

sulting inequality once more with the aid of the relation  $\log(1+x) < x$ , one obtains inequality (54). Of

course, (6) has to be used also. The proof of (54) was just the aim of this section.

## Dissociative Excitation Processes in H<sub>2</sub>O

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(Z. Naturforsch. 28a, 22–26 [1973]; received 5 October 1972)

In a single step process the H<sub>2</sub>O molecule is dissociated into excited atoms or ions. The radiation of these particles — H\*, O I and O II — is investigated by means of VUV spectroscopy. The excitation functions of the various lines show a pronounced structure. An attempt is made to explain these structures by different excitation processes.

Apart from two investigations of the Ly  $\alpha$  line at 1215 Å<sup>1,2</sup> there are no other publications about the radiation in the wavelength region 500–1250 Å caused by dissociative excitation processes from electron collisions in water vapour.

The Lyman series, oxygen atom and oxygen ion lines were investigated. Many structures in the excitation functions were found and an attempt is made to explain these structures by different processes leading to radiation of the same wavelength.

### Apparatus

The apparatus: the electron-molecule collision chamber, the electronic equipment and the vacuum-ultraviolet-monochromator is described in<sup>3</sup>.

In these experiments the intensity of the radiation of different lines was measured in dependence on the electron energy with a multichannel analyzer. The electron energy scale (number of channel) is calibrated by measuring the appearance potentials of some strong atomic lines in the rare gases. The accuracy in the range 12–23 eV amounts to  $\pm 0.5$  eV because there are many calibration points, whereas at about 50 eV it is only  $\pm 2.0$  eV<sup>4</sup>. Special care was taken to purify the water vapour<sup>4</sup>.

### Spectrum

Figure 1 shows a spectrum obtained by electron bombardment of H<sub>2</sub>O molecules at a pressure of 10<sup>−3</sup> Torr and a beam current of 400  $\mu$ A. The electron energy amounted to 150 eV.

Six lines of the Lyman series, three O I lines and five oxygen ion lines were observed. It should be noted that the cross sections of the O II lines are almost of the same order of magnitude as those of the O I lines. Near 600 Å some very weak lines can be seen. Accordingly this part of the spectrum was measured with increased pressure and current and a longer integration time of the rate meter. In this case the signal to noise ratio was about 1/2.

### Excitation Processes

#### a) Excitation of the Lyman series

The experiment covered six transitions in the Lyman series. All excitation functions show structures near the threshold. In the shape of the excitation function of Ly  $\alpha$  there are at least three different onsets, probably even four. At about 40 eV there seems to be a resonance-like structure.

The other Lyman transitions show only two onsets. We probably can not see any others because of the lower intensity.

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<sup>1</sup> J. W. MCGOWAN, J. F. WILLIAMS, and D. A. VROOM, Chem. Phys. Letters 3, 614 [1969].

<sup>2</sup> K. D. BEYER and K. H. WELGE, Z. Naturforsch. 22a, 1161 [1967].

<sup>3</sup> N. BÖSE and W. SROKA, Z. Naturforsch. 26a, 1491 [1971].

<sup>4</sup> N. BÖSE, Diplomarbeit, Hamburg 1972.



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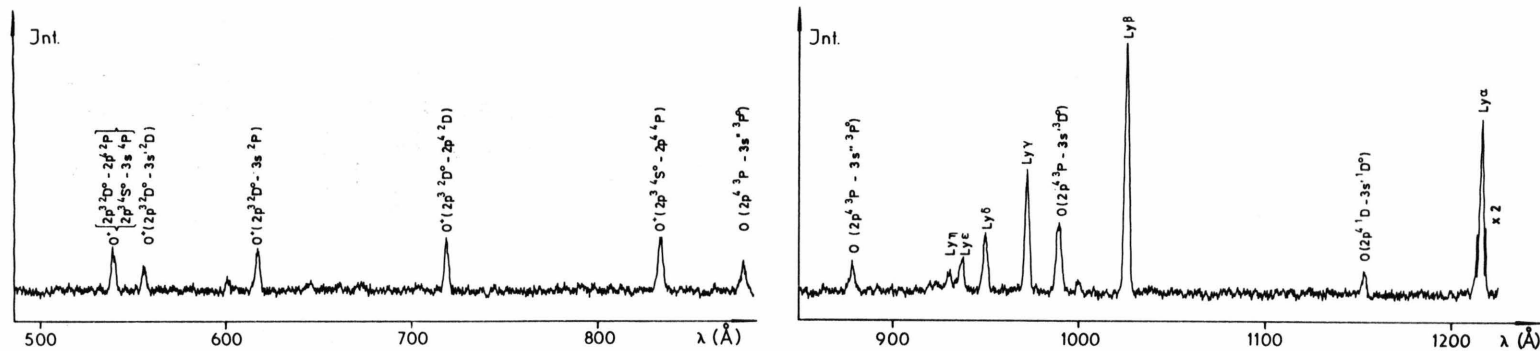


Fig. 1. Dissociation spectrum of  $\text{H}_2\text{O}$ .

Fig. 3. Excitation function of  $\text{Ly } \alpha$  immediately above threshold.

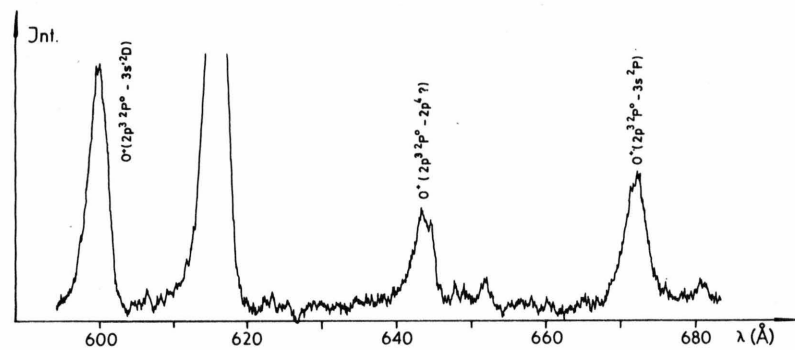
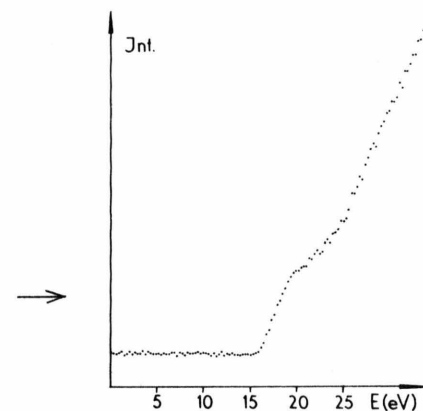


Fig. 2. Weak lines above 600 Å.

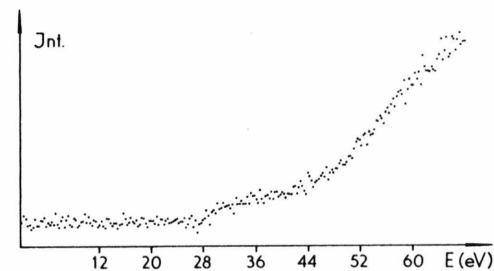


Fig. 4. Threshold behavior of the  $\text{O I}$  line at 879 Å.

By comparing the calculated minimum energies

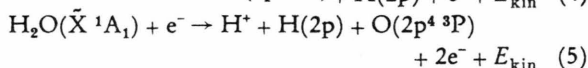
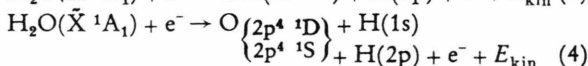
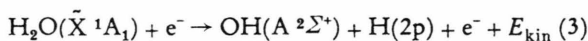
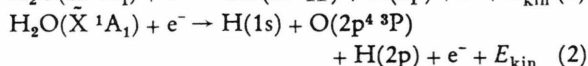
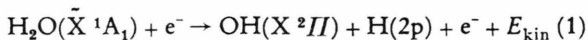
$$E_{\min} = E_{\text{diss}} + E_{\text{exc}} (+ E_{\text{ion}})$$

and the measured onset values it was tried to correlate the measured structures with different excitation processes. The data used for the calculation of the minimum energies can be found in Table 1.

Table 1. Dissociation and ionization energies. The excitation energies are taken from <sup>7</sup>.

$E_{\text{diss}}(\text{H}_2\text{O} \rightarrow \text{H} + \text{OH})$	$= 5.113_6 \text{ eV}^5$ ,
$E_{\text{diss}}(\text{OH} \rightarrow \text{H} + \text{O})$	$= 4.35 \text{ eV}^6$ ,
$E_{\text{diss}}(\text{H}_2 \rightarrow 2\text{H})$	$= 4.476_3 \text{ eV}^6$ ,
$E_{\text{ion}}(\text{O})$	$= 13.617 \text{ eV}^7$ ,
$E_{\text{ion}}(\text{H})$	$= 13.597 \text{ eV}^7$ ,
$E_{\text{ion}}(\text{H}_2)$	$= 15.4 \text{ eV}^8$ ,
$E_{\text{ion}}(\text{H}_2\text{O})$	$= 12.61_8 \text{ eV}^5$ .

There are many processes leading to Ly  $\alpha$  radiation, significant ones are for instance:

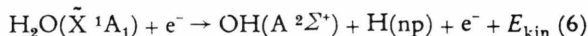


From Table 2 it follows that the first onset is unambiguously due to partial dissociation according to process (1). The second onset could be total dissociation (2) or the simultaneous formation of OH\* (3).

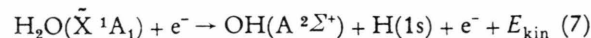
Table 2. Measured onsets and minimum values for the production of Ly  $\alpha$  radiation.

Measured onset eV	Minimum values eV	for the process
$16.1 \pm 0.5$	15.3	(1)
$21.5 \pm 0.8$	19.7	(2)
$26.2 \pm 1.5$	19.4	(3)
ca. 40	21.6 24.0	(4)
	33.3	(5)

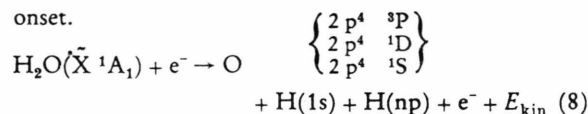
According to <sup>9</sup> the cross section for the formation of OH ( $\text{A}^2\Sigma^+$ ) by electron bombardment of  $\text{H}_2\text{O}$  was found to be  $1.0 \times 10^{-17} \text{ cm}^2$  at 100 eV electron energy. Under the assumption that the main peak is due to process (6)



one obtains for the sum of the cross sections ( $n=2,3,\dots$ ) about the same value as in <sup>9</sup>. This leads to the conclusion that nearly all OH\* are formed via (6) and not via (7).



This is however not reasonable. Therefore we can assume that the third onset should be total dissociation (2), but since simultaneous formation of metastable O atoms can not be excluded, we have to write equation (8) for the process responsible for the third onset.



If both these statements are true then the second onset is probably due to (3). The rise of the slope at about 40 eV could be caused by process (5), but these measurements do not allow for unambiguous interpretations. Only coincidence measurements can substantiate them fully. Also special structures which do not originate from different dissociation processes could be identified by such measurements.

In the case of the other Lyman transitions, where only two critical potentials were observed, the radiation near the first onset must originate from partial dissociation and excitation of an H atom. At the second onset total dissociation combined with ionization of the recoiling H or O atom can be excluded, whereas total dissociation including the formation of metastable O atoms (8) is possible ( $n=3,4,\dots$ ). Measured values and minimum energies see Table 4.

From energy considerations the simultaneous formation of OH\* is possible, but by the same argument as in the case of Ly  $\alpha$  one could conclude that the fract-

<sup>5</sup> G. HERZBERG, Molecular Spectra and Molecular Structure III, D. van Nostrand, New York 1966.

<sup>6</sup> G. HERZBERG, Molecular Spectra and Molecular Structure I, D. van Nostrand, London 1967.

<sup>7</sup> A. R. STRIGANOV and N. S. SVETITSKII, Tables of Spectral Lines of Neutral and Ionized Atoms IFL/Plenum, New York 1968.

ion from this process in the total amount of the cross section at maximum is small.

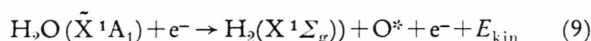
In photodissociation experiments BEYER and WELGE<sup>2</sup> have found Ly  $\alpha$  radiation corresponding to the first onset as measured here. For onsets at higher energy the photon energy used in<sup>2</sup> was not sufficient. In electron-collision processes MCGOWAN et al.<sup>1</sup> have also found two onset energies in the excitation function of Ly  $\alpha$ . The values measured there are  $(15 \pm 1)$  and  $(24 \pm 2)$  eV. It is possible that the authors of<sup>1</sup> could not resolve the second and third onset measured in this work.

### b) Excitation of Oxygen Atoms

The spectrum shows three intense O I lines and one very weak one. The excitation functions of these lines are very similar to each other and show two critical potentials. Here it is more difficult to interpret the structures in the excitation functions.

At the first onset partial and total dissociation are possible, but an additional ionization of the other dissociation products is impossible.

If the first onset is due to partial dissociation (9),



the second one can be total dissociation or simultaneous formation of H<sup>+</sup> or H<sub>2</sub><sup>+</sup> and excitation of an oxygen atom. The cross section as a function of electron energy for the formation of H<sub>2</sub><sup>+</sup> does not show a structure<sup>10</sup>. Since the cross sections for the formation of H<sub>2</sub><sup>+</sup> in<sup>10</sup> and of O\* in this work have the same order of magnitude in the maximum, one should have

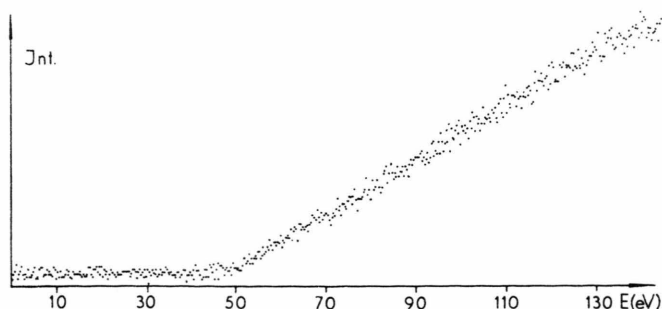
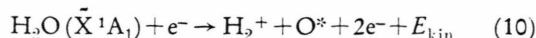


Fig. 5. Excitation function of the transition  $2p^3 4S^\circ - 2p^4 4P$ .

seen such a structure, if process (10) contributes substantially to the formation of O\*.



In the case of the simultaneous production of H<sup>+</sup>, this consideration is not possible because of the great difference between the cross section for the formation of H<sup>+</sup><sup>10</sup> and the excitation cross section of the second peak as measured here.

### c) Excitation of O II lines

We observed five O II lines in the dissociation spectrum of H<sub>2</sub>O. With the exception of the line at about 538 Å the classification of the lines is clear. Because of the low wavelength resolution (3 Å) it was not possible to separate the radiation from the quartet (539 Å) and doublet (538 Å) transition<sup>7</sup>.

There is only one radiation component the excitation function of which is without any structures: see Figure 5. This line at 833 Å belongs to the quartet system. In the threshold region the excitation functions are linear between sharp breaks at the critical potentials: see Figure 6.

The first onsets of the O<sup>+</sup> lines are about 20 eV larger than the minimum energies required for partial dissociation. Therefore it is not possible to interpret these breaks by energy considerations.

In<sup>10</sup> an ionization cross section of  $3.5 \times 10^{-18} \text{ cm}^2$  for the formation of O<sup>+</sup> was given. With a cross section measurement of about  $0.24 \times 10^{-18} \text{ cm}^2$  for excited O<sup>+</sup> ions it follows that approximately 7 % of the ions are excited at 100 eV electron energy.

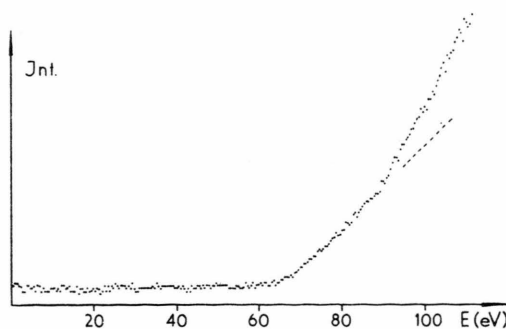


Fig. 6. Structure of the excitation function at 616 Å in the threshold region.

<sup>8</sup> V. I. VEDENEYEV et al., Bond Energies, Ionization Potentials and Electron Affinities, London 1962.

<sup>9</sup> DE HEER, private communication.

<sup>10</sup> J. SCHUTTEN, F. J. DE HEER, H. R. MOUSTAFA, A. J. H. BOERBOOM, and J. KISTEMAKER, J. Chem. Phys. 44, 3924 [1966].

## General Remarks

The dependence of the light intensity on gas pressure and beam current was measured immediately before and after the critical potentials. It was found to be strictly linear, so one can be certain that the excitation is a single-step process.

The intensity ratios of the Lyman series can be found in Table 3.

Table 3. Intensity ratios of the Lyman series at 100 eV  
Int (Ly  $\delta$ ) = 1.

Ly	$\alpha$	$\beta$	$\gamma$	$\delta$	$\epsilon$	$\eta$
	29.5	5.4	2.2	1.0	0.5	0.2

Intensity ratios were also measured in NH<sub>3</sub>, CH<sub>4</sub>, *i*-C<sub>4</sub>H<sub>10</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>2</sub>H<sub>6</sub>. They are nearly the same in all these substances and almost equal to calculated values of atomic hydrogen <sup>11</sup>.

Therefore it may be possible that the main part of the excitation takes place via high Rydberg states. The kinetic energy of the recoiling particles for the different processes is the difference between the measured appearance potential and the necessary minimum energy. In the case of the Ly series for the process of partial dissociation this kinetic energy is of the order of 1 eV. If the interpretation of the other structures is correct, one should find kinetic energies up to 40 eV.

Some of the measurements were repeated with D<sub>2</sub>O instead of H<sub>2</sub>O. In the case of D<sub>2</sub>O the cross sections in the maximum are about 10 % lower. This result was also obtained in <sup>1</sup> for Ly  $\alpha$ .

The onset potentials in D<sub>2</sub>O were measured for Ly  $\alpha$  and the O I line at 879 Å. The first onset in both cases is equal to that in H<sub>2</sub>O, but the other onsets are clearly higher in D<sub>2</sub>O.

Table 4. Summary of the results.

$\lambda$ (Å)	Transition	Measured Appearance Potential (eV)	$E_{\min}$ for the Process (eV)	$\sigma$ (100 eV) $\times 10^{18}$ (cm <sup>2</sup> )
1215.7	Lyman $\alpha$	16.1 $\pm$ 0.5 21.5 $\pm$ 0.8 26.2 $\pm$ 1.5	15.3 OH+H <sup>+</sup> 19.4 H <sup>+</sup> +OH <sup>+</sup> 19.7 O+H+H <sup>+</sup>	7.5
1152.2	O I 2p <sup>4</sup> <sup>1</sup> D – 3s' <sup>1</sup> D <sup>0</sup>	28.0 $\pm$ 2.0 41.0 $\pm$ 3.0	17.7 H <sub>2</sub> +O <sup>+</sup> 22.2 H+H+O <sup>+</sup>	0.2
1025.7	Lyman $\beta$	18.0 $\pm$ 0.5 25.5 $\pm$ 0.8	17.2 OH+H <sup>+</sup> 21.6 O+H+H <sup>+</sup>	1.4
999.5	O I 2p <sup>4</sup> <sup>1</sup> D – 3s'' <sup>1</sup> P <sup>0</sup>	29.5 $\pm$ 2.0 46.0 $\pm$ 4.0	19.3 H <sub>2</sub> +O <sup>+</sup> 23.8 H+H+O <sup>+</sup>	—
990.2	O I 2p <sup>4</sup> <sup>3</sup> P – 3s' <sup>3</sup> D <sup>0</sup>	27.0 $\pm$ 1.0 40.0 $\pm$ 1.5	17.5 H <sub>2</sub> +O <sup>+</sup> 22.0 H+H+O <sup>+</sup>	0.3
972.5	Lyman $\gamma$	18.8 $\pm$ 0.5 26.8 $\pm$ 0.8	17.9 OH+H <sup>+</sup> 22.2 O+H+H <sup>+</sup>	0.6
949.7	Lyman $\delta$	18.9 $\pm$ 0.6 26.4 $\pm$ 0.8	18.2 OH+H <sup>+</sup> 22.5 O+H+H <sup>+</sup>	0.3
937.8	Lyman $\epsilon$	18.9 $\pm$ 0.5 28.3 $\pm$ 1.3	18.3 OH+H <sup>+</sup> 22.7 O+H+H <sup>+</sup>	0.1
930.8	Lyman $\eta$	18.6 $\pm$ 0.5 29.0 $\pm$ 1.0	18.4 OH+H <sup>+</sup> 22.8 O+H+H <sup>+</sup>	0.05
879.1	O I 2p <sup>4</sup> <sup>3</sup> P – 3s'' <sup>3</sup> P <sup>0</sup>	28.0 $\pm$ 2.0 43.5 $\pm$ 3.0	19.1 H <sub>2</sub> +O <sup>+</sup> 23.6 H+H+O <sup>+</sup>	0.1
832.8 -834.5	O II 2p <sup>3</sup> <sup>4</sup> S <sup>0</sup> – 2p <sup>4</sup> <sup>4</sup> P	49.2 $\pm$ 3.0	33.5 H <sub>2</sub> +O <sup>++</sup> 38.0 H+H+O <sup>++</sup>	0.1
718.5	O II 2p <sup>3</sup> <sup>2</sup> D <sup>0</sup> – 2p <sup>4</sup> <sup>2</sup> D	58.5 $\pm$ 2.0 74.5 $\pm$ 5.0	39.2 H <sub>2</sub> +O <sup>++</sup> 43.7 H+H+O <sup>++</sup>	0.06
616.4	O II 2p <sup>3</sup> <sup>2</sup> D <sup>0</sup> – 3s <sup>2</sup> P	66.0 $\pm$ 3.0 91.0 $\pm$ 5.0	42.0 H <sub>2</sub> +O <sup>++</sup> 46.5 H+H+O <sup>++</sup>	0.03
555.1	O II 2p <sup>3</sup> <sup>2</sup> D <sup>0</sup> – 3s' <sup>2</sup> D	63.0 $\pm$ 4.0 84.0 $\pm$ 6.0	44.3 H <sub>2</sub> +O <sup>++</sup> 48.7 H+H+O <sup>++</sup>	0.02
538.3	O II 2p <sup>3</sup> <sup>2</sup> D <sup>0</sup> – 2p <sup>4</sup> <sup>2</sup> P	58.0 $\pm$ 3.0		
539.5	O II 2p <sup>3</sup> <sup>4</sup> S <sup>0</sup> – 3s <sup>4</sup> P	69.0 $\pm$ 3.0 89.0 $\pm$ 3.0	45.0 H <sub>2</sub> +O <sup>++</sup> 49.4 H+H+O <sup>++</sup>	0.03

## Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft. The authors are indebted to Dipl. Phys. H. HERTZ and Mr. H. G. W. MÜLLER for valuable discussions and experimental help.

<sup>11</sup> H. A. BETHE and E. E. SALPETER, Handbuch der Physik XXXV [1957].