp et al.[33] measured the cross section for production of protons with kinetic energies in excess of 0.25 eV. They found that the number of protons produced with above thermal kinetic energies constituted a measurable part of the total ion production. Dunn and Kieffer[31] studied these energetic particles in detail and found that the assumption that all corresponding hydrogen atoms are formed in the ground state does not explain the observed results. This indicates that an appreciable number of the atoms produced in dissociative ionization must be in excited states and will contribute to atomic radiation.

That excited atoms coming from ionization can be important is further emphasized by the fact that the cross section for $H^+$ formation[33–35] is considerably larger than the Balmer-$\alpha$ emission cross section.

In order to gain more information about the possible processes occurring, the cross-section measurements for the Balmer lines were extended to threshold. Since the

instrument used was not designed for low-energy determinations the possibility of errors in the values exists and the results are only included for illustration. Figure 6 gives the threshold for Balmer-$\alpha$ emission (similar results were obtained for the other Balmer lines). The cross-section curve shows three maxima in the region below 100 eV. The first of these comes very close to the threshold and probably is the result of exchange processes (proceeding through intermediate compound states). At about 15 eV above threshold there is a second maximum which may be the result of the optically allowed transitions responsible for the positive slope of the Bethe plot for this line. Above these two rather sharp maxima a very broad peak occurs which reaches its highest point at about 100 eV. The width and energy of this maximum is indicative of ionization processes. As this is the major process the importance of ionizing transitions is emphasized.

There has been no recent determination of Balmer radiation produced by electron impact on molecular hydrogen. However, experimental values have been obtained for proton impact[36–38] in a range which partly overlaps the velocity scale in our electron measurements. The Balmer-$\beta$ results from these investigations have been compared with our electron values in the Bethe plot given in Fig. 7. Also included are preliminary values obtained in this laboratory. The proton
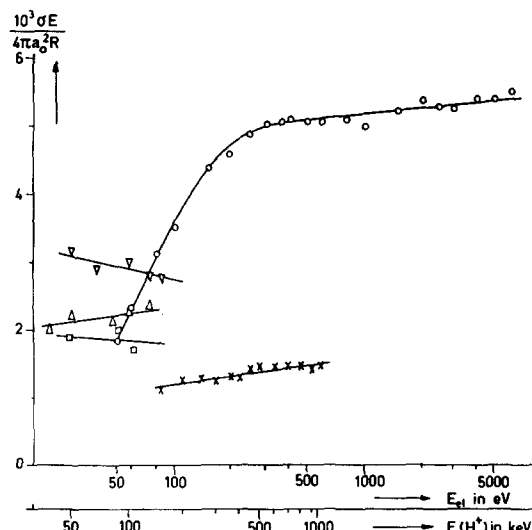


FIG. 7. Comparison of cross sections for Balmer-$\beta$ production in the case of electron and proton impact on $H_2$, $D_2$, plotted as $\sigma E_{el}/4\pi a_0^2 R$ versus $E_{el}$. For protons with energy $E_{H+}$, we take the equivalent electron energy $E_{el} = (m/M) E_{H+}$. O, this work with electrons; $\triangle$, proton data of Hughes et al. (Ref. 37); $\times$, Edwards and Thomas (Ref. 36); $\square$, and Dufay et al. (Ref. 38); $\triangledown$, this laboratory.

[31] G. H. Dunn and L. J. Kieffer, Phys. Rev. **132**, 2109 (1963).
[32] G. H. Dunn and B. van Zyl, Phys. Rev. **154**, 40 (1967).
[33] D. Rapp, P. Englander-Golden, and D. D. Briglia, J. Chem. Phys. **42**, 4081 (1965).
[34] B. Adamczyk, A. J. H. Boerboom, B. L. Schram, and J. Kistemaker, J. Chem. Phys. **44**, 4640 (1966).
[35] M. J. van der Wiel (private communication).

[36] J. L. Edwards and E. W. Thomas, Phys. Rev. **165**, 16 (1968).
[37] R. H. Hughes, S. Lin, and L. L. Hatfield, Phys. Rev. **130**, 2318 (1963).
[38] M. Dufay, J. P. Buchet, M. Carré, J. Desesquelles, M. Druetta, M. Eidelsberg, and M. C. Poulizac (private communication).

and electron results have been plotted on an equal velocity scale.

### F. Isotope Effect

As pointed out previously a large difference in the cross sections for excited-atom production exists between molecular hydrogen and deuterium and is evidence for competing pathways for de-excitation. The results can be used to give further information on the existence and properties of superexcited states.

Platzman[39] pointed out that the number of excitations to molecular states lying above the first ionization potential may be appreciable. These superexcited states have the possibility of preionizing or of decaying by some other mode such as dissociation. The probability for dissociation is related to the term $\eta_n(E)$ given in Eq. (3). The time required for the dissociation to occur depends on the velocity of the outgoing particles and therefore, for a given energy available for dissociation, a change in mass of the particles will influence the dissociation process strongly. Preionization, however, is a process having, presumably, little mass dependence[40] and therefore, if in competition with dissociation, an increase in mass of the particles will enhance the probability of ionization. The heavier particles move apart more slowly and consequently the dissociation is not so much favored.

Since dissociation products are detected in this experiment the molecular states of importance will in general be repulsive and the only processes for de-excitation of the superexcited states will therefore be ionization and dissociation. Such conclusions lead directly to the observed isotope effect. The size of the isotope effect ($\sim$20%–25%) for all atomic emission lines considered indicates the importance of superexcited states.

Since the two processes under consideration are competitive their mean lifetimes must be of the same order of magnitude. Assuming that the atoms are produced in dissociation with 5 eV of kinetic energy [the mean value found for $H(2s)$[5]] and that dissociation can be said to have occurred when the particles are 5 Å apart, one gets a dissociation time of $10^{-14}$ sec. The auto-ionization process must therefore have also a time of about $10^{-14}$ sec. That these two processes are competitive might be taken to imply that in molecules some rearrangement of the atomic nuclei might have to occur before the electron is ejected.

The lower dissociation cross sections for deuterium imply, by the above arguments, that the ionization cross section for $D_2$ should be higher than for $H_2$. Because preionization contributes only part of the ion current the influence would be expected to be small. Nevertheless Jesse[41] observed that for the impact of high-energy electrons on $H_2$ and $D_2$, the latter gas

produced approximately 1% more ions. This is in agreement with our statements.

Similar arguments concerning the influence of the mass of the outgoing particles on the cross section for dissociation processes have also been used by Schulz[42] to explain the very different dissociative attachment cross sections obtained for the impact of low-energy electrons on the isotopic molecules of hydrogen.

In the case of ionic impact on $H_2$ and $D_2$ preliminary experiments in this laboratory indicated that the isotope effect is about 7% for $He^+$ on $H_2$ and $D_2$. This result indicates that the isotope effect found by Van Zyl et al.[28] may be real and not, as they suggest, due to the bandwidth of their detector.

### G. Polarization of the Balmer Radiation

As mentioned previously attempts were made to determine the polarization of the Balmer radiation produced by the dissociation processes. In both hydrogen and deuterium, small but similar polarization was found. The degree of polarization (II) is about +4% at 50-eV impact energy and decreases to about −8% at 1000 eV. The size of the effect was such that it had a very small influence on the absolute cross sections.

Recently, Van Brunt and Zare[8] pointed out that, in general, fluorescence from excited atomic fragments arising from molecular dissociation processes may be polarized, the polarization being related to the form of the anisotropy in the angular distribution of dissociation products. When several molecular states of different electronic symmetry contribute to the dissociative process, however, the anisotropies in the angular distribution tend to be averaged out and the polarization will be reduced. These considerations are consistent with the results found here.

### V. CONCLUSION

The present experiment gives new information on dissociative excitation of molecular hydrogen and deuterium leading to excited atoms. As far as formation of $H(2p)$ and $H(2s)$ is concerned, optically allowed (dipole) transitions in the molecule appear to be relatively important. In the case of $H(2p)$ the predissociation to the $D\,^1\Pi_u$ state appears to form an important contribution. For $H(2s)$ the molecular level giving rise to an important dipole contribution may be a strongly repulsive state in the ionization continuum which has not yet been identified. The extent to which dipole transitions contribute indicates the important role of superexcited states in the excitation process.

The results on Balmer-$\alpha$ radiation ($n=3\rightarrow2$) and Lyman-$\beta$ radiation ($3p\rightarrow1s$) suggest that for $n=3$–6 there may be no strong preference in population of $s$, $p$, and $d$ levels. The results on Balmer radiation show a small dipole contribution in the excitation proc-

[39] R. L. Platzman, Radiation Res. 17, 419 (1962).
[40] M. Inokuti (private communication).
[41] W. P. Jesse, J. Chem. Phys. 38, 2774 (1963).
[42] G. J. Schulz and R. K. Asundi, Phys. Rev. 158, 25 (1967).

ess, which decreases with increasing $n$ number. Because of the relatively large importance of optically forbidden transitions, dissociative ionization may contribute to a large extent to formation of H atoms with $n \geq 3$.

An isotope effect of about 20% is found for the dissociative excitation of $H_2$ and $D_2$, $H_2$ yielding the largest number of atoms. This can be explained in terms of a competition between preionization and predissociation, again emphasizing the role of superexcited states in dissociative excitation and ionization.

## ACKNOWLEDGMENTS

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# Reaction of the Excited Oxygen Atoms (O¹D₂) with Isobutane*

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Reaction of $O^1D_2$ atoms, formed by photolysis of $N_2O$ at 2139 Å, with isobutane has been studied in the gas phase at room temperature and at total pressures between 80 and 1250 torr. The major features of the reaction are similar to those observed previously in this Laboratory with propane. The excited atoms insert indiscriminately into the primary and tertiary CH bonds of isobutane. The "hot" butanols formed by insertion are stabilized at pressures much lower than those required for stabilization of "hot" propanols. The lifetimes of the "hot" butanols have been determined. The reaction mechanism is discussed.

## INTRODUCTION

Information currently available in the literature on the chemical behavior of the electronically excited oxygen atoms ($O^1D_2$) is extremely limited in spite of their importance as a constituent of the upper atmosphere. In earlier studies in this Laboratory considerable information has been accumulated on the effectiveness of deactivation of $O^1D_2$ atoms in collisions with a number of different gases.[1–4] It was also found, in a study with propane,[3] that $O^1D_2$ atoms insert readily and indiscriminately into the CH bonds of paraffins to form highly vibrationally excited alcohol molecules which decompose if not stabilized by collisions with other molecules. However, because of the high exothermicity of these reactions the lifetimes of the "hot" propanols were very short and only partial stabilization was achieved even at pressures as high as 2500 torr. The stabilization curves and some other features of

these reactions could not therefore be examined in as much detail as was desirable. To overcome these limitations it was considered necessary to extend the studies of the reactions of $O^1D_2$ atoms to a greater variety of paraffins. In the present work the reaction with isobutane was investigated since longer lifetimes could be expected for the "hot" butanols in view of the greater number of degrees of freedom in the molecules. The consequent stabilization at considerably lower pressure was expected to permit a more precise determination of the trends in the yields of the three types of products observed with propane[3]: the insertion, the "abstraction," and the fragmentation products.

The excited atoms were generated by direct photolysis of $N_2O$ at 2139 Å, using a zinc lamp as light source. Although $N_2O$ absorbs rather weakly at this wavelength[5] and thus longer irradiations are required, this spectral region has the advantage of a negligible absorption by paraffins and as a rule negligible or only relatively weak absorption by reaction products. In addition, at this wavelength there appears to be enough energy to generate $O^1D_2$ but not the more highly excited $O^1S_0$ atoms.[3,4] The use of $N_2O$ has a further

* Issued as N.R.C. No. 10534.
[1] H. Yamazaki and R. J. Cvetanović, J. Chem. Phys. **39**, 1902 (1963).
[2] H. Yamazaki and R. J. Cvetanović, J. Chem. Phys. **40**, 582 (1964).
[3] H. Yamazaki and R. J. Cvetanović, J. Chem. Phys. **41**, 3703 (1964).
[4] K. F. Preston and R. J. Cvetanović, J. Chem. Phys. **45**, 2888 (1966).

[5] B. A. Thompson, P. Harteck, and R. R. Reeves, Jr., J. Geophys. Res. **68**, 6431 (1963).