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Rydberg series in the absorption spectrum of H₂O and D₂O in the vacuum ultraviolet^{†)}

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The photoabsorption cross section of molecular H₂O and D₂O has been determined in the range from $h\nu = 10$ eV to 20 eV with 0.03 Å resolution. A refined analysis of the Rydberg series including the rotational line shapes of several bands to locate the band origins and a comparison to recent ab initio calculations is given. In the region of continuous absorption we have assigned a p-type and a s-type Rydberg series leading to the ²A₁ and the ²B₂ state respectively with quantum defects $\delta \approx 0.75$ and $\delta \approx 1.36$.

I. Introduction

Water vapour is important because of its nearly universal appearance. Consequently the ground and excited states of the water molecule have been the subject of a large number of detailed investigations. For a discussion of the relevant literature up to 1974 we refer to Herzberg's¹ and Robins² books. In spite of considerable recent theoretical³⁻⁵ and experimental⁶⁻¹² efforts several problems concerning the vacuum ultraviolet (VUV) absorption spectrum of H₂O and D₂O, in particular the nature and assignment of the absorption bands in the ionization continuum region, need further clarification.

We report in the present paper on new measurements of the absorption cross section of H₂O and D₂O under high resolution in the VUV range for photon energies $h\nu = 10$ to 20 eV. In this range we expect transitions originating from the uppermost three orbitals: In the ground state the molecular orbital configuration is

$$(1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^2$$

where the uppermost three orbitals have vertical ionization energies of 12.62 eV, 14.75 eV and 18.54 eV respectively^{13,14}. The aim of our investigation is a detailed assignment of Rydberg series originating from the 1b₂, 3a₁ and 1b₁ orbitals. This is done by comparing our results with high resolution photoelectron spectra¹⁴ and with theoretical calculations⁵⁻⁶. As originally suggested by Mulliken¹⁵ and corroborated quantitatively by the recent calculations of the orbital sizes by Goddard and Hunt⁵ the simplest view of the excited orbitals is to consider each as arising from an n=3 Rydberg atomic orbital modified by the molecular field¹⁶.

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II. Experiments and Results

For our measurements we have exploited the combination of intense synchrotron radiation from the DORIS storage ring at DESY¹⁷ with a high resolution 3m normal incidence scanning monochromator with a vertical dispersion plane^{18,19}. In brief, synchrotron radiation emitted from electrons within the storage ring is focussed onto the entrance slit of the 3m instrument, which has a resolution of 0.03 Å in first order. The light emerging from the exit slit traverses a 60 cm long absorption chamber, is converted into longer wavelength photons by a sodium salicylate screen deposited on a glass window and is detected by a photomultiplier (EMI 9804). The gas pressure in the windowless absorption cell ranged from 1×10^{-1} to 1×10^{-4} Torr, as measured by a membrane - vacuummeter (Datamatrix Model 531).

Spectra for the absolute photoabsorption cross section of H₂O and D₂O are displayed in Fig. 1. Small portions of the spectra are shown in the inserts in Fig. 1, in Fig. 2 and in the insert in Fig. 3 on an expanded scale. From these, an idea of the resolution and accuracy of our data for determining detailed fine structure may be obtained. The spectra shown in Fig. 1 are replotted on a photon energy scale in Fig. 3 together with absorption data at lower photon energies⁹ and with our assignment (see below).

The absorption spectrum (Fig. 1) shows a range of strong structured bands between 1250 Å and ≈ 1000 Å, the range of the A B C and D series first observed by Price²⁰. This is followed to shorter wavelengths by a broad continuum with vibrational progressions superimposed. With the exception of additional details displayed here, the main features of the absorption spectrum are in good agreement with previous absolute cross section measurements as reported by Katayama et al.¹². A small part of the spectrum extending from 1220 Å to 1240 Å has been studied and analyzed previously by Johns²¹ with an even higher resolution of

0.005 Å using photographic recording. Within the limits of our "low" resolution nearly perfect agreement between this study and our measurements was found²². A vibrational analysis of the band systems with origins at 1240 Å and 1219 Å has been given by Bell²³ (see Table 2).

III. Discussion

In the discussion we confine ourselves to the Rydberg transitions originating from the $1b_2$, $3a_1$ and $1b_1$ orbital. The analysis of rotational line shapes using model calculations based on the asymmetric rotator²² enables us to locate precisely the band heads of several Rydberg transitions originating from the uppermost $1b_1$ orbital. The results of such an analysis are presented for the $1b_1 \rightarrow 3p_a(000)$ transition in Fig. 2. The fit has been obtained with the rotational constants as determined by Johns²¹, namely for the ground state: $A = 27.88$, $C = 9.29$ and $\epsilon = -0.44$ and for the excited 1B_1 state $A = 25.67$, $C = 8.55$ and $\epsilon = -0.53$. The agreement of this simple model calculation assuming the same geometry for the ground and excited state with the experiment is excellent.

A summary of our assignment is given in Table 1 where we also make comparison with the results of recent theoretical investigations⁵⁻⁸.

The absorption bands above the first ionization potential are superimposed on a strong continuous background. They are hitherto unassigned, although it has been conjectured^{2,12}, that the structured bands and progressions belong to Rydberg transitions originating from the $3a_1$ and $1b_2$ orbital. We have been guided for our assignment by the close correspondence of a vibrational progression associated with a particular Rydberg transition with the vibrational structure observed for the ionic states^{13,14}. Since it is difficult to identify the 0-0

transitions both in the photoelectron and the optical absorption spectrum we have used for the discussion of term values vertical ionization potentials (IP_v) as derived from the photoelectron spectra^{13,14}. Furthermore, as recently pointed out by Schwarz²⁴, the vertical energy difference of two electronic states is more suitable in many cases for a comparison of experiment with theory.

III.1 s-like series

As regards the s-like Rydberg series in H_2O , Robin⁷ has noted already a remarkable consistency of the term values regardless from which orbital they originate. The broad absorption bands at around 7.44 eV and 9.85 eV have been assigned by him as $1b_1 \rightarrow 3s$ and $3a_1 \rightarrow 3s$ respectively. This yields together with the IP_v 's at 12.62 eV and 14.87 eV term values of 5.18 eV and 5.02 eV respectively. Robin's assignment is also in accord with the most recent ab initio calculations for these transitions (see Table 1). Taking the third IP_v at 18.86 eV and assuming a term value of roughly 5.0 eV, we expect the $1b_2 \rightarrow 3s$ transition at around 13.8 eV. In this range strong continuous absorption and p-like states are observed. The $1b_2 \rightarrow 3s$ transition, which is expected to be broad and diffuse, may well additionally contribute to the cross section in this region. We assign the absorption bands at around 16 eV to 17 eV to the $1b_2 \rightarrow 4s$ transition. This assignment is corroborated by the one to one correspondence between the structure in the absorption cross section and the photoelectron spectrum as determined by Karlsson et al.¹⁴ Furthermore, the resulting term value of 2.0 eV for the 4s transition is consistent with this interpretation. On the basis of this term value one would expect 4s transitions originating from $1b_1$ and $3a_1$ at around 11.0 eV and 12.87 eV respectively. This expectation for the $1b_1 \rightarrow 4s$ assignment is in good agreement with the excitation energy calculated by Goddard and Hunt⁵. For the $3a_1 \rightarrow 4s$ transition it is not possible to give a unique assignment. Nevertheless a contribution of $3a_1 \rightarrow 4s$ to the absorption at around 12.9 eV is not unlikely.

III.2 p- and d-like series

Our assignments for the p- and d-like Rydberg transitions originating from the $1b_1$ orbital are given in Table 1. All the sharp and structured bands at around 11.0 eV can be assigned satisfactorily on the basis of their rotational contours to the four optically allowed $1b_1 \rightarrow 3d$ transitions²² (see also the insert in Fig. 1). Further, we note that for the lower members of the p- and d-like series there is excellent agreement between our assignment and the excitation energies as calculated by Goddard and Hunt⁵. The $3a_1 \rightarrow 4p$ and $\rightarrow 5p$ transitions are indicated in Fig. 3. Although there is a strong overlap of vibrational bands belonging to different p-like transitions as well as to the s-like states, as discussed above, our assignment is supported by the close correspondence of the structures in the absorption and photoelectron spectra as well as by the resulting term values. The detailed fine structure observed for several vibrational bands belonging to these Rydberg transitions (see the insert in Fig. 3) is still a problem. Aside from rotational structure the deviation of the molecular potential from spherical symmetry results in Liehr splitting effects¹⁶ of the p-like final states. At the same time a Renner-Teller splitting²⁵ in the nearly linear geometry of the excited states is expected. Without detailed calculations it is at present premature to give a more elaborate discussion of this point.

Finally we turn to the vibrational analysis for several of the observed transitions. We have summarized the main points in Table 2, where we give the frequencies of the ground state and the ionic states for comparison.²²

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Table 1: Assignment of Rydberg transitions in the absorption spectrum of H₂O and D₂O.
All energies are in eV. Subscript v; vertical energies.

Orbital, ionization energy binding properties (a,b)		transitions								
		assignment	experiment				theory			
			H ₂ O	δ		D ₂ O	H ₂ O		(g)	
H ₂ O	D ₂ O					(d)	(e)	(f)	(g)	
1b ₁ 12.62 12.62 (1st band) non bonding perpendicular to molecular plane		1b ₁ → 3s	7.44 _v (c)				7.30	7.61	7.30	7.22
		4s	10.64				10.64			
		5s					11.66			
		3pa ₁	9.998 0.72	10.011 0.72		10.04	10.06	9.90	9.02	
		3pb ₁	10.171 0.67	10.171 0.65		10.16	10.16	10.32	9.48	
		3da ₁	10.990 0.11	10.966 0.12		11.07			9.61	
		3da ₂	11.041 0.06	11.055 0.07		-				
		3db ₁	11.057 0.04	11.070 0.05		11.17				
		3da ₁	11.122 -0.02	11.130 0.00		11.17				
		4pa ₁	11.374 0.69	11.385 0.71		11.42				
		4pb ₁	11.432 0.60	11.427 0.65		11.48				
		4da ₁	11.729 0.08	11.752 0.08						
		4db ₁	11.770 -0.01	11.793 -0.01						
		5p	11.890 0.66	11.901 0.70						
		5d	12.061 0.05	12.075 0.08						
		6p	12.120 0.74	12.155 0.69						
		6d	12.235 0.02	12.254 0.04						
		7p	12.288 0.52	12.300 0.65						
		7d	12.337 0.01	12.365 -0.07						
		8p	12.361 0.63	12.386 0.65						
8d	12.399 0.07	12.423 0.03								
9p	12.411 0.77	12.438 0.75								
9d	12.448 -0.03	12.468 0.03								
∞p	12.612 0.67	12.637 0.70								
∞d	12.612 0.03	12.638 0.01								
3a ₁ 13.897 13.988 (1st band) 14.87 _v 14.96 _v weakly O-H bonding parallel to molecular plane		3a ₁ → 3s	9.85 (c)				9.82	9.80	9.54	
		4s	~12.9							
		4p	13.5 _v 0.83	13.9 _v 0.75		11.47	11.21	11.92	11.72	
		5p	14.1 _v 0.74	14.2 _v 0.70		12.08				
∞	~14.9 _v	~15.0 _v								
1b ₂ 17.22 17.26 strongly O-H bonding parallel to molecular plane		1b ₂ → 3s	~13.8 _v		~13.8 _v					
		4s	16.9 _v 1.38	17.0 _v 1.35						
		∞	18.9 _v	19.0 _v						

(a) D.W. Turner et al., Ref. 13; (b) L. Karlsson et al., Ref. 14; (c) M.B. Robin, Ref. 2;
(d) W.A. Goddard III and W.J. Hunt, Ref. 5; (e) N.W. Winter et al. Ref. 8;
(f) R.J. Buenker and S.D. Peyerimhoff, Ref. 6; (g) D. Yeager et al., Ref. 7

Table 2: Vibrational energies for the ν_1 and ν_2 mode observed in the present work for various states of H_2O and D_2O as compared to the energies of the same modes in the ground and ionic states. All energies are in meV.

state	H_2O		D_2O	
	ν_1 (meV)	ν_2 (meV)	ν_1 (meV)	ν_2 (meV)
ground state ^(a)	453	198	331	146
ionic state $2B_1$ ^(b)	402	177	293	132
$3pb_1$ this work	399	204	298	153
$3pb_1$ Bell ^(c)	405	203	295	152
$3pa_1$ this work	395	173	287	131
$3pa_1$ Bell ^(c)	394	174	290	129
$3da_1$	381	-	286	-
$3da_2, 3db_1$	407	-	315	-
$3da_1'$	400	-	300	-
ionic state $2A_1$ ^(b)		122		89
$3a_1 \rightarrow 4p$		117		90
$3a_1 \rightarrow 5p$		128		92
ionic state $2B_2$ ^(b)	365	185	267	134
$1b_2 \rightarrow 4sa_1$	342	180	259	133

References to Table 2

(a) G. Herzberg, Ref. 1

(b) L. Karlsson et al., Ref. 14

(c) S. Bell, Ref. 23

Figure Captions

Fig. 1 Absolute absorption cross section of molecular H_2O and D_2O in the range 1250 Å to 600 Å. The range of the $1b_1 \rightarrow 3d$ transitions is shown on an expanded scale in the insert. For the assignments see Table 1 and text.

Fig. 2 Comparison of the experimentally determined band profile for the $1b_1 \rightarrow 3pa_1(000)$ transition with a band profile calculated for an asymmetric rotator.

Fig. 3 Rydberg assignments for the absorption bands in the spectra of H_2O . For the range below 10 eV the spectra as determined by Watanabe et al.⁹ are shown. The dashed curves are the vibrational bands observed in the photoelectron spectra¹⁴. The insert for H_2O shows the observed fine structure for some of the bands in more detail.

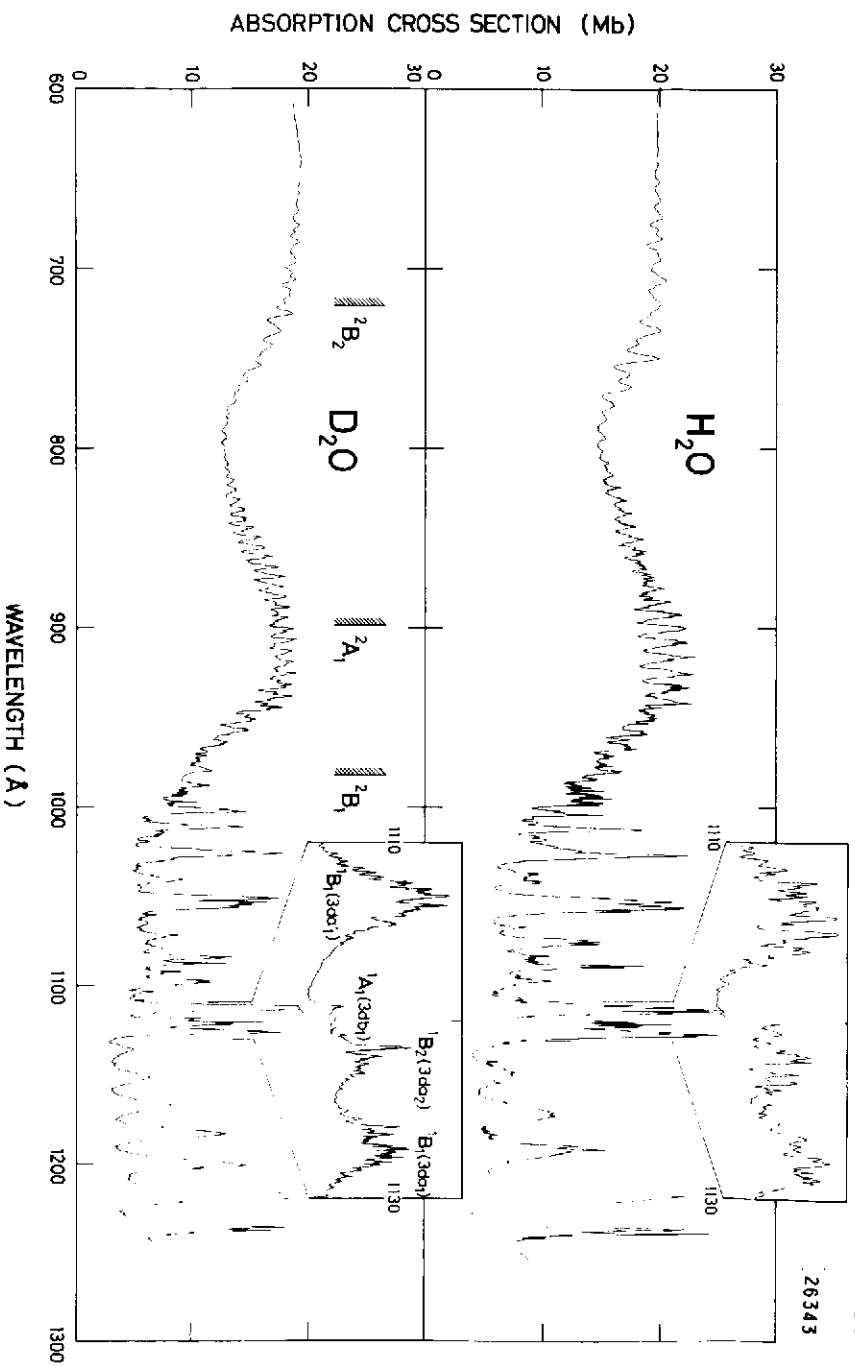
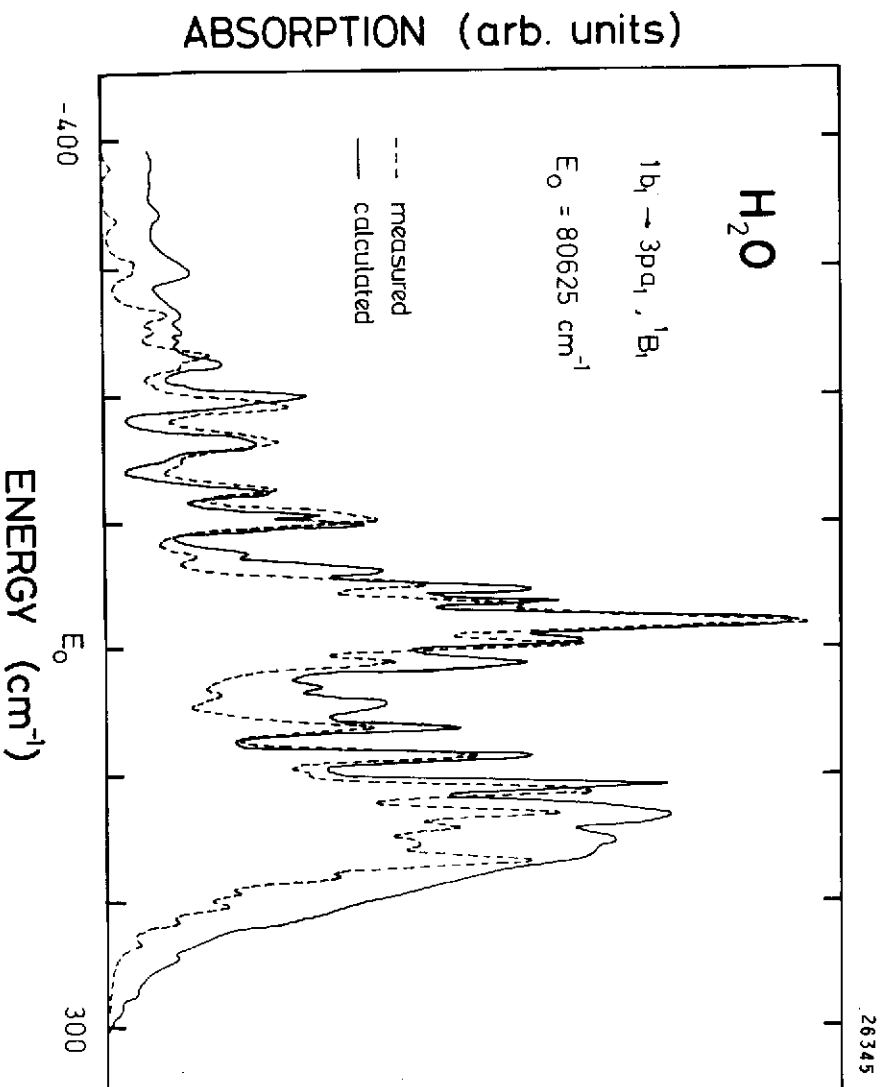


Fig. 1



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Fig. 2

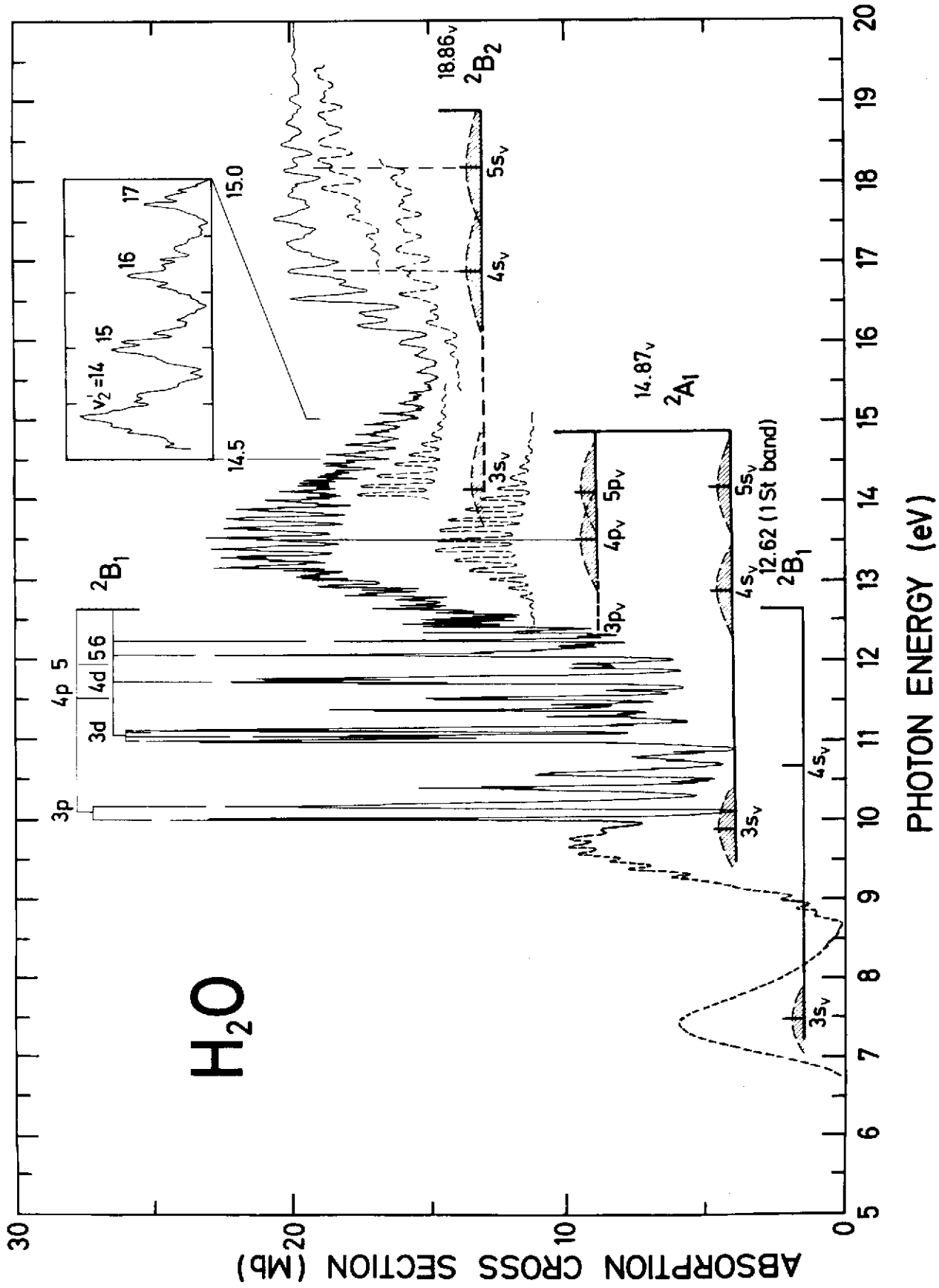


Fig. 3