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On apparent contradictions in some photophysical properties of liquid water

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Abstract

Apparent inconsistency has appeared between essentially two sets of data relative to the optical absorption limit of liquid water on the one hand and to its photoionization threshold and band-gap energy on the other. Recent data prompt a renewed examination. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Optical absorption limit; Photoionization threshold; Band-gap energy

So far, the results dealing with the ultraviolet absorption spectrum of liquid water have been somewhat contradictory.

Most authors [1–4] – from transmission experiments – claim that a weak structureless absorption persists down to about 6 eV, showing a steep rise around 6.1–6.5 eV. On the other hand, a semiempirical method based on reflectance techniques and calculation of the energy-loss function indicates an optical absorption starting at about 7.2 eV with the first absorption band peaking at 8.2 eV [5–7] [1]. A recent review did not settle the question [8].

More recent convincing measurements of liquid water transmission in the 4–10.8 eV photon energy range confirm the existence of a structureless weak absorption below 7.2 eV extending to about 6 eV or even below [9]. Below 7.2–7.4 eV, the absorption coefficient decreases exponentially with decreasing excitation energy [9], in accordance with the observations of Onaka and Takahashi [1] and Williams et al. [3].

The latter authors [1,3] emphasize such exponential variation in the red tail region, which is reminiscent of the exponential distribution of localized states (Urbach tail) below the conduction band. However, the presumed extension of the Urbach tail in liquid water (~0.5 eV) [8], leading to ~8.2 eV for the lowest unoccupied levels, would not permit a direct vertical transition for an excitation energy of ~6 eV.

By analogy to charge-transfer-to-solvent (CTTS) spectra, Sander et al. [10] suggest that the low-energy tail may be partially attributed to an optical charge-transfer (CT) transition. The CTTS state, populated by this transition, is then believed to decay via a proton transfer, hence an electron transfer from the negatively charged complex [10].

Another approach applied to the first excited state $\tilde{A}^1B_1$ of the H_2O molecule follows from matrix-isolation spectroscopy. Absorption thresholds and maxima are found differently affected in the various matrices used (rare gases and ice) [11,12]. The blue gas-to-matrix shifts at maximum are attributed to the predominantly Rydberg character of the $\tilde{A}$ state at the equilibrium distance of H_2O. On the other hand, much weaker shifts at threshold are attributed to its predominantly valence character [11,12], the latter associated with large H–OH internuclear distances. The red tail of condensed water would thus correspond to molecules whose OH bond is fully extended.

Provided that such interpretation is also valid in the case of liquid water, we now suggest that the extension of the H–OH bond would facilitate a proton transfer. With such a model or from a CT mechanism, the production of excess electrons would thus be accounted for as soon as liquid water begins to absorb, that is, around 6 eV.

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[1] Recent measurements of inelastic X-ray scattering spectra of liquid water – an alternative to reflectance experiments – by Hayashi et al. [7] are essentially in accordance with the data of Kerr et al. [5] and of Heller et al. [6], at least in the ~7–15 eV energy range.

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As to the photoionization threshold (IP) of liquid water, two sets of values have been proposed with or without an explicit definition of the quantity involved.

The values ranging from about 6 to 6.5 eV [13–16], referred to as 'the ionization potential of liquid water', were all determined upon hydrated electron (e_{aq}^-) recording – $-e_{aq}^-$ or e_{aq}^- scavenging products. The IP was then the minimum photon energy required to create a pair of quasi-free independent charges.

To interpret such low IP values, it has been stressed repeatedly that the excess electron production may not be a simple one-step electron ejection. Instead, it may involve a sequence of reactions, such as a concerted proton–electron transfer [14,17,18], or/and imply the intervention of hot H atoms [19,20]. The 6–6.5 eV threshold would then correspond to an electron 'appearance potential' [21,22], as proposed by Mozumder [19], and in no way to a band-gap energy.

On the other hand, the liquid photoionization process has been considered to imply a band-to-band transition, in which case the condensed phase IP corresponds to a band-gap width (E_g) [23]. For water, the latter has been indirectly estimated at 8.9 eV [23–25]. More recently, it has been semiempirically determined using the magneto-optical Faraday rotation effect and the measurement of the Verdet constant [26–28]. Values ranging from 8.3 to 9.2 eV have been obtained and a mean value of 8.7 eV then proposed [8].

Another approach, semiempirical and elaborate, has been recently developed by Coe et al. [29]. It is based essentially on various experimental hydrated-electron-cluster data and on the knowledge of thermodynamic quantities, especially the hydration energy of OH. The role of the water reorganization energy (RE) is emphasized and a value RE=1.6 eV is estimated. The latter value permits an evaluation of the conduction-band edge relative to the vacuum level (V_0), namely, $V_0 \geq -0.12$ eV,[2] which in turn leads to $E_g = 6.9$ eV [29]. Such a low value, however, seems difficult to conciliate with femtosecond time-resolved measurements [10,30–36] of e_{aq}^--H_3O^+/OH geminate recombination upon various photon excitation energies.

On the other hand, a recent direct analysis of the water absorption spectrum in the 6–10.8 eV energy range and subtraction of the gaussian peak centered at ~8.5 eV from the overall absorbance curve have shown a threshold at 8.8 eV, considered to be the onset of a 'true' ionization of water [9]. Such a value will be provisionally retained for E_g.

In conclusion, in the light of recent data, it becomes clearer how excess electrons can be photoproduced in liquid water around 6–6.5 eV while a classical ionization process would require about 2 eV more.

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References

[1] R. Onaka, T. Takahashi, Vacuum UV absorption spectra of liquid water and ice, J. Phys. Soc. Japan 24 (1968) 548–550.

[2] J.A. Ghormley, C.J. Hochanadel, Production of H, OH, and H_2O_2 in the flash photolysis of ice, J. Phys. Chem. 75 (1971) 40–44.

[3] F. Williams, S.P. Varma, S. Hillenius, Liquid water as a lone-pair amorphous semiconductor, J. Chem. Phys. 64 (1976) 1549–1554.

[4] T.I. Quickenden, J.A. Irvin, The ultraviolet absorption spectrum of liquid water, J. Chem. Phys. 72 (1980) 4416–4428.

[5] G.D. Kerr, R.N. Hamm, M.W. Williams, R.D. Birkhoff, L.R. Painter, Optical and dielectric properties of water in the vacuum ultraviolet, Phys. Rev. A 5 (1972) 2523–2527.

[6] J.M. Heller Jr., R.N. Hamm, R.D. Birkhoff, L.R. Painter, Collective oscillation in liquid water, J. Chem. Phys. 60 (1974) 3483–3486.

[7] H. Hayashi, N. Watanabe, Y. Udagawa, C.-C. Kao, Optical spectra of liquid water in vacuum UV region by means of inelastic X-ray scattering spectroscopy, J. Chem. Phys. 108 (1998) 823–825.

[8] A. Bernas, C. Ferradini, J.-P. Jay-Gerin, On the electronic structure of liquid water: Facts and reflections, Chem. Phys. 222 (1997) 151–160.

[9] J.-M. Jung, personal communication.

[10] M.U. Sander, K. Luther, J. Troe, Excitation energy dependence of the photoionization of liquid water, J. Phys. Chem. 97 (1993) 11489–11492.

[11] M. Chergui, N. Schwentner, Experimental evidence to Rydbergization of antibonding molecular orbitals, Chem. Phys. Lett. 219 (1994) 237–242.

[12] M. Chergui, N. Schwentner, V. Stepanenko, Absorption by dissociative continua in condensed matter: H_2O in rare gas and ice matrices, Chem. Phys. 187 (1994) 153–162.

[13] J.W. Boyle, J.A. Ghormley, C.J. Hochanadel, J.F. Riley, Production of hydrated electrons by flash photolysis of liquid water with light in the first continuum, J. Phys. Chem. 73 (1969) 2886–2890.

[14] M. Anbar, G.A. St. John, H.R. Gloria, R.F. Reinisch, Effect of state of condensation on the ionization potential of associated liquids, in: H.H.G. Jellinek (Ed.), Water Structure at the Water–Polymer Interface, Plenum Press, New York, 1972, pp. 85–105.

[15] D.N. Nikogosyan, A.A. Oraevsky, V.I. Rupasov, Two-photon ionization and dissociation of liquid water by powerful laser UV radiation, Chem. Phys. 77 (1983) 131–143.

[16] A. Iwata, N. Nakashima, Y. Izawa, C. Yamanaka, One-photon ionization of liquid water upon 193 nm laser irradiation, Chem. Lett. (1993), 1939–1940.

[17] P. Han, D.M. Bartels, H/D isotope effects in water radiolysis. 2. Dissociation of electronically excited water, J. Phys. Chem. 94 (1990) 5824–5833.

[18] A. Bernas, D. Grand, On the so-called ionization potential of water and associated liquids, J. Phys. Chem. 98 (1994) 3440–3443.

[19] P. Han, D.M. Bartels, H/D isotope effects in water radiolysis. 4. The mechanism of $(H)_{aq} \rightleftarrows (e^-)_{aq}$ interconversion, J. Phys. Chem. 96 (1992) 4899–4906.

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[2] Note that adopting the calculated value of 1 eV for RE [8] – instead of 1.6 eV – would result in $V_0 = -0.72$ eV, a value quite close to that obtained on the basis of Henglein's formulation [8].

[20] R.A. Crowell, D.M. Bartels, Multiphoton ionization of liquid water with 3.0–5.0 eV photons, J. Phys. Chem. 100 (1996) 17940–17949.

[21] S.M. Pimblott, A. Mozumder, Structure of electron tracks in water. 2. Distribution of primary ionizations and excitations in water radiolysis, J. Phys. Chem. 95 (1991) 7291–7300.

[22] A. Mozumder, Distribution of primary ionization and excitation in water radiolysis, in: J. Dobó, L. Nyikos, R. Schiller (Eds.), Proc. 7th Tihany Symp. on Radiation Chemistry, Hungarian Chemical Society, Budapest, 1991, pp. 3–8.

[23] I.G. Kaplan, A.M. Miterev, Interaction of charged particles with molecular medium and track effects in radiation chemistry, Adv. Chem. Phys. 68 (1987) 255–386.

[24] T. Goulet, A. Bernas, C. Ferradini, J.-P. Jay-Gerin, On the electronic structure of liquid water: Conduction-band tail revealed by photoionization data, Chem. Phys. Lett. 170 (1990) 492–496.

[25] A. Bernas, T. Goulet, J.-P. Jay-Gerin, C. Ferradini, Photoionization of water or aqueous solutes: on the electronic structure of liquid water, in: J. Dobó, L. Nyikos, R. Schiller (Eds.), Proc. 7th Tihany Symp. on Radiation Chemistry, Hungarian Chemical Society, Budapest, 1991, pp. 17–24.

[26] A. Balbin Villaverde, D.A. Donatti, Verdet constant of liquids; measurements with a pulsed magnetic field, J. Chem. Phys. 71 (1979) 4021–4024.

[27] W. Grevendonk, J. Dauwen, P. Van den Keybus, B. Vanhuyse, Dispersion of the Verdet constant of water: A band model interpretation, J. Chem. Phys. 81 (1984) 3746–3747.

[28] A. Balbin Villaverde, E. Munin, Interband Faraday rotation in liquids: Band parameter determination, J. Chem. Soc. Faraday Trans. 88 (1992) 1245–1247.

[29] J.V. Coe, A.D. Earhart, M.H. Cohen, G.J. Hoffman, H.W. Sarkas, K.H. Bowen, Using cluster studies to approach the electronic structure of bulk water: Reassessing the vacuum level, conduction band edge, and band gap of water, J. Chem. Phys. 107 (1997) 6023–6031.

[30] H. Lu, F.H. Long, R.M. Bowman, K.B. Eisenthal, Femtosecond studies of electron-cation geminate recombination in water, J. Phys. Chem. 93 (1989) 27–28.

[31] F.H. Long, H. Lu, X. Shi, K.B. Eisenthal, Intensity dependent geminate recombination in water, Chem. Phys. Lett. 185 (1991) 47–52.

[32] Y. Gauduel, S. Pommeret, A. Migus, A. Antonetti, Femtosecond dynamics of geminate pair recombination in pure liquid water, J. Phys. Chem. 93 (1989) 3880–3882.

[33] J.L. McGowen, H.M. Ajo, J.Z. Zhang, B.J. Schwartz, Femtosecond studies of hydrated electron recombination following multiphoton ionization at 390 nm, Chem. Phys. Lett. 231 (1994) 504–510.

[34] A. Reuther, A. Laubereau, D.N. Nikogosyan, Primary photochemical processes in water, J. Phys. Chem. 100 (1996) 16794–16800.

[35] D. Houde, C. Pépin, T. Goulet, J.-P. Jay-Gerin, Dynamics of solvated electrons in polar liquids using 2 eV femtosecond laser pulses, in: M. Piché, P.W. Pace (Eds.), Mode-Locked and Solid State Lasers, Amplifiers, and Applications, Proc. SPIE, vol. 2041, International Society for Optical Engineering, Bellingham, WA, 1993, pp. 139–152.

[36] C. Pépin, T. Goulet, D. Houde, J.-P. Jay-Gerin, Observation of a continuous spectral shift in the solvation kinetics of electrons in neat liquid deuterated water, J. Phys. Chem. A 101 (1997) 4351–4360.