

## OPTICAL ABSORPTION SPECTRA OF $(\text{H}_2\text{O})_n^-$

Joshua JORTNER

*School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel*

Uzi LANDMAN and R.N. BARNETT

*School of Physics, Georgia Institute of Technology, Atlanta, GA 30332, USA*

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We provide theoretical information from quantum path integral molecular dynamics simulations on the size dependence of the mean optical excitation energy of the localized excess electron in  $(\text{H}_2\text{O})_n^-$  ( $n=8-128$ ) cluster. We consider the energetics and the nature of the electronic excitation, i.e. bound-continuum and bound-bound transitions, and their interrelationship to the excess electron localization modes via surface and interior states in water clusters.

Excess electron states in fluids [1-3] encompass a broad spectrum of systems which include polar solvents, e.g. liquid water and ammonia [4-6], supercritical polar vapors ( $\text{H}_2\text{O}$  and  $\text{NH}_3$ ) [7-9], liquid rare gases [10-14], non-polar liquids [15] and metal-molten salt systems [16,17]. Theoretical studies of localized excess electron states in polar liquids [18-21] constituted some of the early explorations of electronic states of fluids. During the last decade the problem of electron localization in a finite cluster of polar molecules, e.g.  $(\text{H}_2\text{O})_n^-$  or  $(\text{NH}_3)_m^-$  [18-27] constituted an experimental and theoretical challenge. From the experimental point of view [22-27] weak electron binding in small  $(\text{H}_2\text{O})_n^-$  clusters ( $n=2, 5, 6$ ) was documented [23-25], and strongly bound negatively charged water  $(\text{H}_2\text{O})_n^-$  [22-27] and ammonia  $(\text{NH}_3)_m^-$  [22] clusters were observed for  $n \geq 11$  and  $m \geq 35$ , respectively, with accurate values of the vertical binding energies for  $(\text{H}_2\text{O})_n^-$  clusters ( $n=2, 5, 6$  and  $11 \leq n \leq 40$ ) being obtained via photoelectron spectroscopy [24,25]. From the theoretical point of view, these systems are interesting for the elucidation of distinct surface and interior excess electron localization modes in finite systems and the delicate dependence of their stability on the nature of electron-molecule and intermolecular interactions. Employing the quantum path integral molecular dynamics

method (QUPID) [28-38], which rests on the path integral formulation of quantum statistical mechanics and on isomorphism between the quantum problem and a classical one, in conjunction with a new electron-molecule pseudopotential [36-40], we have explored [36-40] the structure, charge distribution, energetics and stability of electron attachment to  $(\text{H}_2\text{O})_n^-$  and  $(\text{NH}_3)_m^-$  clusters over a broad range of cluster sizes. A major conclusion emerging from our studies is that electron localization in medium-sized  $(\text{H}_2\text{O})_n^-$  clusters  $8 \leq n < 64$  constitutes a novel excess electron surface state, while for large  $(\text{H}_2\text{O})_n^-$  clusters localization in interior states requires cluster sizes of  $n \geq 64$ . In contrast to  $(\text{H}_2\text{O})_n^-$  clusters, the onset of stable electron localization in  $(\text{NH}_3)_m^-$  clusters occurs solely via internal localization requiring  $n \geq 32$  molecules, and is not preceded by surface localized states for smaller clusters [40].

Experimental interrogation of the microscopic structure of  $(\text{H}_2\text{O})_n^-$  and  $(\text{NH}_3)_m^-$  clusters can utilize structural determinations [38] and measurements of the cluster dipole moment [38]. The energetics of the system can be explored by photoelectron spectroscopy [24,25,37-40] and by optical absorption studies. The electron vertical binding energies (EVBE) in the ground electronic state for  $(\text{H}_2\text{O})_n^-$   $11 \leq n \leq 40$  clusters, experimentally determined by photoelectron detachment spectroscopy

[24,25], are in quantitative agreement with the theoretical EVBE values for surface states [37–40]. Optical absorption spectra of the localized excess electron states in polar clusters are expected to provide central information regarding

- (i) the nature of excited electronic states,
- (ii) ground and excited state energetics,
- (iii) bound–continuum and bound–bound transitions and their interrelationship to electron localization (surface versus internal) modes,
- (iv) symmetry breaking of degenerate electronically excited states [41,42], and
- (v) energy fluctuations which together with (iv) determine the optical lineshape [19–22,41,42].

The experimental information regarding optical spectroscopy of these excess electron polar clusters is meagre. Absorption spectroscopy of excess electron states generated by pulse radiolysis in subcritical and supercritical gaseous  $D_2O$  [8], which are reproduced in fig. 1, reveal that the peak energies, EOP, of the broad absorption bands are located in the range  $EOP=0.90\text{--}1.05$  eV in the density region  $0.02\text{--}0.125$   $g\text{ cm}^{-3}$ , exhibiting a weak density de-

pendence [8]. On the basis of the weak density dependence of EOP in conjunction with an examination of the critical densities for electron localization in supercritical polar fluids [8] it was concluded [8] that electron localization in these systems is due to the formation of a trapped electron localized in a large cluster of polar molecules. Thus the spectra of fig. 1 originate from  $(D_2O)_n^-$  clusters of unspecified size. Some information on optical absorption cross sections of size-selective  $(H_2O)_n^-$  clusters at a few fixed wavelengths emerged from photofragmentation spectra of these clusters [43]. In this note we provide some theoretical information on the size dependence of the optical excitation energies of  $(H_2O)_n^-$  clusters obtained from QUPID simulations. We limit ourselves to mean excitation energies EOP, which correspond approximately to the peak energy of the optical absorption band. The interesting problems of line broadening of the optical absorption band are not considered [41,42,44]. Rather, we focus on the problem of the nature of the electronic excitation, i.e. bound–continuum and/or bound–bound transitions and their relation to surface and interior excess electron states in water clusters. These theoretical predictions provide guidelines and challenge for experimental work.

Extensive work in the area of the optical spectroscopy of the solvated electron in bulk polar liquids, which was explored by approximate condensed matter methods [14,18,20] and by QUPID simulations [28,32–35,41], indicated that the major contribution to the absorption spectrum originated from a single electronic transition from a ground electronic state, which according to QUPID simulations [32–40] is approximately spherically symmetrical, to a single (degenerate) electronically excited state,  $e$ , which undergoes symmetry breaking, resulting in the splitting of this degenerate state [41,42]. For the calculations of EOP this effect will not be explicitly considered. The vertical electron excitation energy is

$$EOP = EVBE_e - EVBE, \quad (1)$$

where  $EVBE$  is the electron vertical binding energy in the equilibrium nuclear configuration of the ground electronic state, while  $EVBE_e$  is the electron vertical binding energy in the electronically excited state  $e$  at the equilibrium nuclear configuration of

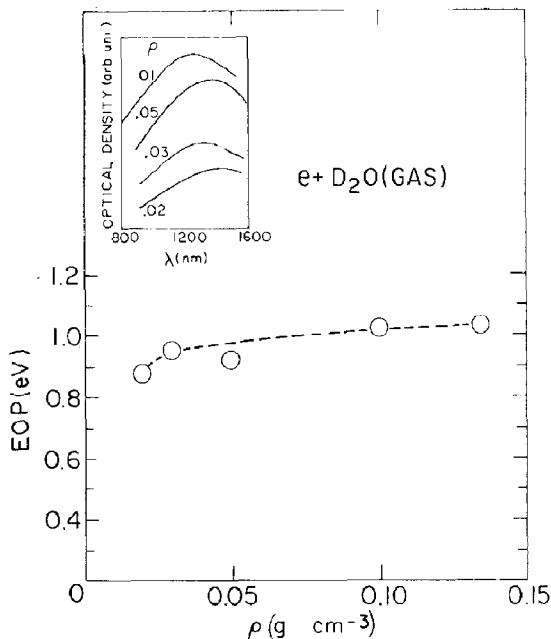


Fig. 1. The density ( $\rho$ ) dependence of the energies of the peaks of the absorption bands of the localized electron in  $D_2O$  gas. The insert shows several typical absorption spectra at densities ( $g\text{ cm}^{-3}$ ) indicated on the figure. Data from ref. [8].

the *ground electronic state*. For bound-continuum transitions  $EVBE_e = 0$  and

$$EOP = -EVBE, \quad (2)$$

while for bound-bound transitions  $EVBE_e < 0$  and EOP is given by eq. (1).

Eq. (2) can be used as a diagnostic criterion for the identification of bound-continuum transitions. The excitation energies for surface excess electron states in  $(H_2O)_n^-$  ( $8 \leq n \leq 64$ ) are obtained [38] from the analysis of the imaginary time correlation function  $\mathfrak{R}(t-t')$  for the quantum particle, which is represented by a necklace with  $P$  beads [38,45],  $\mathfrak{R}(t-t') = \langle |r(t) - r(t')|^2 \rangle$ ;  $t-t' \in (0, \beta\hbar)$  where  $r(t)$  is the position vector along the electron path at time  $t$  and  $\beta = (k_B T)^{-1}$ . Results for eq. (1), obtained from QUPID simulations, were used to estimate the excitation energies  $\epsilon_{0m} = \beta(E_m - E_0)$  (where  $E_m$  and  $E_0$  are the electronic energies of the ground and excited state, respectively) by fitting to the relationship [38]

$$\mathfrak{R}(j\beta\hbar/P) = \mathfrak{R}(\frac{1}{2}\beta\hbar) + \sum_{m=1}^{m_{\max}} R_{0m}^{(2)} \exp(-\epsilon_{0m}) \times \{ \cosh[(j/P - \frac{1}{2})\epsilon_{0m}] - 1 \}, \quad (3)$$

where the matrix element is

$$R_{0m}^{(2)} = \int dr \int dr' \psi_0(r) \psi_m^*(r) |r-r'|^2 \psi_0^*(r') \psi_m(r'), \quad (4)$$

with  $\psi_0$  and  $\psi_m$  being the one-electron wavefunctions of the ground and electronically excited states, respectively. The best fit of the QUPID data to eq. (3) was accomplished for both surface and internal states with one electronically excited state, which is identified with the state  $e$ .

In fig. 2 we compare the excitation energies for surface states of small and medium-sized  $(H_2O)_n^-$  [38] with the corresponding EVBE data. From these results it is apparent that for  $n=8, 12, 18$  and possibly  $n=32$  the diagnostic criterion for bound-continuum transitions is satisfied. For the  $n=64$  surface state  $-EVBE > EOP$  and this surface state is presumably characterized by a bound-bound transition; however, for the large  $(H_2O)_{64}^-$  the excess electron localization mode may involve not a surface

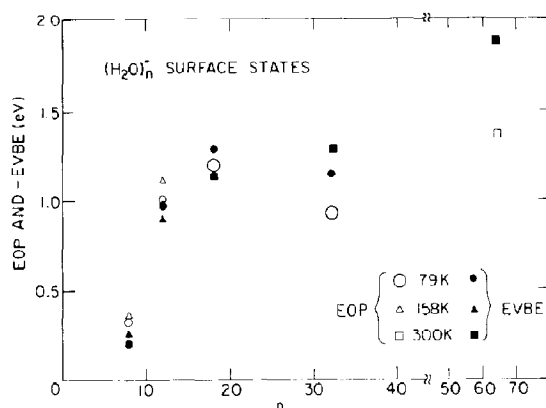


Fig. 2. The size dependence of the optical excitation energy (EOP) and the vertical ground-state electron binding energy of surface electron states in  $(H_2O)_n^-$  clusters obtained from QUPID calculations at several temperatures [38].

state but rather an interior state, whose optical excitation will be considered.

The electronic excitation of internal excess electron states, which are energetically favored for large ( $n \geq 64$ ) clusters, fall again into two categories of bound-continuum and bound-bound transitions, whose energies are given by eqs. (2) and (1), respectively. The EOP for the interior state of the  $(H_2O)_{128}^-$  clusters obtained from the QUPID calculations of  $\mathfrak{R}(t-t')$  [38],  $EOP = 2.48$  eV, is considerably lower than  $-EVBE = 3.55$  eV. Accordingly, this electronic excitation in the large cluster corresponds to a bound-bound transition. This conclusion is supported by recent fast Fourier transform simulations by Barnett, Landman and Nitzan [42,44] of excess electron states in  $(H_2O)_n^-$  ( $n=64$  and 128) clusters, which reveal that the first electronically excited state is bound with  $EVBE_e = -0.91$  eV for  $n=64$  and  $EVBE_e = -1.66$  eV for  $n=128$ .

The size dependence of the excitation energies of interior excess electron states in large polar clusters can be quantitatively described in terms of the dielectric model [39] adopted for finite systems. Provided that the radii of gyration  $R_g^{(g)}$  and  $R_g^{(e)}$  of the electron in the ground and excited electronic states, respectively, are both smaller than the (mean) cluster radius  $\bar{R}$ , the excitation energies can be related to  $n^{-1/3} = r_s/\bar{R}$ , where  $r_s$  is the mean radius of the water molecule. We have established the linear relationship of the ground-state vertical binding energy [39]

$$\text{EVBE}(\bar{R}) = \text{EVBE}(\infty) + An^{-1/3}, \quad \bar{R} > R_g^{(g)}, \quad (5)$$

with

$$A = (e^2/2r_s)(1 + D_{\text{op}}^{-1} - 2D_s^{-1}), \quad (6)$$

where  $D_{\text{op}}$  and  $D_s$  are the optical and static dielectric constants of the cluster, respectively. The rhs of eq. (5) also provides a description of  $\text{EVBE}_e(\bar{R})$  for  $R_g^{(e)} < \bar{R}$ . We can infer from eqs. (2), (5) and (6) that for bound-continuum transitions of interior states,  $\text{EOP}(\bar{R}) = -\text{EVBE}(\infty) - An^{-1/3}$ . This result is only of marginal interest for water clusters where the interior states are characterized by bound-bound transitions. For bound-bound transitions of interior states, eqs. (1), (5) and (6) result in

$$\text{EOP}(\bar{R}) = \text{EOP}(\infty) \quad (7)$$

with EOP for sufficiently large clusters being independent of the cluster size. This conclusion is borne out by fast Fourier transform simulations of the excitation energies [42,44] of interior states in  $(\text{H}_2\text{O})_{64}^-$  and  $(\text{H}_2\text{O})_{128}^-$  clusters (fig. 3), whose values are not far from the experimental value of EOP of the hydrated electron in bulk water.

Fig. 3 provides an overview of the theoretical predictions regarding the nature and energetics of the electronic excitations of  $(\text{H}_2\text{O})_n^-$  clusters. The experimental optical excitation energy of the solvated electron [6] was also included. From these results it is apparent that:

(1) Surface excess electron states in small and medium-sized clusters ( $8 \leq n \leq 32$ ) are characterized by bound-continuum transitions.

(2) For the bound-continuum transitions of surface states EOP increases fast for small ( $n < 12$ ) clusters while in the range  $12 \leq n \leq 32$  EOP exhibits a weak size dependence.

(3) The optical spectra of localized excess electron states in gaseous  $\text{D}_2\text{O}$  [8] are attributed to surface states of  $(\text{D}_2\text{O})_n^-$  clusters with  $n \approx 10-30$ . This assignment rests on the weak density dependence of EOP and its values ( $\text{EOP} = 0.88$  eV for  $\rho = 0.02$  g  $\text{cm}^{-3}$  to  $\text{EOP} = 1.02$  eV for  $\rho = 0.135$  g  $\text{cm}^{-3}$ ) in conjunction with the theoretical data (figs. 2 and 3).

(4) Energetically stable interior excess electron states in large  $(\text{H}_2\text{O})_n^-$  ( $n \geq 64$ ) clusters are characterized by bound-bound transitions.

(5) The energies of bound-bound transitions of

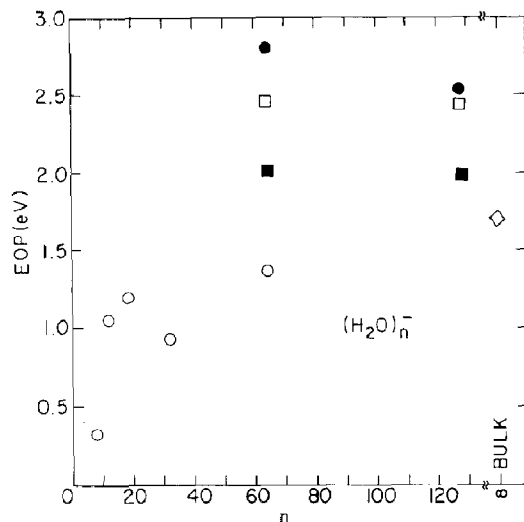


Fig. 3. An overview of the theoretical predictions regarding the nature and energetics of the electronic excitations of  $(\text{H}_2\text{O})_n^-$  clusters. Data for surface and interior states were obtained from QUPID simulations [38] while data for interior states were obtained from the fast Fourier transform (FFT) method for transitions from the ground to the first electronically excited state (filled squares [42]) and for transitions to the mean energy of the first three excited states (empty squares [44]). For clusters with  $8 \leq n \leq 32$  bound-continuum (BC) excitations of surface states are exhibited. For large clusters with  $n > 64$  bound-bound (BB) excitations of interior states prevail. The experimental value of EOP for the hydrated electron in bulk water is also shown.  $\circ$ , BC excitations of surface states (QUPID).  $\bullet$ , BB excitations of interior states (QUPID).  $\blacksquare$ , BB excitations to first electronically excited state of interior states (FFT).  $\square$ , BB excitations to the mean of the lowest three excited states of interior states (FFT).  $\diamond$ , EOP (BULK) experimental [6].

interior states in large clusters exhibit a weak size dependence.

(6) The "transition" between energetically stable surface and bulk excess electron states upon increasing the cluster size is expected to be manifested by an abrupt marked increase in EOP.

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