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M. S. Banna, B. H. McQuaide, R. Malutzki, and V. Schmidt

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The photoelectron spectrum of water in the 30–140 eV photon energy range

M. S. Banna[a] and B. H. McQuaide
Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235
R. Malutzki and V. Schmidt
Department of Physics, Freiburg University, 7800 Freiburg, Federal Republic of Germany

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Synchrotron radiation from the German storage ring BESSY has been used to study the photoelectron spectrum of the water molecule. Asymmetry parameters and relative photoionization cross sections have been measured for all four molecular orbitals ($2a_1$, $1b_2$, $3a_1$, and $1b_1$) in the 30–140 eV photon energy range. The results have been compared with the $X\alpha$ calculations of Roche, Salahub, and Messmer and good agreement was found. Comparison was also made with a number of previous measurements, including those obtained by $(e,2e)$ spectroscopy. Finally, the inner valence ($2a_1$) region has been studied at 60 and 100 eV photon energies and the relative intensities of some of the satellites were found to change as the exciting energy was varied.

I. INTRODUCTION

Interest in the electron spectroscopy of water continues unabated, the most recent studies being those of the valence orbitals using electron momentum spectroscopy.[1,2] In the present work, we report relative partial photoionization cross sections and asymmetry parameters for the four valence molecular orbitals. Since both of these quantities have been calculated theoretically, most recently by Roche, Salahub, and Messmer,[3] our results allow for a rigorous test of the various computations carried out on this very important molecule. In addition, we have studied the inner valence region for which the one-particle model is known to break down.[4] The data in this region were obtained at higher resolution than any of the previously reported studies; this was possible because of the high photon flux available from the storage ring BESSY. Here, too, comparison is made with a number of previous theoretical investigations.[1,5–9]

Our work is in part an extension of the previous study of photoionization cross sections (σ) and asymmetry parameters (β) at energies up to 30 eV by Truesdale *et al.*,[10] and of the study of σ values up to 60 eV by Tan *et al.*[11] Here we report measurements up to $\sim$140 eV and in addition we report measurements of σ and β for the deepest valence orbital, $2a_1$.

This study of water is part of a broader effort to obtain photoionization quantities for the first-row hydrides. Thus HF and NH_3 have also been studied and the results will be reported in the near future.

II. EXPERIMENTAL

The German storage ring BESSY was used in the present study, and the monochromator was of the toroidal grating type with a bandpass (for 1mm slits) of 1.0 eV for 60 eV photons and 2.0 eV for 110 eV photons. The corresponding photon fluxes were $\sim 7\times 10^{12}$ and $\sim 3\times 10^{12}$ photons/s, respectively.

Photoelectrons from the interaction region were energy analyzed with a double-sector CMA located and rotatable in the plane perpendicular to the photon beam direction.[12(a)] In addition, a fixed analyzer (also a CMA sector) monitored a signal for normalization with respect to the (decreasing) light intensity from the storage ring and to possible variations in the target density.

For the determination of β parameters, measurements were made at two angles close to both rotation limits of the analyzer and at a third intermediate angle. Helium was used to determine the azimuthal angle λ for the rotation of the polarization ellipse with respect to the plane of the ring, and the Stokes parameter P_1.[12(b)] The latter was found to decrease monotonically from $\sim$70% at 50 eV to $\sim$66% at 110 eV.

The differential and integrated cross sections are related in our experimental setup by the relationship

$$\frac{d\sigma}{d\Omega}(\theta) = \frac{\sigma}{4\pi}\left[1 + \frac{\beta}{4}(1 + 3P_1 \cos 2\theta)\right], \qquad (1)$$

where β is the asymmetry parameter, θ is the angle between the main polarization axis and the photoelectron direction, and P_1 is the Stokes parameter (degree of polarization). We have performed a least-squares fit of the three angular intensities (areas) obtained for each molecular orbital at each energy. This makes possible the determination of both β and the relative σ. The latter are obtained by dividing the intensity of each peak by the kinetic energy corresponding to its mean in order to correct for the change in the dispersion of the spectrometer with kinetic energy. At lower kinetic energy ($\leqslant$10 eV) a loss of transmission through the electron energy analyzer as well as a reduction of the channeltron detection probability might occur. These effects have been estimated by Kämmerling[13] and taken into account in the evaluation of intensities. Additional statistical precision can be achieved by taking the average of the two quantities (β or σ) obtained from the two CMA sectors.

Some of the measurements reported in this work, notably those for the inner valence region, were carried out at the *quasimagic angle*. From the angular distributions equation (1) above, this angle is given by

$$\theta_{QM} = \tfrac{1}{2}\cos^{-1}(-\tfrac{1}{3}P_1), \qquad (2)$$

[a] Alexander von Humboldt fellow.

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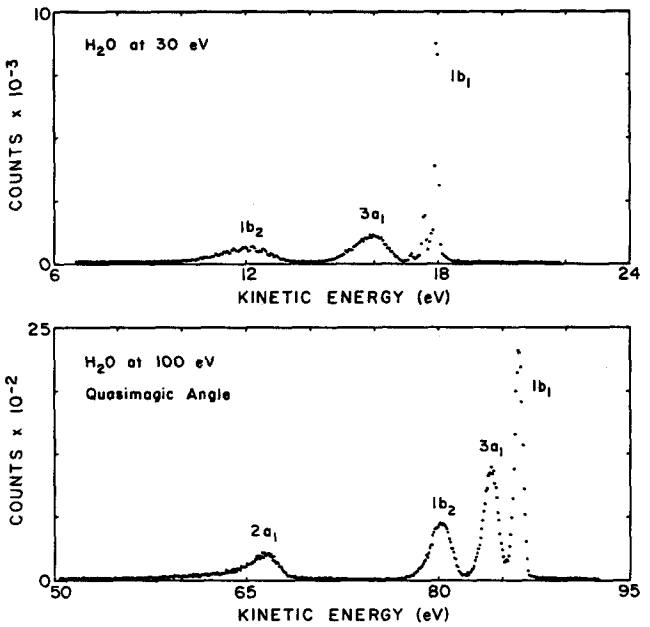

FIG. 1. Top: The outer three molecular orbitals of water obtained with 30 eV photons at an angle of ~22° with respect to the main polarization axis. Bottom: The four molecular orbitals of water obtained using 100 eV photons at the quasimagic angle.

TABLE I. Asymmetry parameters for the molecular orbitals of water.

$h\nu$ (eV)	$2a_1$	$1b_2$	$3a_1$	$1b_1$
30.0		0.49(1)	0.93(2)	1.31(3)
32.0		0.58(2)	1.01(2)	1.36(3)
34.4		0.60(4)	1.05(5)	1.36(6)
36.5		0.67(2)	1.09(4)	1.39(5)
38.5		0.71(3)	1.12(4)	1.38(5)
42.7	1.27(7)	0.80(2)	1.21(3)	1.48(3)
46.8	1.49(6)	0.85(2)	1.25(3)	1.49(3)
48.9	1.41(5)	0.92(2)	1.33(3)	1.56(4)
50.9	1.44(9)	0.90(2)	1.33(3)	1.54(4)
54.0	1.52(4)	0.94(2)	1.34(3)	1.52(3)
57.2	1.53(4)	0.97(2)	1.42(4)	1.57(3)
60.3	1.56(4)	1.00(2)	1.35(4)	1.53(4)
63.5	1.60(5)	1.02(5)	1.40(4)	1.58(4)
67.6	1.55(5)	1.09(8)	1.47(4)	1.59(4)
71.9	1.60(4)	1.07(3)	1.45(3)	1.55(3)
77.2		1.11(3)	1.48(4)	1.57(4)
82.4		1.14(3)	1.51(4)	1.58(4)
87.8		1.15(3)	1.50(4)	1.57(4)
93.2	1.76(5)	1.17(3)	1.55(4)	1.59(4)
98.5		1.17(4)	1.53(4)	1.58(4)
103.8	1.72(5)	1.24(4)	1.56(6)	1.60(4)
114.7	1.80(6)	1.28(4)	1.57(6)	1.60(4)
138.9		1.50(20)	1.84(18)	1.79(17)

and the cross sections are proportional to the integrated cross sections in this case.

The high resolution possible at lower photon energies is illustrated by the example in Fig. 1(a); it compares favorably with that in the reported spectrum using He II radiation,[14(a)] which is not as good as the resolution in the He I spectrum.[14(b)] All four MO's are shown in Fig. 1(b), obtained with 100 eV photons at the quasimagic angle. Again, the resolution is good for this energy.

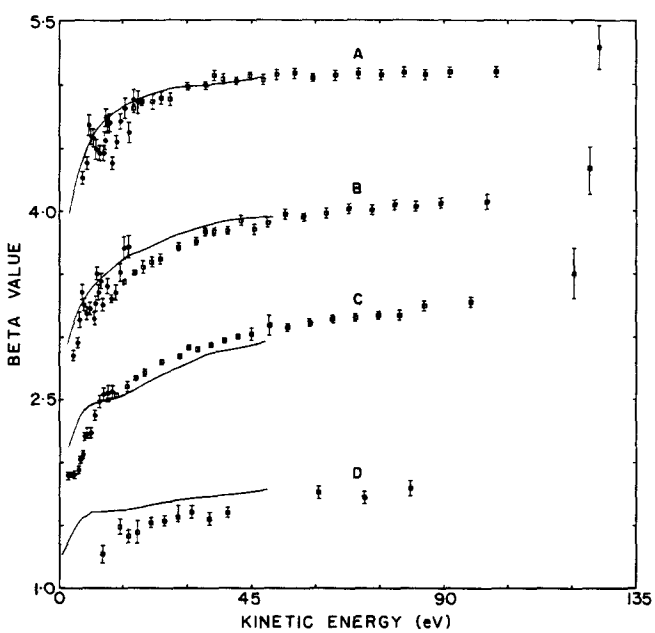

FIG. 2. The asymmetry parameters of the MO's of water (binding energies are: $1b_1$ 12.6 eV, $3a_1$ 14.8 eV, $1b_2$ 18.6 eV, and $2a_1$ 32.6 eV) as a function of kinetic energy of the photoelectron. Our measurements are denoted by squares, those of Truesdale *et al.* (Ref. 10) by solid circles, and the theoretical results of Roche *et al.* (Ref. 3) are shown as a solid line. Data labeled A are for $(1b_1)^{-1}$, those labeled B are for $(3a_1)^{-1}$, those labeled C are for $(1b_2)^{-1}$, and those labeled D are for $(2a_1)^{-1}$. For clarity, the first three sets of values are incremented by 3.5, 2.5, and 2.0, respectively.

TABLE II. Relative partial photoionization cross sections for the molecular orbitals of water.

$h\nu$ (eV)	$2a_1$	$1b_2$	$3a_1$	$1b_1$
30.0		1.15(6)	0.97(2)	1.00
32.0		1.05(5)	0.92(1)	1.00
34.4		1.04(3)	0.95(3)	1.00
36.5		0.99(3)	0.90(1)	1.00
38.5		0.94(3)	0.88(1)	1.00
42.7	0.31(3)	0.89(2)	0.88(1)	1.00
46.8	0.31(3)	0.83(1)	0.86(1)	1.00
48.9	0.27(2)	0.81(1)	0.86(1)	1.00
50.9	0.31(2)	0.80(1)	0.86(1)	1.00
54.0	0.33(1)	0.79(1)	0.85(1)	1.00
57.2	0.40(1)	0.74(1)	0.82(1)	1.00
60.0[a]	0.37(1)	0.77(1)	0.89(1)	1.00
60.3	0.37(1)	0.72(1)	0.87(1)	1.00
63.5	0.38(1)	0.78(1)	0.86(2)	1.00
67.6	0.46(1)	0.67(1)	0.82(2)	1.00
71.9	0.46(3)	0.70(1)	0.83(2)	1.00
77.2		0.71(1)	0.85(2)	1.00
82.4		0.70(1)	0.85(1)	1.00
87.8		0.67(1)	0.84(1)	1.00
93.2	0.56(1)	0.68(1)	0.83(1)	1.00
98.5		0.67(3)	0.89(4)	1.00
100.0[a]	0.49(1)	0.64(3)	0.89(4)	1.00
114.7	0.77(1)	0.67(1)	0.89(2)	1.00
138.9		0.73(6)	0.95(4)	1.00

[a] From measurements made at the quasimagic angle [Eq. (2)] only while all other σ values are obtained from angle-dependent measurements followed by the use of Eq. (1) to calculate σ as explained in the text.

TABLE III. Absolute partial photoionization cross sections for water (Mb).

	$1b_1$		$3a_1$		$1b_2$		$2a_1$		Total σ	
$h\nu$ (eV)	Ref. 11	This work[a]	Ref. 11	This work[a]	Ref. 11	This work[a]	Ref. 11	This work[a]	Ref. 11[b]	Ref. 17
30.0		5.1		4.9		5.8				15.8
30.5	4.37		4.16		5.19				13.7	
31.5	4.27		3.74		5.05				13.1	
32.0		4.7		4.4		5.0				14.1
32.5										
34.4										
34.5	3.58		3.25		3.76		1.05		11.6	
36.5	3.70		2.96		3.29		1.05		11.0	
37.5	3.44		2.84		3.00		1.12		10.4	
38.5	3.19		2.85		2.98		0.94		10.0	
39.5	3.35		2.80		2.68		0.94		9.8	
40.5	3.05		2.55		2.83		1.01		9.4	
41.5	2.94		2.36		2.86		0.84		9.0	
42.5	2.97		2.52		2.29		0.93		8.7	
42.7		3.0		2.7		2.7		0.9		9.3
43.5	2.86		2.39		2.16		0.99		8.4	
44.5	2.58		2.24		2.33		1.02		8.2	
45.5	2.49		2.29		2.17		0.82		7.8	
46.5	2.39		2.05		2.06		1.00		7.5	
46.8		2.6		2.3		2.2		0.8		7.9
47.5	2.33		2.04		1.95		0.96		7.3	
48.5	2.35		1.93		1.99		0.89		7.2	
48.9		2.5		2.2		2.0		0.7		7.4
49.5	2.28		1.98		1.77		0.90		6.9	
50.5	2.10		1.98		1.78		0.95		6.8	
50.9		2.3		2.0		1.9		0.7		6.9
51.5	2.20		2.00		1.60		0.87		6.7	
52.5	2.32		1.82		1.56		0.98		6.7	
53.5	1.89		1.47		1.65		0.95		6.0	
54.0		2.1		1.8		1.6		0.7		6.2
54.5	1.78		1.78		1.50		0.83		5.9	
55.5	1.72		1.64		1.47		0.92		5.8	
56.5	1.76		1.61		1.45		0.70		5.5	
57.2		1.9		1.6		1.4		0.8		5.7
57.5	1.59		1.64		1.36		0.88		5.5	
58.5	1.66		1.54		1.44		0.75		5.4	
60.0		1.7		1.5		1.3		0.6		5.2
60.3		1.7		1.5		1.2		0.6		5.1
60.5	1.45		1.34		1.44		0.95		5.2	
63.5		1.6		1.3		1.2		0.6		4.7
67.6		1.4		1.1		0.9		0.6		4.1
71.9		1.2		1.0		0.9		0.6		3.7
93.2		0.7		0.6		0.5		0.4		2.1
100.0		0.6		0.5		0.4		0.3		1.8
114.7		0.4		0.4		0.3		0.3		1.4

[a] Cross sections obtained by partitioning the photoionization cross sections from Ref. 17, given in the last column, using the relative cross sections from Table II.

[b] Cross sections obtained by multiplying the measured absolute photoabsorption oscillator strength by the ionization efficiency. The resulting photoionization cross sections were partitioned using measured branching ratios to yield the results given in the table.

III. RESULTS AND DISCUSSION

A. Asymmetry parameters

Truesdale *et al.*[10] reported asymmetry parameters for the outer three MO's of water up to a photon energy of 31 eV. Their results are plotted along with ours as a function of kinetic energy in Fig. 2. In the region of overlap there is reasonable agreement except for the $3a_1$ MO where their results are over 0.1 greater than ours.

We have also measured β's for the deepest MO ($2a_1$). The values obtained are also plotted in Fig. 2 and given in Table I along with the values for the other three MO's.

Roche *et al.*[3] carried out SCF-$X\alpha$-scattered wave calculations of both σ and β. Their results for β are shown as solid lines in Fig. 2. The comparison shows qualitative agreement with experiment as can be expected.[15] It was noted previously[3] that the O2p lone-pair character of the $1b_1$ and $3a_1$ orbitals is reflected in the similarity of their β plots to that of O2p of atomic oxygen, also calculated by Roche *et al.*[3] On the other hand, the effect of bonding to the hydrogens is exhibited by the β's of $1b_2$ as a displacement to lower values compared to $1b_1$ and $3a_1$.[3] Finally, the $2a_1$ β's are large (ap-

proaching 2) since this orbital is predominantly O2*s* (with a β value of 2).

B. Photoionization cross sections

Experimentally, the photoionization cross sections of water have been studied to a greater extent than the asymmetry parameters. For example, Banna and Shirley[16] reported relative photoionization cross sections at a photon energy of 132.3 eV (the $YM\zeta$ line) over a decade ago. Unfortunately, many of the earlier measurements were carried out using a 90° geometry between the photon and photoelectron beams. Thus it was not possible to obtain true partial cross sections since the asymmetry parameters were not known accurately. A notable exception to this trend is the work of Tan *et al.*[11] who reported partial photoionization cross sections over a range up to 60 eV photon energy using the (*e*,2*e*) quasiphoton impact technique.

In this section we compare our partial photoionization cross sections with those obtained previously, particularly the results of Tan *et al*,[11] as well as with the $X\alpha$ scattered wave calculations of Roche *et al.*[3] Although our experiment yields relative cross sections most directly, it is possible to obtain absolute values as well by normalizing to existing total photoabsorption cross section measurements.[17]

The relative cross sections are given in Table II. If we assume that the four ionic states corresponding to single ionization from $2a_1$, $1b_2$, $3a_1$, and $1b_1$ are the only possible final states (with shake up states included in the case of $2a_1$, see Sec. III C below, but direct double ionization processes also neglected) then the total photoionization cross section at each energy[17] can be partitioned thus yielding absolute partial cross sections. The values thus obtained are given in Table III where comparison is also made with the direct measurements of Tan *et al.*[11] Figure 3 provides a comparison of our results with theory as well as with (*e*,2*e*) quasiphotoionization. There is good agreement among all three sets of results.

It is interesting to examine how the ratio of the total cross section of the three outer molecular orbtials to the inner orbital cross section changes with photon energy. From the relative cross sections in Table II it can be seen that the ratio decreases from 10:1 at ~40 eV photon energy to 7:1 at ~60 eV. Tan *et al.*[11] observed a somewhat more dramatic change, the ratio decreasing from 8:1 at 40 eV to 4.5:1 at ~60 eV.[18] Such an intensity change has been explained before, for example by Banna and Shirley,[16] albeit in a different energy range. (Excitation was with Mg$K\alpha$ radiation with an energy of 1254 eV vs $YM\zeta$ radiation with an energy of 132 eV.) There it was noted that the molecular orbitals with 2*s* composition gain over those originating from 2*p* orbitals with increasing photon energy. This behavior may be useful in determining the orbital composition of the states present in the inner valence region which is discussed in Sec. III C below.

Next we compare our results with a selection of previously reported photoelectron spectroscopic measurements of differential photoionization cross sections, and with some of the calculations predicting this quantity. In all these cases a right-angle geometry was used; this means that a knowledge of β is necessary for a meaningful comparison with the present results. Since unpolarized radiation (from x-ray tubes or discharge lamps) was used in the previous studies, Eq. (1) should be modified to read

$$\frac{d\sigma}{d\Omega}=\frac{\sigma}{4\pi}\left[1+\frac{\beta}{4}(3\cos^2\theta'-1)\right], \tag{3}$$

where θ' is now the angle between the direction of propagation of the photon beam and the photoelectron beam. When $\theta'=90°$,

$$\left(\frac{d\sigma}{d\Omega}\right)_{90°}=\frac{\sigma}{4\pi}\left(1+\frac{\beta}{4}\right). \tag{4}$$

Thus knowing σ and β for a molecular orbital makes possible the determination of $\sigma_\perp$ for that orbital. In Table IV we compare the relative $\sigma_\perp$'s extracted from our data [using Eq. (4)] with those measured directly.[16,19,20] We also compare with the theoretical results of Yarzhemsky *et al.*[21] who used the Gelius model,[22] which gives the molecular orbital cross section as a sum of atomic orbital cross sections each weighted by the electron population of the respective atomic orbital, coupled with theoretically obtained (random-phase approximation with exchange, or RPAE) atomic σ's and β's to calculate $\sigma_\perp$'s using Eq. (4). In general, our results agree

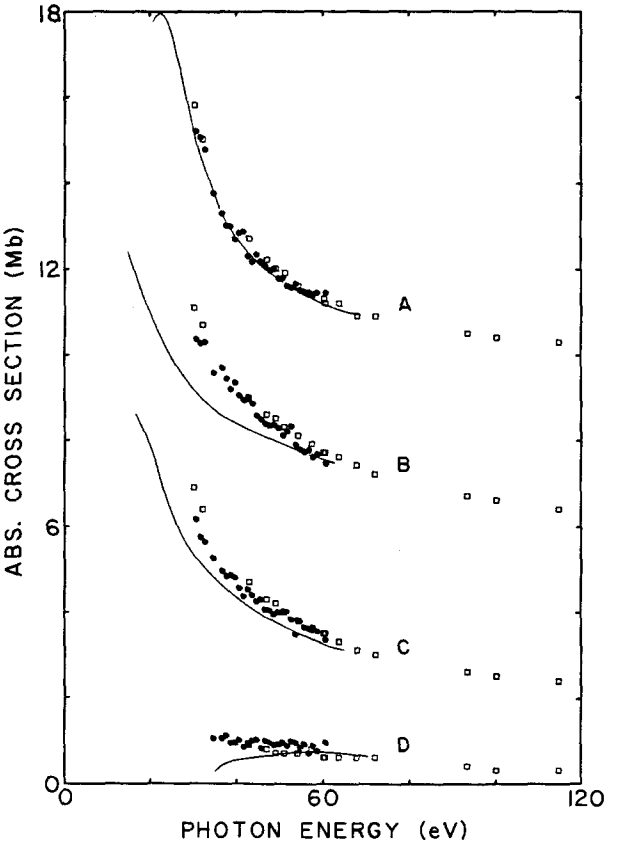

FIG. 3. Absolute partial photoionization cross sections of the molecular orbitals of water as a function of photon energy. □, this work, using total photoionization cross sections from Ref. 17; ●, Ref. 11; solid line, $X\alpha$ results from Ref. 3. Data labled A are for $(1b_2)^{-1}$, those labeled B are for $(1b_1)^{-1}$, those labeled C are for $(3a_1)^{-1}$, and those labeled D are for $(2a_1)^{-1}$. For clarity, the first three sets of values (A, B, and C) are displaced by 10, 6, and 2 Mb, respectively.

TABLE IV. Relative differential photoionization cross sections (σ_1) for the molecular orbitals of water.

(A) $h\nu = 41$ eV MO	This work[a]	Ref. 19	Ref. 20	Theory[b]
$1b_1$	1.00	1.00	1.0	1.00
$3a_1$	0.84	1.04	0.8	0.82
$1b_2$	0.78	0.83	0.6	0.77
$2a_1$	0.30			0.32
(B) $h\nu = 132$ eV MO	**This work[c]**	**Ref. 15**	**Theory[b]**	
$1b_1$	1.00	1.00	1.00	
$3a_1$	0.96	1.13	0.85	
$1b_2$	0.70	0.76	0.64	
$2a_1$		1.09	0.65	

[a] Actually measured at $h\nu = 42.7$ eV.
[b] Reference 21. See the text for a brief explanation of the method used.
[c] Actually measured at 139 eV.

quite well with previous measurements. Furthermore, there is excellent agreement with theory at 41 eV; this agreement with experiment was not as apparent when only the He II results were available.[19,20]

C. The inner valence region

It is well known that the inner valence region of many molecules is rich in satellites corresponding to multielectron excitation. This region in water has been studied with both monochromatized Al$K\alpha$ x rays[23] and lower-energy radiation (132.3 eV[16] and 151.4 eV[20]). In principle, this should allow for a comparison of relative satellite intensities as a function of photon energy. Unfortunately, the statistics in the lower-energy spectra were not sufficient to make this procedure meaningful. Recently, however, the powerful technique of binary $(e,2e)$ has been used to probe this region with better sensitivity than previously possible.[1,2] Cambi *et al.*[1] point out that the interpretation of relative intensities is much more straightforward in binary $(e,2e)$ than in photoelectron spectra. This enabled them to compare their inner-valence results with some of the many available calculations.[5–9]

Synchrotron radiation provides an excellent source for studying the dependence of shake-up intensities on photon energy. In this work we report two measurements at 60 and 100 eV, and attempt to determine if there is an accompanying change in the appearance of the inner valence region. Cambi *et al.*[1] concluded that the features above 25 eV are "*s*-type" based on the change in relative intensities when the relative azimuthal angle ϕ is varied. Banna and Shirley[16] reached a similar qualitative conclusion earlier by noting the behavior of the cross section with large changes (order of magnitude) in photon energy. Cambi *et al.*[1] also confirmed the presence of weak features at ~ 27 eV, as noted earlier.[23]

The spectra obtained at 60 and 100 eV are shown in Figs. 4 and 5, respectively. It is interesting that the resolution here, especially at 60 eV was superior to that in any of the previously reported spectra of the inner-valence region, as evidenced by the partial resolution of vibrational structure in the first band (somewhat obscured by the compact energy scale of Fig. 4). Yet no new features are resolved in the inner region compared to those in the spectrum of Martensson *et al.*[23] This suggests that the peaks are inherently broad or that the overlap between adjacent peaks is substantial.

Our spectra are in agreement with previous results concerning the weak feature at ~ 27 eV. One of the interesting observations to note here is that this structure weakens in going from 60 to 100 eV excitation. Qualitatively, its intensity appears to track that of the outer three MO's. From Table II, the combined intensity of the first three MO's relative to the inner region decreases from 7.2 to 5.2 in going from 60 to 100 eV excitation. As a sample comparison with theory we show (as vertical bars) the multireference double excitation configuration interaction (MRD-CI) results of Cambi *et al.*[1] It is interesting that the states at 27 eV, assigned by them predominantly to $1b_1^{-1}1b_1^{-1}4a_1$ are inexplicably absent in the

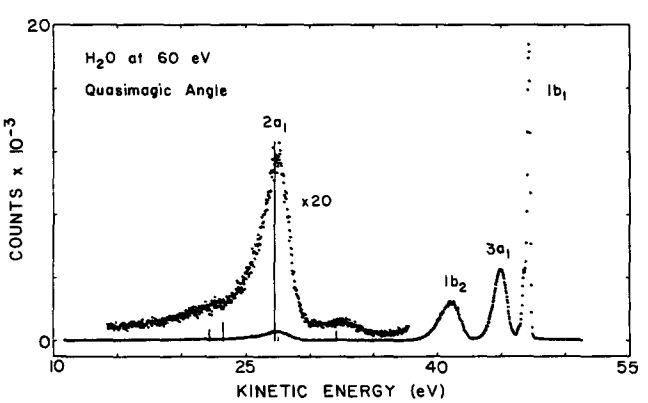

FIG. 4. The $2a_1$ region of water at 60 and the quasimagic angle. To give some idea about the resolution, the outer valence region is also shown. The vertical bars (only the relative heights are significant) are the results of MRD-CI calculations by Cambi *et al.* (Ref. 1). The main corresponding configurations are (from right to left) $1b_1^{-1}1b_1^{-1}4a_1$, $3a_13a_1^{-1}4a_1$, $2a_1^{-1}$, $3a_1^{-1}1b_1^{-1}2b_1$ (and $3a_1^{-1}1b_2^{-1}2b_2$), and $3a_1^{-1}1b_1;2b_1$ (and $3a_1^{-1}1b_2^{-1}2b_2$).

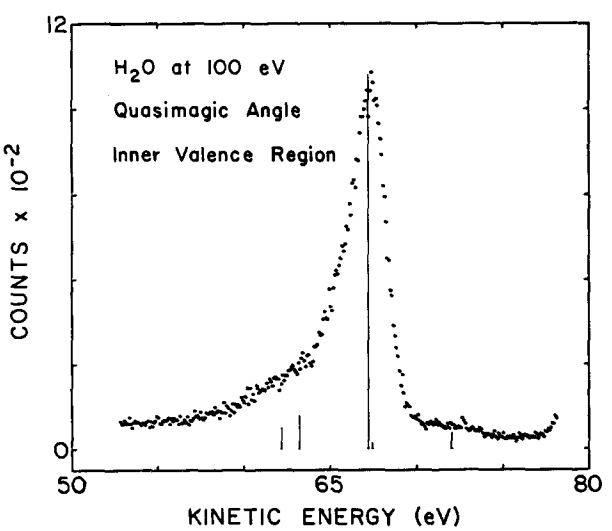

FIG. 5. The $2a_1$ region of water at 100 eV and the quasimagic angle. Theory is the same as in Fig. 4.

symmetry-adapted-cluster CI calculations of Nakatsuji and Yonezawa.[9] Quantitative comparison between experimental and theoretical relative intensities must await accurate calculations of photoionization cross sections of the various states as well as better calculations of the pole strengths. Therefore, at this stage we merely note that theory appears to predict the experimental spectrum reasonably well.

In conclusion, this work has provided a check on previous experimental measurements using a variety of techniques and new data which should spur more accurate theoretical work. We have shown that in the photon energy range of interest in this work it is now possible to utilize synchrotron radiation to meaningfully study the inner valence region despite the small cross sections of the states involved.

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