Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Trapped Electrons in Ice

P. S. Julienne [a] & L. P. Gary [a b]

[a] Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27514

[b] Crystal Growth Laborastory, Department of Physics, University of North Carolina, Chapel Hill, North Carolina, 27514

Version of record first published: 21 Mar 2007.

To cite this article: P. S. Julienne & L. P. Gary (1968): Trapped Electrons in Ice, Molecular Crystals, 5:1, 135-139

To link to this article: http://dx.doi.org/10.1080/15421406808082934

Molecular Crystals. 1968. Vol. 5, pp. 135–139

Trapped Electrons in Ice†

P. S. JULIENNE‡ and L. P. GARY§
Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

Received April 1, 1968

Since the successful recording of the transient absorption spectrum of the hydrated electron by Keene[1] and Hart and Boag[2] using pulse radiolysis, an enormous amount of experimental and theoretical data[3] has been presented confirming the existence of the hydrated electron in water (at room temperature). In comparison, however, the solvated electron in *pure* ice was identified only recently by Eiben and Taub.[4] They irradiated pure ice samples at 77°K with ^{60}Co gamma radiation, recorded and analyzed the absorption spectra of the irradiated samples, and subsequently assigned the observed absorption maximum at 6400 Å (1.9 eV) to the hydrated electron. The observed absorption was thermally stable at 77°K and could be photobleached using visible radiation. Working with *pure* ice samples in the temperature range of 200°K to 260°K, V. N. Shubin *et al.*[5] employed the techniques of pulse radiolysis to map the absorption spectra of short-lived species (typical lifetimes of 10^{-3}–10^{-5} sec) in ice, and they attributed the observed transient absorption centered around 6400 Å to the hydrated electron.

The experimental confirmation of a stable bound electron in *pure* ice provides an opportunity to ascertain the validity of the polaron model suggested for the hydrated electron in ice.[6] We have examined the binding of an electron in pure ice using the simple polaron model of Jortner.[7] The electron is assumed to be bound to

† Work supported in part by the Army Research Office (Durham), National Science Foundation, and Advanced Research Projects Agency through Contract SD-100.

‡ National Science Foundation Predoctoral Fellow, 1965–1968.

§ Present address: Crystal Growth Laboratory, Department of Physics, University of North Carolina, Chapel Hill, North Carolina 27514.

a spherical cavity of radius R_0 in a continuous dielectric medium. We have calculated the ground state (E_{1s}) and first excited state (E_{2p}) energies for several values of the parameter R_0 in order to evaluate the optical absorption properties for the 1s → 2p transition of an electron in ice. Jortner[7] has shown that the energy E_n of a bound state n is given by

$$E_n = W_n + S_n \tag{1}$$

where W_n is the energy of the electron in the potential well formed by the "permanent" polarization (atomic and dipole) of the medium and is calculated from a one-parameter hydrogenlike variational wave function; S_n is the electronic polarization energy, which effectively lowers the energy of the bound state n.

The calculated energies W_n, S_n, and E_n for the ground state (1s) and first excited state (2p) and the transition energy $h\nu = E_{2p} - E_{1s}$ as a function of the cavity parameter R_0 are listed in Tables 1 and 2 for an electron bound in pure ice. In order to evaluate completely

TABLE 1 Energies of a Trapped Electron in Pure Ice at 77°K ($D_s = 3.0$ and $D_{op} = 1.76$)

R_0 (Å)	State (n)	Transition energy[a] (eV)	$-E_n$ (eV)	$-W_n$ (eV)	$-S_n$ (eV)
0	1s	1.20	1.67	0.75	0.92
	2p		0.47	0.19	0.28
0.5	1s	1.10	1.57	0.71	0.86
	2p		0.47	0.19	0.28
1.0	1s	0.94	1.41	0.65	0.76
	2p		0.47	0.19	0.28
1.5	1s	0.81	1.27	0.59	0.68
	2p		0.46	0.19	0.27
2.0	1s	0.68	1.14	0.53	0.61
	2p		0.46	0.19	0.27
2.5	1s	0.59	1.05	0.49	0.56
	2p		0.46	0.19	0.27
3.0	1s	0.53	0.97	0.45	0.52
	2p		0.44	0.18	0.26

[a] Experimental absorption maximum of 1.9 eV in ice at 77°K.[4]

TABLE 2 Energies of a Trapped Electron in Pure Ice at 77°K ($D_s = 75$ and $D_{op} = 1.76$)

R_0 (Å)	State (n)	Transition energy (eV)	$-E_n$ (eV)	$-W_n$ (eV)	$-S_n$ (eV)
0	1s	4.66	6.36	4.19	2.17
	2p		1.70	1.05	0.65
0.5	1s	3.52	5.22	3.49	1.73
	2p		1.70	1.05	0.65
1.0	1s	2.47	4.15	2.79	1.36
	2p		1.68	1.04	0.64
1.5	1s	1.81	3.43	2.31	1.12
	2p		1.62	1.01	0.61
2.0	1s	1.37	2.93	1.97	0.96
	2p		1.56	0.98	0.58
2.5	1s	1.11	2.57	1.72	0.85
	2p		1.46	0.93	0.53
3.0	1s	0.90	2.29	1.53	0.76
	2p		1.39	0.89	0.50

the polaron model for ice at 77°K two different degrees of orientational polarization of the dielectric medium by the electron were considered.

Case (1)—Assuming that the dipolar medium molecules surrounding the electron are unable to uniformly orient themselves with respect to the electronic charge (effectively, there is a large relaxation time[8]), then complete orientational polarization of the surrounding medium is hindered. This is the actual condition in ice at 77°K and is characterized by the small static dielectric constant D_s; for the calculations in Case (1) we used $D_s = 3.0$.[6, 9] A summary of the results for Case (1) is shown in Table 1. If it is assumed that the observed absorption maximum (1.9 eV) in pure ice at 77°K reported by Eiben and Taub[4] for the hydrated electron corresponds to a 1s → 2p optical transition of the polaron model, then it is clear that there is insufficient polarization for the model to give a potential well deep enough to account for the observed transition energy.

Case (2)—Assuming that the dipolar medium molecules are free to rotate, then polarization of the medium by the electron produces a cavity similar to that found in water. For this hypothetical situation of a high degree of rotational freedom in ice at 77°K a static dielectric constant of 75 was used. The calculated results for Case (2) are listed in Table 2. Under these conditions the model potential well is deep enough to account for the experimental transition energy.

Previously the simple polaron model was used to estimate the cavity radius at 77°K for trapped electrons in 2-methyltetrahydrofuran[10] (2-MTHF) and triethylamine[11] (TEA) glasses. The experimental threshold photobleaching energy was equated to the ground state energy E_{1s} of the trapped electron, yielding cavity radii of $R_0 \sim 2.0$ Å for 2-MTHF and $R_0 = 2.3 - 4.3$ Å for TEA. In these glasses the static dielectric constant is sufficiently large to permit the polaron model to account for the stabilization of the electron.

The observed thermal stability[4] of trapped electrons in ice at 77°K, together with the inability of the polaron model to predict enough stabilization with the real static dielectric constant, leads us to conclude that the electrons are most likely trapped at immobile physical defects. If the medium about such a defect is characterized by some random frozen-in orientation, the potential well of the electron could be deepened enough to explain the observed stabilization [cf. Case (2) above]. Thus, we picture the electron to be trapped in a lattice defect region, the contribution to the trapping potential coming from two sources, namely medium polarization and an additional potential resulting from the presence of the defect region.

REFERENCES

1. Keene, J. P., *Nature* **197**, 47 (1963).
2. Hart, E. J. and Boag, J. W., *J. Am. Chem. Soc.* **84**, 4090 (1962).
3. Reviews containing typical examples with references:
   (a) Dorfman, L. M. and Matheson, M. S., "Pulse Radiolysis", in *Progress in Reaction Kinetics*, ed. by G. Porter (Pergamon Press, London, 1965), Vol. III, p. 237.
   (b) "Solvated Electron", *Advances in Chemistry*, Series No. 50 (American Chemical Society, Washington, D.C., 1965).

(c) Jortner, J., Rice, S. A., and Wilson, E. G., "Theories of Electron Binding in Solution", in *Metal-Ammonia Solutions*, ed. by G. Lepoutre and M. J. Sienko (W. A. Benjamin, Inc., New York, 1964), p. 222.
4. Eiben, K. and Taub, I. A., *Nature* **216**, 782 (1967).
5. Shubin, V. N., Zhigunov, V. I., Zolitarevskii, V. I., and Dolin, P. I., *Dokl. Akad. Nauk SSSR* **174**, 416 (1967) [English translation: *Dokl. Phys. Chem.* **174**, 373 (1967)].
6. See, for example, Kevan, L., "Chemical Reactions of Radiation-Produced Electrons in Ice and in Organic Solids", in *Progress in Solid State Chemistry*, ed. by H. Reiss (Pergamon Press, New York, 1965), Vol. 2, p. 304.
7. Jortner, J., *J. Chem. Phys.* **30**, 839 (1959).
8. Auty, R. P. and Cole, R. H., *J. Chem. Phys.* **20**, 1309 (1952).
9. Landolt-Börnstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1959), Vol. 2, Teil 6.
10. Fueki, K., *J. Chem. Phys.* **44**, 3140 (1966).
11. Tsujihawa, H., Fueki, K., and Kuri, Z., *J. Chem. Phys.* **47**, 256 (1967).