Letters to the Editor

Communications

Localized excess electrons in water vapor

Ariel Gaathon and Gideon Czapski

Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel

and

Joshua Jortner

Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

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Electron localization in polar liquids[1,2] is a well-established phenomenon. Localized electron states are expected to be stable in dense polar vapors[3] and their absorption spectra were recorded in supercritical ammonia[4] down to density of 0.1 g cm^{-3} and in supercritical water[3,5] down to 0.2 g cm^{-3}. We report the observation of the absorption spectra of localized excess electrons in moderately dense D_2O vapor, down to the density of 0.02 g cm^{-3}. Such experimental data are relevant for the understanding of the mechanism of electron localization in a polar medium and for the elucidation of a proper theoretical description of these states.

Utilizing the pulse radiolysis technique, we have studied the transient ir absorption spectra observed in D_2O vapor which are assigned to the localized electron (e_{loc}). Samples were contained in a high pressure (up to 400 atm) cell (optical path 7 cm) which was thermostated in the range 30–400°C (accuracy ±2°C). Irradiation was performed by a 7715 Varian linear accelerator delivering 1.4 μsec, 6 MeV, 160 mA pulses. The optical detection system consisted of a germanium photodiode (ENL 653) characterized by a risetime of ≤ 0.5 μsec and by the spectral range 5000–17 000 Å. A typical oscilloscope trace is presented in Fig. 1. Vapor densities were determined from the experimental thermodynamic data.[6] We have also determined the absorption spectra in liquid D_2O at the same temperatures.

In Fig. 1 we display the absorption spectra of excess localized electrons in water vapor at moderately low densities (down to 0.02 g cm^{-3}). The experimental spectroscpic data in the liquid and in the gas phase are compared in Table I. From these results we conclude

the following:

(a) Excess electrons are localized in water vapor down to the density of 0.02 g cm^{-3}, which corresponds to the lowest density which could be studied utilizing the present setup.

(b) The OD of the e_{loc} band maximum (extrapolated to account for the pulse width) is proportional to the fluid density in the range 0.1–0.02 g cm^{-3}, whereupon the formation yield is density independent within ±25%.

(c) There is a striking similarity (see Table I) between the absorption spectra of e_{loc} in the vapor and in the subcritical liquid.

(d) The absorption band exhibits a weak density dependence in the liquid, while in the low density vapor a moderate decrease of the transition energy (corrected for the T variation) with density[3] is observed (see Table I).

(e) The observation of the absorption spectra of e_{loc} in water vapor and their weak density dependence implies the crucial role of short range structure in the theoretical description[7] of the solvated electrons.

(f) The weak density dependence and the decrease of e_{loc} with density $\lesssim 0.1$ g cm^{-3} are in agreement with the results of theoretical calculations[3] based on the molecular model[7] which incorporates both short range interactions beyond it.

(g) The present data provide conclusive evidence that solvated electrons in polar liquids cannot be adequately described in terms of the continuum dielectric model[8,9] or by the "molecular" model[10] based on the open icelike structure of water.

Low energy mass spectrometric gas phase data indicate that the electron affinity of the H_2O molecule

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TABLE I. Optical properties of the localized electron in liquid and in Vapor D_2O.

Temperature (°K)	Gas density (g cm^{-3})	$h\nu$[a,b] in gas (eV)	Δ[a,c] in gas (eV)	Liquid density (g cm^{-3})	$h\nu$[a,b] in liquid (eV)	Δ[a,c] in liquid (eV)
523	0.022	0.88	0.41	0.88	1.12	0.45
546	0.033	0.95	0.35	0.83	1.03	0.52
578	0.055	0.92	0.38	0.80	1.02	0.47
618	0.11	1.02	0.41	0.65	1.00	0.44

[a] Accuracy of energy values is ±0.05 eV.

[b] $h\nu$ represents the maximum of the absorption band.

[c] Δ represents the half-width of absorption band at half-maximum intensity.

is negative.[11] Furthermore, theoretical calculations demonstrate that a cluster of four water molecules does not localize[3,12] an excess electron. Gaathon and Jortner[3] considered electron localization within a cluster of four water molecules. An electrostatic charge-dipole potential was adopted to account for attractive interactions, while short range repulsive electron–molecule interac-

tions were handled in terms of a model potential which is specified by an effective hard core radius for each water molecule. The total ground state energy E_T was evaluated as a sum of the electronic energy, the dipole–dipole repulsions, and the short range molecular repulsions within the coordination layer. This calculation resulted in $+E_T \simeq 0.02$ eV $\lesssim k_B T$, and we assert that the supermolecule is unstable. This conclusion concurs with the results of the extensive detailed SCF calculations of Newton,[12] who has demonstrated that a cluster of four water molecules does not localize an excess electron. These recent results are not in conflict with the theoretical study of Ray,[13] who has applied an SCF scheme to handle electron binding to a water molecule at a center of four effective dipoles, characterized by a dipole moment[14] $\mu = \mu_{\text{eff}} = 3.8$ D, which results in an energetically stale configuration. For the case under consideration, one should take $\mu = \mu_{H_2O} = 1.84$ D, whereupon Ray's electron localization center will become energetically unstable.[15] Consequently, no localized electron states are expected to exist in the limit of zero density. We were unable to establish experimentally the existence of a "critical" density for the transition between the localized and quasifree electron in polar vapor in analogy to the case of helium gas.[16] Our experimental data provide an upper limit for this "critical" density.

FIG. 1. Absorption spectra of e_{loo} in D_2O vapor. The vapor densities (relative to liquid at 4°C) are indicated by the numbers above the curves. A typical oscilloscope trace presented at the right hand lower side of the figure represents the time resolved absorption formed in D_2O at 0.033 g cm^{-3} monitored at 1490 mm.

[1] E. J. Hart and M. Anbar, *The Hydrated Electron* (Wiley, New York, 1970).

[2] (a) G. Lepoutre and M. J. Sienko, *Metal–Ammonia Solutions* (Benjamin, New York, 1964); (b) J. J. Lagowski and M. J. Sienko, *Metal-Ammonia Solutions* (Butterworths, London, 1970).

[3] A. Gaathon and J. Jortner, Proceedings of Colloque Weyl III, Metal–Ammonia Solutions, Israel, 1972 (to be published).

[4] R. Olinger, U. Schindelwolf, A. Gaathon, and J. Jortner, Ber. Bunsenges. Physik. Chem. 75, 690 (1971).

[5] B. D. Michael, E. J. Hart, and K. H. Schmidt, J. Phys. Chem. 75, 1798 (1971).

[6] R. W. Bain, *Steam Tables 1964* (H. M. Stationery Office, London, 1964).

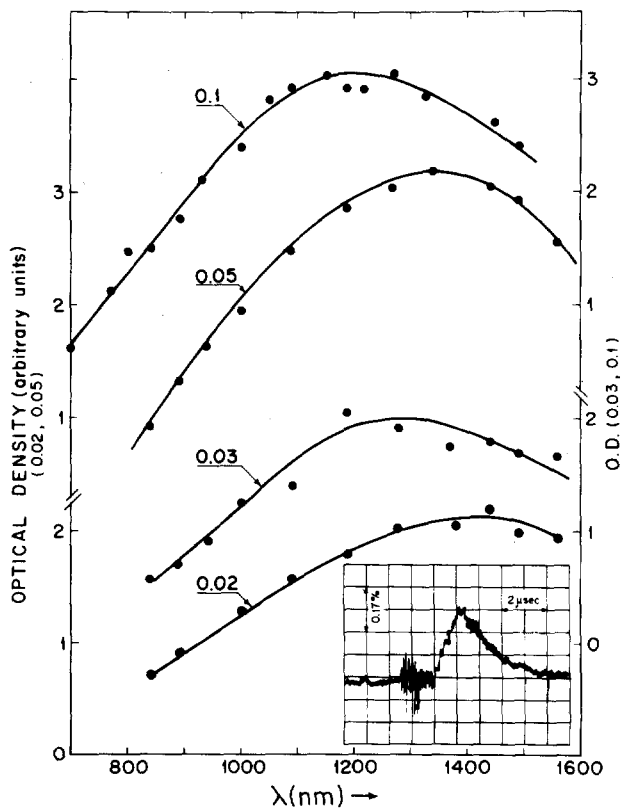[7] D. Copeland, N. R. Kestner, and J. Jortner, J. Chem. Phys. 53, 1189 (1970).

[8] J. Jortner, J. Chem. Phys. 30, 899 (1959).
[9] K. Iguchi, J. Chem. Phys. 48, 1735 (1969).
[10] G. Nillson, J. Chem. Phys. 56, 3427 (1972).
[11] L. G. Christophorou, *Atomic and Molecular Radiation Physics* (Wiley–Interscience, New York, 1971), p. 469.
[12] M. Newton (unpublished).
[13] S. Ray, Chem. Phys. Letters 11, 573 (1971).
[14] L. Onsagerand M. Dupuis, in *Electrolytes*, edited by B. Pesce (Pergamon, London, 1962).

[15] Ray's interaction potential[13] due to the four dipoles is proportional to μ, and the total energy is very sensitive to the relative dipole orientation specified[13] by the angles ϕ_N, $N = 1$–4. When $\phi_N = 0$ for all N, $E_1 = -1.79$ eV, while for $\phi_1 = \phi_3 \simeq \pi/2$ and $\phi_2 = \phi_4 = 0$, $E_2 = +2.31$ eV. A rough estimate for the energy E of such an isolated cluster in $E \sim E_2 + (E_1 - E_2)(\mu_{H_2O}/\mu_{eff})$ is $+0.36$ eV resulting in an energetically unstable configuration.
[16] J. L. Levine and T. M. Sanders, Phys. Rev. Letters 8, 159 (1962).

Nitrogen-14 nuclear quadrupole resonance in isoxazole*

Enrique G. Sauer

Department of Physics, Brown University, Providence, Rhode Island 02912

and

Tõnis Oja

Department of Physics, University of Denver, Denver, Colorado 80210
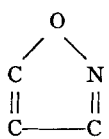
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Nitrogen-containing five-membered rings have interested a considerable number of microwave and nuclear quadrupole resonance (NQR) spectroscopists during the last six to ten years.[1] In the field of NQR, results in five-membered rings have been particularly difficult to obtain since many of the spectral absorption lines are at low frequencies and have long relaxation times.

In this Communication we report the first observation of the nitrogen-14 NQR spectrum in isoxazole. The results were obtained with a pulsed spectrometer[2]

TABLE I. Nuclear quadrupole resonance spectrum of isoxazole at 77°K.

$\nu_+ = 5226$ kHz	$e^2qQ/h = 5428$ kHz [a]
$\nu_- = 2916$ kHz	$\eta = 0.8511$ [b]
$\nu_d = 2310$ kHz	

[a] $e^2qQ/h = \frac{2}{3}(\nu_+ + \nu_-)$.
[b] $\eta = 3(\nu_+ - \nu_-)/(\nu_+ + \nu_-)$.

operated in the 90°–180°-echo mode. The absorption lines are relatively broad and have long relaxation times. Observed transition frequencies were obtained at 77°K and are listed in Table I. Due to the large linewidths involved, the errors associated with the location of the lines are in all cases ±5 kHz. The observed transition frequencies lead to the following values of the quadrupole coupling tensor in the principal axes system: $e^2q_{zz}Q/h = \mp 5428$ kHz, $e^2q_{xx}Q/h = \pm 404$ kHz, and $e^2q_{yy}Q/h = \pm 5024$ kHz. These values are in serious

disagreement with the results of the gaseous phase microwave measurements reported by Mackrodt et al.[3]: $e^2q_{ii}Q/h < 1$ MHz $(i = x, y, z)$, but are reasonably close to the theoretical values calculated by Kochansky and collaborators[4,5]: $e^2q_{zz}Q/h = -6021$ kHz, $e^2q_{yy}Q/h = 5129$ kHz, and $e^2q_{xx}Q/h = 892$ kHz.

A preliminary Townes and Dailey[6] analysis indicates that the sigma N–O bond in isoxazole is highly polarized towards the oxygen atom. If the occupation numbers of the N–C and N–O bonds are σ_{NC} and σ_{NO}, respectively, and provided that σ_{NC} does not deviate appreciably from the values in open-chain compounds $(\sigma_{NC} = 1.20$–$1.24)$, one can obtain σ_{NO} from the following relation[7]:

$$\sigma_{NO} = \sigma_{NC} + [2(\xi^2 - \Delta^{1/2})/(2-\xi)^2](2 - \sigma_{NC}),$$

$$\Delta = 4\xi^2(\xi - 1) + |4(2-\xi)\nu_+/3(2 - \sigma_{NC})A|^2, \quad (1)$$

where $\xi = 1 - \cot^2 CNO/2$, and A is the coupling constant of a $2p$ electron, here taken to be 10 MHz. For $\sigma_{NC} = 1.24$ and $CNO = 105.8°$,[8] Eq. (1) leads to $\sigma_{NO} = 0.56$, a value appreciably lower than the range of values obtained in oximes[7] $(RR'CNOH)$: $\sigma_{NO} = 0.76$–0.80. This difference can be explained in terms of electron repulsion effects at the oxygen atoms. In oximes, the two lone pairs of the oxygen atom are essentially localized and consequently the net "π charge"[9] of the atom is zero. On the other hand, the oxygen atom in isoxazole has one lone pair conjugating with the ring system and therefore bears a positive net π charge. The effect of this positive charge is to enhance the σ electronegativity of the oxygen atom, therefore reducing σ_{NO}. The opposite behavior is observed for the NO_2 group in nitrobenzene. For that case the oxygen atoms