

THE RYDBERG NATURE AND ASSIGNMENTS OF EXCITED STATES OF THE WATER MOLECULE*

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We report ab initio theoretical calculations on 32 excited states of H₂O found to lie below 11.7 eV. Of the eight states observed experimentally, the average discrepancy between theoretical and experimental excitation energies is 0.1 eV. We find that the excited states can each be characterized as arising from an excitation to a Rydberg orbital. Our results indicate that the \bar{E} and \bar{F} states are both 3d-like excited states rather than one 3d state and one 4s state as previously assumed and similarly for the two Rydberg series joining onto \bar{E} and \bar{F} . The $n\sigma a_1$ Rydberg series is found to have a quantum defect of 1.38, joining onto the $\bar{A}(^1B_1)$ state. We have assigned the 9.81 eV transition observed by electron impact as the $1b_1 \rightarrow 3p b_1$ excitation to a 3A_1 state.

1. Introduction

There has been a great deal of interest in the excited states of the H₂O molecule in recent years [1–3] with a number of experimental [4–8] and theoretical [9–17] studies reported. Despite this great amount of work only about one fourth of the excited states are known experimentally, and no consistent treatment of more than a few of the excited states has been previously reported. Here we report ab initio theoretical calculations of the vertical excitation energies to the 32 excited states of water we find to lie below 11.7 eV (all corresponding to excitations from the $1b_1$ and $3a_1$ nonbonding orbitals[#] of H₂O).

2. Computational details

The Hartree–Fock wavefunction of water contains five doubly-occupied orbitals

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2, \quad (1)$$

where $1a_1$ corresponds to an O1s orbital; $2a_1$ and $1b_2$ are usually considered as combinations of OH bonding orbitals, and $3a_1$ and $1b_1$ are σ and π nonbonding orbitals, respectively. The $1b_1$ and $3a_1$ orbitals have the lowest and second lowest ionization potentials; hence the low-lying excited states are expected to arise from these orbitals.

Low-lying excited states are obtained by exciting an electron from the doubly occupied orbital, ϕ_n , to an empty orbital, ϕ_ν (and combining with appropriate spin functions to obtain singlet and triplet states).

In the improved virtual orbital (IVO) method [9, 18] for excited states, we use the proper variational equations

$$H_\nu \phi_\nu = \epsilon_\nu \phi_\nu, \quad (2a)$$

$$H_\nu = \sum_i (2J_i - K_i) + (J_n \pm K_n), \quad (2b)$$

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We choose the standard coordinate system with the origin at the oxygen, the x axis perpendicular to the molecular plane, and the z axis bisecting the HH vector. In this case b_1 orbital are π orbitals with a nodal plane through all three atoms.

in solving for the excited orbitals but do not allow the unexcited orbitals of the ground state to readjust. Since $H_\nu(2)$ is independent of ϕ_ν , all excited states are obtained by solving (2) once each for the singlet and triplet state. Thus the solutions for all excited states arising from exciting of ϕ_n are obtained with about the same cost as one HF iteration for the ground state. The advantage of the IVO approach is that it removes the well known difficulties associated with regular virtual orbitals [9] but avoids the tedious solution of self-consistent orbitals for each state of a system.

The energy related quantity solved for directly in the IVO method is the orbital energy ϵ_ν in (2), which corresponds to the negative of the ionization potential of the excited orbital. Calculations [18] on H_2O , C_2H_4 , CO , N_2 , and O_2 [19] indicate that for Rydberg excited states these IP's are within 0.1 to 0.2 eV of the experimental value. The reason is that the correlation error in a Rydberg excited state is comparable to that in the positive ion (due to the diffuse nature of the excited orbital). To obtain the excitation energy from the ground state, we must subtract the IP's of the ground and excited states

$$\Delta E_{n \rightarrow \nu} = \text{IP}_n - \text{IP}_\nu = \epsilon_\nu - \epsilon_n. \quad (3)$$

However, Hartree-Fock calculations generally lead to poor values for ionization potentials from the ground state. For this reason we use in (3) the experimental value of ϵ_n .

The calculations reported herein were carried out with the Caltech SCF/GVB wavefunction programs [20] and the Polyatom integral programs. The basis used is the $(9s\ 5p\ |4s) \rightarrow [4s\ 3p\ |2s]$ contracted gaussian basis of Huzinaga and Dunning [21][†]. In order to describe the diffuse Rydberg orbitals of excited states, this basis was supplemented with appropriate diffuse s, p, and d gaussian functions ($\xi_s = 0.08, 0.02, 0.005, 0.00125$; $\xi_p = 0.05, 0.0125, 0.003125$; $\xi_d = 0.036358, 0.010769$) chosen from studies of the Rydberg states of O atom [18]. The geometry used is $R_{\text{OH}} = 1.8111 a_0$ and $\angle \text{HOH} = 104.45^\circ$.

[†] The hydrogen basis set is scaled for a Slater exponent of 1.2. Using the $[4s, 3p\ |2s]$ valence basis, we obtain an energy for the ground state of H_2O of -76.0105 h.

3. Results and discussion

The calculated excitation energies to the states below 11.7 eV are listed in table 1[‡] along with comparisons to other theoretical and experimental results. The properties of these excited states are tabulated in table 2. Here $\rho(\text{O})$ is the density of the excited orbital at the oxygen nucleus and $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$ are moments of the ϕ_ν charge density with respect to the oxygen nucleus.

Of the eight states observed experimentally [4, 23, 24], the average difference between the experimental and theoretical excitation energies is 0.1 eV.

3.1. The Rydberg nature of the excited states of H_2O

From an analysis of the results reported herein, we conclude that the simplest view of the excited orbitals is to consider each as arising from an $n \geq 3$ Rydberg atomic orbital, a view originally suggested by Mulliken [25][☆]. Thus the sequence of states obtained by exciting from either the $1b_1$ or $3a_1$ orbital is

3s, 3p, 4s, 3d, 4p, 5s, ...,

with splitting of each degenerate atomic orbital in the molecular field. Some of the evidence leading to this conclusion is summarized below.

3.1.1. Orbital sizes

From table 2 we see that for each excited state the excited orbital is very large in extent. Thus for the most compact valence orbital (ϕ_{3s} for 3B_1), the excited orbital has an $\langle r^2 \rangle$ of $17.5a_0^2$ whereas the occupied orbitals of the ground state all have $\langle r^2 \rangle$ less than $3.0a_0^2$. Comparing the sizes of the 3p orbitals we see that $\langle r^2 \rangle = 23.2a_0^2$ for $3p_{b_2}$ while it is 47.5 for $3p_{b_1}$ and 54.7 for $3p_{a_1}$. Thus the size ($\langle \{r^2\}^{\frac{1}{2}} \rangle$) of the $3p_{b_2}$ orbital is

[‡] In calculating excitation energies from (3), we have taken the experimental vertical ionization potentials [22] as $\text{IP}_{1b_1} = 12.62$ eV (which corresponds to the 0-0 first ionization of H_2O), and $\text{IP}_{3a_1} = 14.68$ eV (which corresponds to the ionization to the $\nu = 7$ vibrational state of the second ion state of H_2O). These IP's correspond to the vertical ionization potentials and hence yield vertical excitation energies in (3).

[☆] In eq. (8) of this paper $2 \times a_1$ should be $2 \times b_1$.

Table 1
Calculated and experimental vertical excitation energies for H₂O. All energies in eV

State	Present work ^{a)} (IVO)	Experimental		Other calculations			Bishop and Wu [13] (approx. SCF)
		photon spectry.	electron spectry. [4]	Hunt and Goddard [9] (IVO) ^{a)}	Claydon et al. [10] (INDO)	Miller et al. [11] (SCF)	
1b ₁ → 3sa ₁ 1 ³ B ₁	6.68			6.63	6.20	7.3 ^{a)}	
1 ¹ B ₁	7.30	≈ 7.49(Å) ^{e)}	7.40	7.28	7.43	7.7 ^{a)}	x ^{b)}
1b ₁ → 3pb ₂ 1 ³ A ₂	8.68			8.83	7.49		
1 ¹ A ₂	9.04			9.20	8.03		
→ 3pb ₁ 3 ³ A ₁	9.70		9.81	9.85			
1 ¹ A ₁	10.16	10.172(D̄) ^{e)}	10.17	10.26			y + 1.51
3pa ₁ 3 ³ B ₁	9.96			9.99			
1 ¹ B ₁	10.04	9.996(C̄) ^{e)}	10.00	10.08			x + 3.26
1b ₁ → 4sa ₁ 3 ³ B ₁	10.51			10.56			
1 ¹ B ₁	10.64	(10.63) ^{d)}		10.69			x + 3.61
1b ₁ → 3db ₂ 3 ³ A ₂	10.79						
1 ¹ A ₂	10.87						
→ 3da ₁ 3 ³ B ₁	11.05						
1 ¹ B ₁	11.07	10.99(Ē) ^{a, f)}					x + 5.17
→ 3da ₂ 3 ³ B ₂							
1 ¹ B ₂		(11.07) ^{d)}					
→ 3db ₁ 3 ³ A ₁	11.16						
1 ¹ A ₁	11.17	11.12(F̄) ^{f)}					y + 2.75
→ 3da ₁ 3 ³ B ₁	11.16						
1 ¹ B ₁	11.17	11.12(F̄) ^{f)}					x + 5.33
1b ₁ → 4pb ₂ 3 ³ A ₂	11.18						
1 ¹ A ₂	11.21						
→ 4pb ₁ 3 ³ A ₁	11.32						
1 ¹ A ₁	11.48	11.41(D̄ ₂) ^{f)}					y + 2.89
→ 4pa ₁ 3 ³ B ₁	11.40						
1 ¹ B ₁	11.42	11.37(C̄ ₂) ^{f)}					x + 5.59
1b ₁ → 5sa ₁ 3 ³ B ₁	11.62						
1 ¹ B ₁	11.66	(11.61) ^{d)}					x + 5.81
1b ₁ → 4db ₂ 3 ³ A ₂	11.64						
1 ¹ A ₂	11.67						
3a ₁ → 3sa ₁ 3 ³ A ₁	9.02			9.01	8.67		
1 ¹ A ₁	9.92	9.73(B̄) ^{e)}	9.5	9.94	10.85		y ^{b)}

Table 1 (continued)

$3a_1 \rightarrow 3pb_2$	1^3B_2	10.81		9.43
	1^1B_2	11.46	(≈ 11.4) ^{d)}	11.06

- a) The excitation energies are calculated from (3) using experimental ionization potential for ϵ_n (see footnote †, p. 465).
 b) Absolute energies of excited states were not reported (except that they were not in good agreement with experiment). Energies were reported with respect to the first excited state of the symmetry.
 c) In ref. [9], the IP of excited orbitals was reported but the ΔF reported used the HF ϵ_n instead of the experimental value.
 d) Transitions to these states are dipole allowed but have not yet been identified in the spectra. In each case we have listed the energy of an unidentified band from the spectra of Watanabe et al. [8]. Such assignments are tentative.
 e) Johns, ref. [6], f) Price, ref. [24].

about 68 % of the size of the other 3p orbitals. Although this is a significant contraction (see section 3 below for an explanation), the $3pb_2$ orbital is still quite diffuse compared to the $n = 2$ orbitals and can be considered as a Rydberg orbital.

3.1.2. Orbital properties for the na_1 sequence

Consider the sequence of excited a_1 orbitals, which we assign as $4a_1 = 3s$, $5a_1 = 3p$, $6a_1 = 4s$, $7a_1 = 3d$, $8a_1 = 3d$, $9a_1 = 4p$, and $10a_1 = 5s$. (For simplicity we consider just the 3B_1 states obtained from $1b_1 \rightarrow na_1$.) The orbitals assigned as 3s, 4s, 5s have calculated quantum defects of $\delta = 1.487$, 1.461, and 1.311, the orbitals assigned as 3p and 4p have quantum defects of $\delta = 0.738$ and 0.660, while the orbitals assigned as 3d have quantum defects of $\delta = 0.056$ and -0.053 . These quantum defects are all consistent with the above assignments.

Comparing the charge densities at the oxygen nucleus we find $\rho(O) = 0.962$, 0.179, and 0.065 au for the 3s, 4s, and 5s orbitals; $\rho(O) = 0.034$ and 0.006 au for the 3p and 4p orbitals; and $\rho(O) = 0.001$ and 0.0003 au for the 3d orbitals. Again these results are consistent with the Rydberg assignments.

The quadratic moments $\langle r^2 \rangle$, etc., are also consistent with the above assignments although the results here are not so persuasive since corresponding atomic values are not presented.

3.2. Assignments of the experimental transitions

3.2.1. Notation

The excited states of H_2O have been denoted several ways. Following Price [27], the upper states of the 10.00, 10.17, 10.99, and 11.12 eV transitions have been denoted as A, B, C, and D with subscripts sometimes

used to indicate the members of the Rydberg series joining onto the above states. Recently, Herzberg [23] has modified the notation, using \tilde{A} , \tilde{B} , \tilde{C} , \tilde{D} , \tilde{E} , and \tilde{F} to denote the upper states of the 7.50, 9.75, 10.00, 10.17, 10.99 and 11.12 eV transitions.

When reporting the whole spectrum of states (as in this paper) of a molecule, it would be convenient to identify the states as 1^1B_1 , 2^1B_1 , 3^1B_1 , etc. in analogy to notation for atomic states. However, such notation does not immediately specify the nature of the transitions. For example, 1^3A_1 , 2^3A_1 , and 3^3A_1 would be $3a_1 \rightarrow 3sa_1$, $1b_1 \rightarrow 3pb_1$, and $1b_1 \rightarrow 3db_1$, respectively. In addition this notation would have obvious problems above the first ionization limit. We will instead use a simple MO based notation such that the above transitions are denoted as

$$^3A_1(3a_1 \rightarrow 3sa_1) \text{ or } ^3A_1(3sa_1),$$

$$^3A_1(1b_1 \rightarrow 3pb_1) \text{ or } ^3A_1(3pb_1),$$

$$^3A_1(1b_1 \rightarrow 3db_1) \text{ or } ^3A_1(3db_1),$$

where the simpler notation on the right (indicating only the nature of the excited orbital) can be used in this paper without ambiguity.

3.2.2. Previous assignments

Mulliken [25] suggested that the first strong absorption in H_2O (at 7.5 eV) arises from $1b_1 \rightarrow 3sa_1$ and that the other excitations are to $n \geq 3$ Rydberg orbitals. Price [24] confirmed this by showing that the observed transitions above 10 eV all fit into four Rydberg series. From this basis, Johns [6] concluded that the 10.0 and 10.17 eV transitions must be $1b_1 \rightarrow 3pa_1$ and $1b_1 \rightarrow 3pb_1$. Based on his analysis of the rotational structure

Table 2
Calculated properties for excited states of water molecules

State	Orbital properties (au)				Quantum defect δ	$\Delta IP(eV)^c$ $\epsilon_{atom} - \epsilon_{molec}$
	$\rho(O)^a$	$\langle \alpha^2 \rangle^b$	$\langle \gamma^2 \rangle^b$	$\langle z^2 \rangle^b$		
$1b_1 \rightarrow 3sa_1$ 3B_1	0.962	4.129	6.430	6.887	1.487	1.47
1B_1	0.692	5.079	7.578	8.548	1.401	
$1b_1 \rightarrow 3pb_2$ 3A_2	0.0	4.084	13.276	5.887	1.142	1.07
1A_2	0.0	5.230	16.549	6.996	1.051	
$\rightarrow 3pb_1$ 3A_1	0.0	28.138	9.379	9.957	0.841	0.05
1A_1	0.0	42.959	14.320	15.372	0.667	
$\rightarrow 3pa_1$ 3B_1	0.034	14.067	14.120	26.519	0.738	-0.21
1B_1	0.025	14.850	15.443	28.148	0.704	
$1b_1 \rightarrow 4sa_1$ 3B_1	0.179	42.077	32.203	53.794	1.461	0.33
1B_1	0.152	48.006	36.288	60.571	1.379	
$1b_1 \rightarrow 3db_2$ 3A_2	0.0	19.465	58.454	22.271	0.273	0.29
1A_2	0.0	19.466	58.504	24.847	0.212	
$\rightarrow 3da_1$ 3B_1	0.001	28.703	69.445	18.280	0.056	0.03
1B_1	0.0009	29.149	71.700	20.334	0.037	
$\rightarrow 3db_1$ 3A_1	0.0	54.264	18.088	53.076	-0.053	-0.08
1A_1	0.0	56.508	18.836	52.843	-0.063	
$\rightarrow 3da_1$ 3B_1	0.0003	35.642	21.449	69.119	-0.053	-0.08
1B_1	0.0002	39.382	19.725	68.460	-0.063	
$1b_1 \rightarrow 4pb_2$ 3A_2	0.0	26.136	78.432	58.331	0.926	0.11
1A_2	0.0	30.259	90.321	59.605	0.894	
$\rightarrow 4pb_1$ 3A_1	0.0	184.852	61.617	62.707	0.765	-0.03
1A_1	0.0	254.068	89.689	86.209	0.545	
$\rightarrow 4pa_1$ 3B_1	0.006	80.910	75.142	170.338	0.660	-0.11
1B_1	0.005	81.665	80.579	184.486	0.633	
$1b_1 \rightarrow 5sa_1$ 3B_1	0.065	195.179	175.106	230.099	1.311	0.04
1B_1	0.050	229.216	215.565	256.094	1.235	
$1b_1 \rightarrow 4db_2$ 3A_2	0.0	83.834	251.501	89.979	0.274	0.12
1A_2	0.0	79.908	239.756	87.682	0.216	
$3a_1 \rightarrow 3sa_1$ 3A_1	0.855	4.280	6.982	7.624	1.450	1.19
1A_1	0.696	6.567	9.360	9.200	1.309	
$3a_1 \rightarrow 3pd_2$ 3B_2	0.0	4.083	13.316	5.953	1.125	1.10
1B_2	0.0	7.196	22.094	8.437	0.944	

Table 2 (continued)

ion states	2B_1	296.730	4.137	2.668	3.732
	2A_1	295.933	5.029	2.456	2.793
ground state	$1a_1$	141.426	0.018	0.018	0.018
orbitals	$2a_1$	6.142	0.498	0.737	0.674
	$3a_1$	0.797	0.460	0.643	1.390
	$1b_2$	0.0	0.417	1.760	0.790
	$1b_1$	0.0	1.352	0.451	0.451

- a) Electronic charge density of the Rydberg orbital at the oxygen nucleus.
 b) Origin at the oxygen nucleus.
 c) Using IP of quintet states of atom [26].

of the 10.17 eV transition, Johns correctly assigned it as 1A_1 ($1b_1 \rightarrow 3pb_1$). Based on Walsh's suggestion [27] that the quantum defects, δ , in H_2O be similar to those in O atom ($\delta_s = 1.20$, $\delta_p = 0.76$, and $\delta_d = 0.03$). Johns concluded that the 10.99 eV state (C or \tilde{E}) arises from $1b_1 \rightarrow 4sa_1$ while the 11.12 eV state (D or \tilde{F}) arises from $1b_1 \rightarrow 3d$. He suggested that the 11.12 eV transition should be looked at in high resolution to determine if it is composed of several lines.

Bell [7] analyzed the vibrational overtones of the 10.00 and 10.17 eV transitions, finding three bands below 10.99 eV that could *not* be so identified. These states (at 10.46, 10.63, and 10.84 eV, respectively) were found to each have different rotational structure, and Bell suggested that they may correspond to three different electronic states. He assigned them tentatively as the three allowed 3d transitions not involved in the 10.99 and 11.12 transitions.

3.2.3. Theoretical assignments

As indicated in table 1, we agree with the usual assignments of the \tilde{A} , \tilde{B} , \tilde{C} , and \tilde{D} bands. However, we calculate the ${}^1B_1(4sa_1)$ state to be at 10.64 eV, and we find three dipole allowed transitions to 3d states [${}^1B_1(3da_1)$, ${}^1A_1(3db_1)$, and ${}^1B_1(3da'_1)$] at 11.07, 11.17, and 11.17 eV, where the $3da_1$ and $3da'_1$ orbitals have the form

$$3da_1 = -0.50x^2 + 0.67y^2 - 0.17z^2,$$

$$3da'_1 = -0.57x^2 + 0.17y^2 + 0.73z^2.$$

There is one further dipole allowed transition to a 3d

orbital, $1b_1 \rightarrow 3da_2$; however we did not solve for excited orbitals of a_2 symmetry. Experimentally [8], bands are observed at 10.99, 11.07, and 11.12 eV and we conclude that these bands all involve transitions to excited 3d orbitals. Our results are not sufficiently precise to allow us to unambiguously identify which $1b_1 \rightarrow 3d$ transition is responsible for the three observed bands. The calculated relative oscillator strengths are 1.0, 0.13, and 0.22 to ${}^1B_1(3da_1)$, ${}^1A_1(3db_1)$, and ${}^1B_1(3da'_1)$. The ${}^1B_2(3da_2)$ state is expected to be below ${}^1A_1(3db_1)$ and of about the same strength. From these considerations the tentative assignments are ${}^1B_1(3da_1)$ at 10.99 eV, ${}^1B_2(3da_2)$ at 11.07 eV, and both ${}^1A_1(3db_1)$ and ${}^1B_1(3da'_1)$ at 11.12 eV. The assignment of the C and D states (i.e., \tilde{E} and \tilde{F}) as both due to transitions to 3d orbitals is consistent with the coalescing of these bands observed [24] for $n \geq 5$.

We find the ${}^1B_1(3sa_1)$, ${}^1B_1(4sa_1)$, and ${}^1B_1(5sa_1)$ states to be at 7.30, 10.64, and 11.66 eV, corresponding to quantum defects of $\delta = 1.40$, 1.38, and 1.24. Our basis set is only moderately adequate for the $5sa_1$ orbital and a better estimate of its energy is probably obtained by use of $\delta = 1.38$ from the $4sa_1$ orbital; this leads to the ${}^1B_1(5sa_1)$ state at 11.58 eV and the ${}^1B_1(6sa_1)$ state at 11.98 eV. The fitting of even the $3sa_1$ level so well onto this series helps confirm the Rydberg nature of the first excited state of H_2O . Except for $n = 3$, the members of this series have not been reported. Identification in the experimental spectra of the transitions to these states is complicated by the presence of vibrational overtones of the transitions to the np states. However, as noted above, Bell concluded that transitions at 10.46, 10.63, and 10.84 eV were not due to transitions

to the 3p states. If so the 10.63 feature could well be due to the $^1B_1(4s a_1)$ state (calculated at 10.64 eV). Indeed it is possible that the 10.84 eV features could arise from the dipole forbidden (but vibronically allowed) transition to $^1A_2(3db_2)$ calculated at 10.87 eV. There are also unidentified bands at 11.61 eV and 11.93 eV that could conceivably be due to the $^1B_1(nsa_1)$ states (in addition to npa_1 and npb_1 upper states).

Assignments of specific bands to specific states, especially those in the previous paragraph are premature at the present. One should be careful to remove possible vibrational overtones to all currently assigned states and to remove any contributions from hot bands, impurities, etc. On the theoretical side, we need to obtain more reliable oscillator strengths and energies to ≈ 0.03 eV. This may well require self-consistent orbitals for the excited states. On the other hand, our transition energies are sufficiently accurate so as to help greatly along with proper experimental studies in assigning the bands.

3.3. Comparison with the new states observed by electron impact

3.3.1. The 9.81 eV transition

The electron impact spectra [4] of H_2O yield a transition at 9.81 eV not observed in the optical spectrum. Trajmar et al. [4] have shown that the differential cross section for this transition is consistent only with it being a triplet state. As shown in table 1, we find $^1A_1(1b_1 \rightarrow 3pb_1)$ and $^1B_1(1b_1 \rightarrow 3pa_1)$ states at 10.16 and 10.04 eV, in good agreement with the spectroscopic values of 10.17 and 10.00 eV, respectively. In addition we find the corresponding 3A_1 and 3B_1 states at 9.70 and 9.96 eV. As a result, we assign the upper state of the 9.81 eV transition as the $^3A_1(1b_1 \rightarrow 3pb_1)$ state. Due to the large size of the $K_{1b_1,3pb_1}$ exchange integral (as compared to the $K_{1b_1,3pa_1}$ exchange integral), the $^3A_1 \rightarrow ^1A_1$ splitting is calculated to be 0.46 eV compared to only 0.08 eV for $^3B_1 \rightarrow ^1B_1$. As a result, the 9.81 eV triplet corresponds to the 10.17 eV singlet, not to the 10.00 eV singlet as one might have guessed.

3.3.2. The 4.5 eV transition

The other feature discovered in H_2O by electron impact spectroscopy [4] is the very weak transition at 4.5 eV. This has also been interpreted [4] as a singlet-trip-

let transition although the evidence is not as strong as for the 9.81 eV transition. The IVO results indicate that the lowest vertical single excitation is to the $^3B_1(1b_1 \rightarrow 3sa_1)$ state at 6.68 eV and hence the 4.5 eV transition cannot represent a vertical transition to an excited electronic state of H_2O (at least not to an excitation describable in terms of exciting one orbital of the ground state). We earlier [18] suggested that the 4.5 eV transition may be due to the H_2O dimer rather than the H_2O monomer. The reasoning was that the IP of the dimer should be much lower (≈ 1.5 eV) than the monomer and hence the excitation energies might be lower.

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