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Submitted to Chemical Physics Letters

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PHOTOIONIZATION CROSS SECTIONS FOR PRODUCTION
OF THE $(2a_1)^{-1}$ STATE OF H_2O UP TO 200 eV

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February 1986

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LBL-20530

PHOTOELECTRON BRANCHING RATIOS AND PARTIAL PHOTOIONIZATION CROSS SECTIONS FOR PRODUCTION OF THE $(2a_1)^{-1}$ STATE OF H_2O UP TO 200 eV

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The photoelectron branching ratio for the production of the $(2a_1)^{-1}$ state of H_2O^+ has been measured in the 50-200 eV photon-energy range using synchrotron radiation and magic-angle photoelectron spectroscopy. Partial photoionization cross sections are derived from the measured branching ratios using previously reported absolute photoabsorption cross sections. The results are consistent with earlier measurements from threshold to 60 eV obtained with dipole (e, 2e) spectroscopy.

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I. Introduction

Partial photoionization cross sections for the outer-valence orbitals of gaseous H_2O molecules have been measured using photoelectron spectroscopy with synchrotron radiation in the photon-energy range from 18 to 40 eV [1] and by dipole (e,2e) spectroscopy from 16 to 60 eV [2-5]. Photoionization of the $2a_1$ inner-valence orbital, which is principally of oxygen 2s character [6,7], has been less well-studied because of its relatively low cross section (<1 Mb) and higher ionization threshold (~ 30 eV). However, Tan et al. [2] measured the $(2a_1)^{-1}$ photoelectron branching ratio using dipole (e,2e) spectroscopy [8-10] over the photon-energy range from near threshold to 60 eV. These branching-ratio values were converted to partial photoionization cross sections (dipole oscillator strengths) by using the corresponding values of the absolute photoabsorption cross section measured by dipole (e,e) spectroscopy [2]. The photoionization efficiency was found to be unity above 20 eV from a consideration of the associated dipole (e,e+ion) data [2].*

Single-particle calculations of H_2O valence-shell partial cross sections have been reported at low photon energies by several authors using a variety of theoretical treatments [11-16]. Diercksen et al. [12] have given a detailed discussion of the various theoretical

*It should be noted that dipole (e,e), (e,2e) and (e,e+ion) spectroscopies provide quantitative equivalents to tunable energy photoabsorption, photoelectron spectroscopy, and photoionization mass spectrometry, respectively [8-10].

methods and have compared the results with experiment. With two exceptions [11,13], these theoretical studies have included calculations for the inner-valence $(2a_1)^{-1}$ photoionization cross section in fair agreement with experiment out to the limit of existing data at 60 eV [2]. There are no published experimental or theoretical data for the $(2a_1)^{-1}$ partial cross section beyond 60 eV photon energy.

Removal of a $2a_1$ inner-valence electron of H_2O is not well-described by a single-particle (Koopman's) picture due to extensive final-state electron-correlation effects in the ionization process. Such effects have been predicted theoretically for numerous molecules, notably by the many-body Green's function calculations reported by Cederbaum and co-workers [17,18]. In the case of the inner-valence $(2a_1)^{-1}$ ionization process in H_2O , such effects have been observed experimentally in binding-energy spectra obtained with X-ray photoelectron spectroscopy [19,20], dipole $(e,2e)$ spectroscopy [2], and by electron-momentum spectroscopy [also known as binary $(e,2e)$ spectroscopy] [6,7,21]. Detailed comparisons of experiment and the various calculations [22-26] have been given by Bawagan et al. [7] and also by Cambi et al. [21]. These studies [6,7,21-26] have shown that the $(2a_1)^{-1}$ ionization strength is distributed over the binding-energy range of 25-40 eV, and likely consists of at least four major ionic configurations, each of which has a dissociative width of approximately 2.26 eV [7]. Any accurate measurement of the $(2a_1)^{-1}$ partial cross section must include the

complete manifold of many-body states.

In the present work we report new measurements of the $(2a_1)^{-1}$ photoelectron branching ratio and partial photoionization cross section for gas-phase H_2O in the photon-energy range 50–200 eV using synchrotron radiation and photoelectron spectroscopy. The many-body states mentioned above were not resolved in our spectra, thus all of the results reported here pertain to the complete manifold of $(2a_1)^{-1}$ final states. The experimental technique is described in Sec. II, and the $(2a_1)^{-1}$ results are presented in Sec. III.

II. Experimental

Photoelectron spectra of the valence-shell region of H_2O were measured using a time-of-flight (TOF) electron spectrometer [27] sampling photoelectrons at the magic angle (54.7°) to the polarization direction of the photon beam. Pulsed (780 ns period, 0.3 ns pulse length) highly polarized synchrotron radiation was obtained from Beam Line III-1 at the Stanford Synchrotron Radiation Laboratory (SSRL). The radiation was monochromatized using a grasshopper monochromator (2–3Å bandpass). Vapor from the outgassed, distilled, water sample was allowed to leak into the interaction region of the TOF electron spectrometer at an ambient pressure of $\sim 1 \times 10^{-4}$ torr.

The presence of higher-order radiation can often be a serious problem in using monochromatized synchrotron radiation. However, for most molecular valence-shell studies, the higher-order radiation present in the monochromator output produces higher-energy valence

photoelectrons that can be resolved easily from the valence photoelectrons produced by the first-order radiation. Such operation with higher orders permits the simultaneous coverage of a wide spectral range with the use of only a limited number of monochromator settings, allowing greater efficiency in the use of beam time. This mode of operation works well for ionization of the $(2a_1)^{-1}$ inner-valence orbital of H_2O , which is well separated from the three (more closely spaced) outer-valence bands. We have taken photoelectron spectra using first-order photon energies of 50.7, 60.7, and 80.0 eV, yielding, for example, higher-order binding-energy spectra for the photon energies 101.4, 152.1, and 202.8 eV (2nd, 3rd, and 4th order at 50.7 eV). Figure 1 shows the photoelectron spectra obtained from all orders at a first-order energy setting of 50.7 eV. Even at fourth order the TOF analyzer is able to separate the $(2a_1)^{-1}$ inner-valence peak from the (unresolved) outer-valence region. At each photon energy the binding-energy spectra were integrated to obtain the $[(2a_1)^{-1}/\text{total}]$ branching ratio.

III. Results and Discussion

Branching ratios for $(2a_1)^{-1}$ photoionization in H_2O are shown in Table 1 and in the top of Fig. 2 (open circles). Also shown in Fig. 2 are the branching-ratio data reported earlier by Tan et al. from dipole (e,2e) measurements (solid circles) [2,5]. Agreement of the two data sets in the 50–60 eV region is good with the present data fitting smoothly with the results of the dipole (e,2e) measurements.

The increase of the $(2a_1)^{-1}$ branching ratio with photon energy is attributable to the dominant $0\ 2s$ component of the $2a_1$ orbital. At higher energies, the $0\ 2s$ cross section is expected to decrease more slowly than the $0\ 2p$ cross section, which is the major contribution to the outer-valence orbitals. A similar effect is observed for the Ne $2s$ and $2p$ partial cross sections.¹⁹

The photoelectron branching ratios have been converted to partial photoionization cross sections by taking the product with the absolute total photoionization cross section [2,4] at each energy. The photoionization cross section in the region above 50 eV is equal to the absolute total photoabsorption cross section because the photoionization efficiency has been shown to be unity at photon energies above 20 eV [2]. The photoabsorption cross sections, which are obtained from dipole (e,e) measurements by Tan et al. [2,4] over the range 10–300 eV, are in quite good agreement with direct photoabsorption measurements [28–30] covering various portions of this region. The $(2a_1)^{-1}$ partial photoionization cross sections so obtained are shown in the bottom panel of Fig. 2. The measured cross-section data show a physically sensible shape, monotonically decreasing to higher energies. This fact together with the good agreement with the independent dipole (e,2e) data at lower energies lends confidence to the results of the present PES measurements. The results of several calculations at lower energies [12,14–16] are included for comparison. Unfortunately no published theoretical values above 60 eV are available.

Acknowledgements

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and also by the Natural Sciences and Engineering Research Council of Canada. It was performed at the Stanford Synchrotron Radiation Laboratory, which is supported by the Department of Energy's Office of Basic Energy Sciences. One of us (CEB) acknowledges a Canada Council Killam Research Fellowship (1984-1986), and another (MNP) acknowledges a Fulbright scholarship during this project.

References

1. C.M. Truesdale, S. Southworth, P.H. Kobrin, D.W. Lindle, G. Thornton, and D.A. Shirley, *J. Chem. Phys.* 76, 860 (1982).
2. K.H. Tan, C.E. Brion, Ph.E. van der Leeuw, and M.J. van der Wiel, *Chem. Phys.* 29, 299 (1978).
3. C.E. Brion and F. Carnovale, *Chem. Phys.* 100, 291 (1985).
4. C.E. Brion and J.P. Thompson, *J. Electron Spectrosc.* 33, 301 (1984).
5. C.E. Brion and J.P. Thompson, *J. Electron Spectrosc.* 33, 287 (1984).
6. S.T. Hood, A. Hamnett, and C.E. Brion, *J. Electron Spectrosc.* 11, 205 (1977).
7. A.O. Bawagan, L.Y. Lee, K.T. Leung, and C.E. Brion, *Chem. Phys.* 99, 367 (1985).
8. C.E. Brion and A. Hamnett, in *Advances in Chemical Physics* 45, edited by J.W. McGowan (Wiley, New York, 1981).
9. C.E. Brion, in Physics of Electronic and Atomic Collisions, edited by S. Datz (North-Holland, Amsterdam, 1982).
10. C.E. Brion, *Comm. At. Mol. Phys.* 16, 249 (1985).
11. G.R.J. Williams and P.W. Langhoff, *Chem. Phys. Lett.* 60, 201 (1979).
12. G.H.F. Diercksen, W.P. Kramer, T.N. Rescigno, C.F. Bender, B.V. McKoy, S.P. Langhoff, and P.W. Langhoff, *J. Chem. Phys.* 76, 1043 (1982).
13. J.J. Delaney, V.R. Saunders, and I.H. Hillier, *J. Phys. B* 14, 819 (1981).

14. M. Roche, D.R. Salahub, and R.P. Messmer, *J. Electron Spectrosc.* 19, 273 (1980).
15. P.R. Hilton, S. Nordholm, and N.S. Hush, *Chem. Phys. Lett.* 64, 515 (1979).
16. I. Cacelli, R. Moccia, and V. Carravetta, *Chem. Phys.* 90, 313 (1984).
17. W. von Niessen, J. Schirmer, and L.S. Cederbaum, *Comput. Phys. Reports* 1, 57 (1984).
18. L.S. Cederbaum, W. Domcke, J. Schirmer, and W. von Niessen, *Advances in Chemical Physics* (Wiley, New York) (in press).
19. K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P.F. Hedèn, K. Hamrin, U. Gelius, T. Bergmark, L.O. Werme, R. Manne, and Y. Baer, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).
20. N. Mårtensson, P.A. Malmquist, S. Svensson, E. Basilier, J.J. Pireaux, U. Gelius, and K. Siegbahn, *Nouv. J. de Chim.* 1, 191 (1977).
21. R. Cambi, G. Ciullo, A. Sgamellotti, C.E. Brion, J.P.D. Cook, I.E. McCarthy, and E. Weigold, *Chem. Phys.* 91, 373 (1984); 98, 166 (1985).
22. H. Ågren and H. Siegbahn, *Chem. Phys. Lett.* 69, 424 (1980).
23. W. von Niessen, L.S. Cederbaum, J. Schirmer, G. Diercksen, and W.P. Kramer, *J. Electron Spectrosc.* 28, 45 (1982).
24. H. Nakatsuji and T. Yonezawa, *Chem. Phys. Lett.* 87, 426 (1982).
25. M. Mishra and Y. Ohrn, *Chem. Phys. Lett.* 71, 549 (1980).
26. R. Arneberg, J. Muller, and R. Manne, *Chem. Phys.* 64, 249 (1982).

27. M.G. White, R.A. Rosenberg, G. Gabor, E.D. Poliakoff, G. Thornton, S.H. Southworth, and D.A. Shirley, Rev. Sci. Instrum. 50, 1268 (1979).
28. L. de Reilhac and N. Damany, J. Quant. Spectrosc. Rad. Trans. 18, 121 (1977).
29. J.A.R. Samson and G.N. Haddad (private communication).
30. J. Gallagher, C.E. Brion, J.A.R. Samson, and P.W. Langhoff (to be published).

Table 1

Photoelectron Branching Ratios for $(2a_1)^{-1}$ Photoionization in H_2O .

Photon Energy (eV)	Branching Ratio ^a
50.7	0.120(2)
60.7	0.143(2)
80.0	0.230(7)
101.4	0.242(2)
121.4	0.253(4)
152.1	0.304(7)
160.0	0.30(4)
182.1	0.34(1)
202.8	0.40(2)

^aEstimated statistical uncertainties are shown in brackets.

Figure Captions

- Fig. 1. TOF binding-energy spectra of the valence shell of H₂O. The first-order photon energy is 50.7 eV. Higher-order spectra are also visible (see text). The spectra are uncorrected for the TOF analyzer transmission function, although it is essentially constant for the kinetic energies of interest.
- Fig. 2. Photoelectron branching ratios (top) and partial photoionization cross sections (bottom) for the $(2a_1)^{-1}$ orbital in H₂O: open circles - synchrotron radiation, this work; solid circles - dipole (e,2e) spectroscopy, reference [2]. The solid curves are drawn for clarity. The other curves in the bottom panel represent theoretical calculations: C (Ref. 16); D (Ref. 12); GIPM (Ref. 15); and χ_α (Ref. 14).

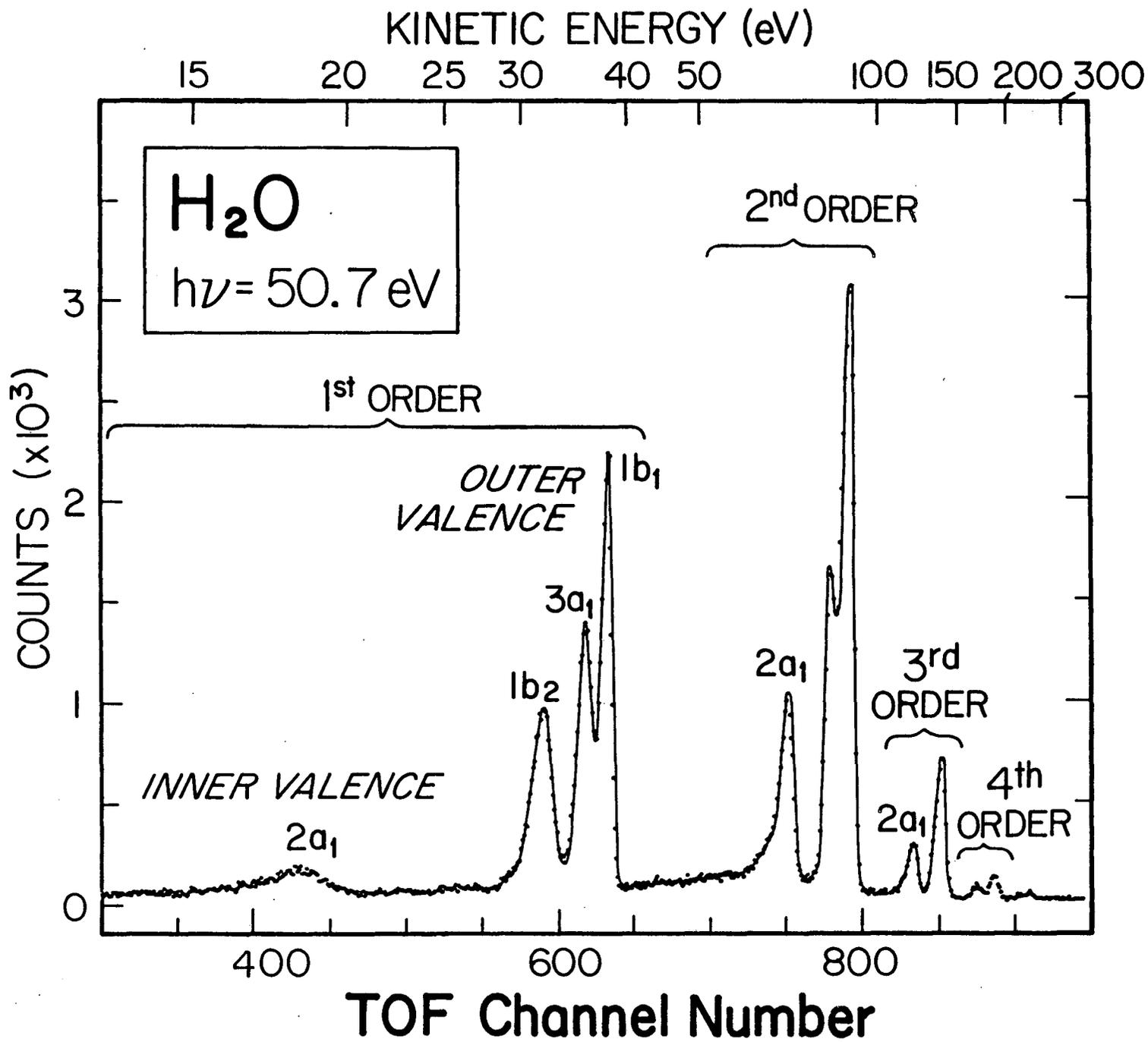


Figure 1

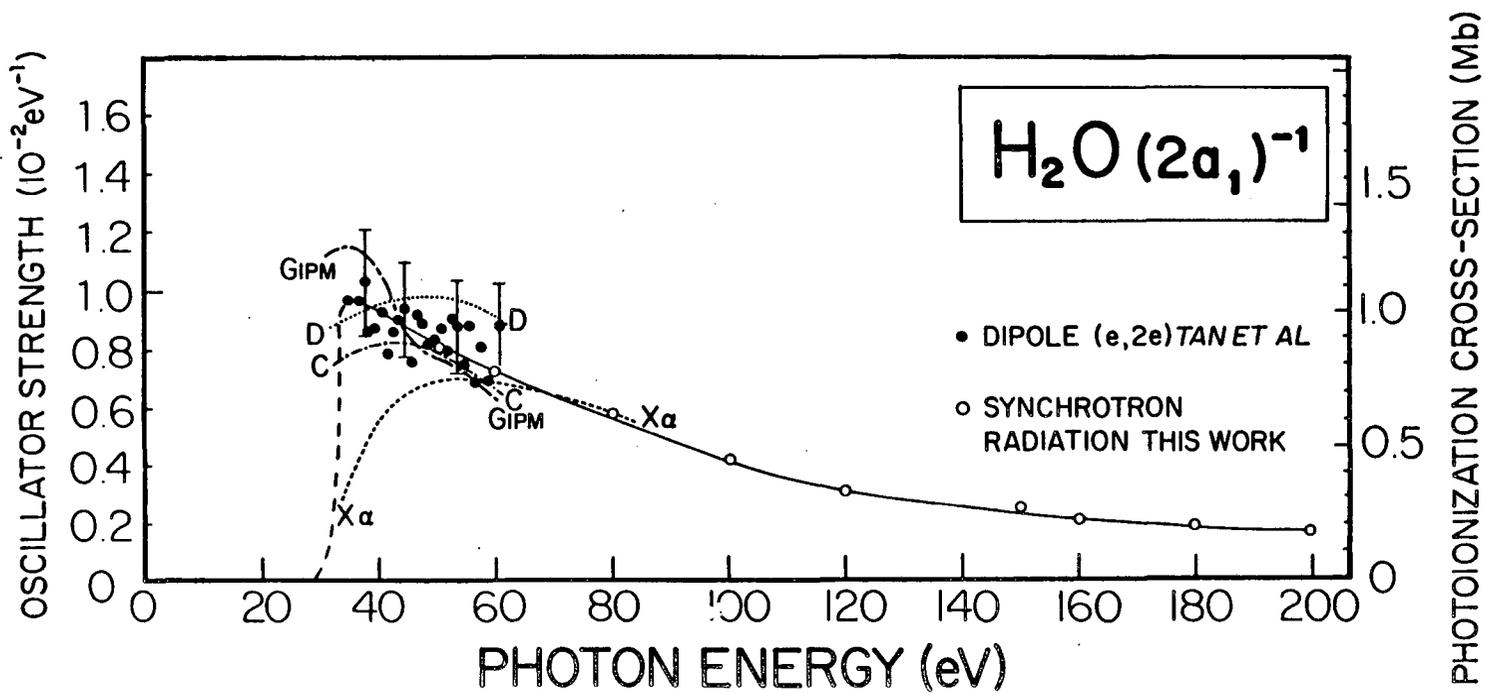
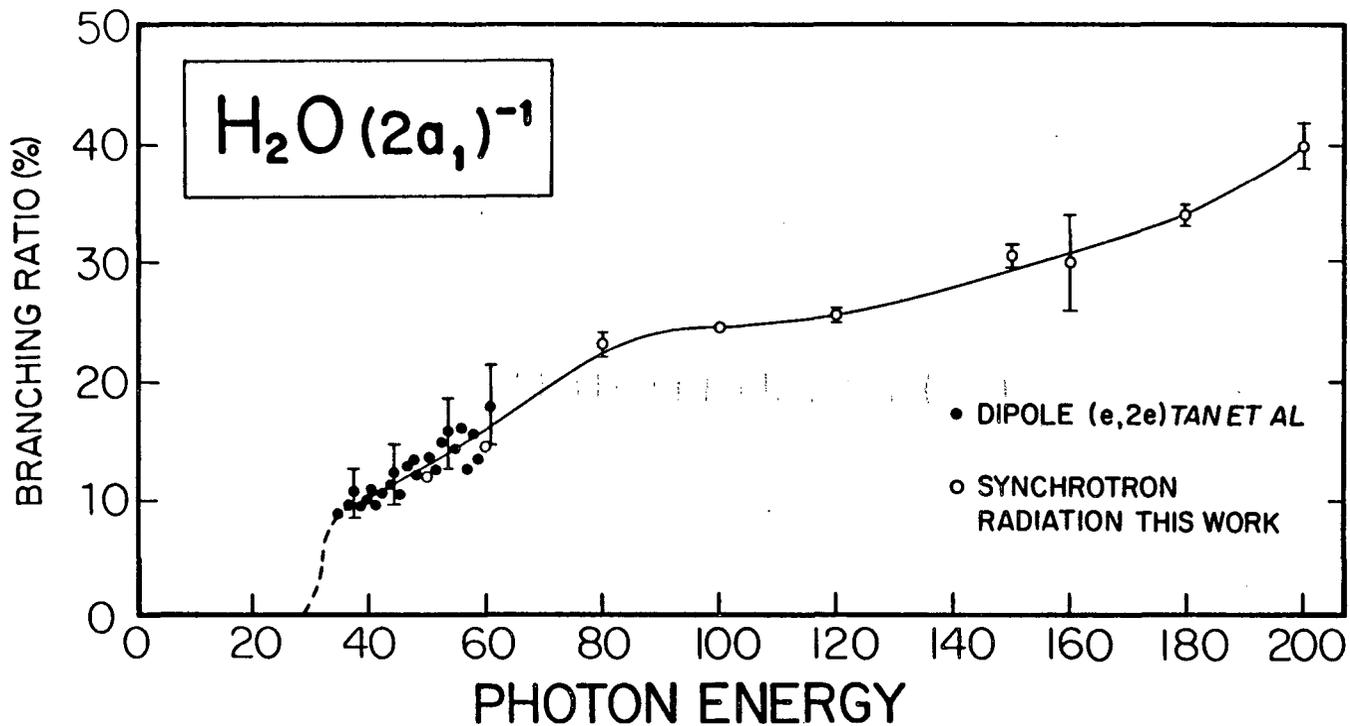


Figure 2

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