

Evidence for Electron Binding in Frozen Aqueous Solutions

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THE existence of a stable bound state of an electron in water and in similar media is of particular interest in radiation and photochemistry of aqueous solutions. Recent kinetic evidence indicates that electrons produced in irradiated aqueous solutions have a sufficiently long lifetime to react with specific scavengers.¹ The use of rigid glasses prepared from aqueous solutions at liquid-nitrogen temperature affords an efficient method for the investigation of electron binding in such systems. Trapped electrons produced by photo-ionization of organic molecules in EPA glasses were identified.² Recently spectroscopic evidence for electron trapping in γ -irradiated organic glasses was reported.³

We have carried out an investigation of electron binding in glasses prepared from frozen 10N KOH-NaOH aqueous solutions at liquid-nitrogen temperature (77°K). Air-free samples were prepared in quartz cells for photochemistry and in Pyrex cells for radiation chemical studies. The glasses were maintained at 77°K during irradiation and subsequent spectrophotometric measurements.

Irradiation of glasses containing 5N NaOH+5N KOH by 200-kV x rays leads to the production of a broad absorption band originating at 350 $m\mu$, with $\lambda_{\max}=586 m\mu$. The absorption center is stable at 77°K, while heating to 160°K leads to thermal annihilation. The absorption band is efficiently bleached by illumination. Using optical filters it was shown that the 579- $m\mu$ Hg line is efficient in bleaching this absorption band.

In this glass x-ray irradiation leads to ionization processes, i.e., $H_2O \rightarrow H_2O^+ + e$ and $OH^- \rightarrow OH + e$. The H_2O^+ ion may react with an OH^- ion leading to the formation of an OH radical characterized by an absorption band at 311 $m\mu$.⁴ The 586- $m\mu$ band is assigned to an electron trapped in the glass.

In order to yield further evidence for the identification of this band we attempted to produce trapped electrons in the NaOH-KOH glass by photo-ionization of organic molecules.^{2,5} Glasses containing 10^{-2} – 10^{-3} M phenol were irradiated with an unfiltered low-pressure Hg lamp at 77°K. After stopping the irradiation, delayed luminescence was observed.^{2,6} The resulting irradiated glass is blue. The absorption spectrum in the region 450–700 $m\mu$, with $\lambda_{\max}=586 m\mu$, produced by the photo-ionization of the phenolate ion is practically identical with the band obtained by x-ray irradiation of the glass. The band produced by photo-ionization is annihilated by heating to 170°K and bleached by irradiation with visible light.

A new feature of the absorption spectrum produced by photo-ionization of the phenolate anion, which is not observed in the x-irradiated glass involves two weak bands at 385 and 410 $m\mu$. These bands are attributed to a $\pi \rightarrow \pi^*$ transition of the phenoxy radical, and were previously observed in flash photolysis and photolysis of phenol in organic glasses.⁷ We failed to detect any bands at 430 and 450 $m\mu$ as previously reported.⁸ As, under our conditions, the phenolate anion is photolyzed, the two bands observed by us have to be assigned to the phenoxy radical C_6H_5O and not to the protonated radical $C_6H_5OH^+$, thus supporting the interpretation of Porter *et al.*⁷

The nature of the trapping center giving rise to the blue band should be considered. The electron may be bound in the glass by polarization of the medium as in the case of infinitely dilute metal ammonia solution.⁹ This electron center is characterized by an infrared absorption band $\lambda_{\max}=1500 m\mu$ at 240°K,⁹ and $\lambda_{\max}=$

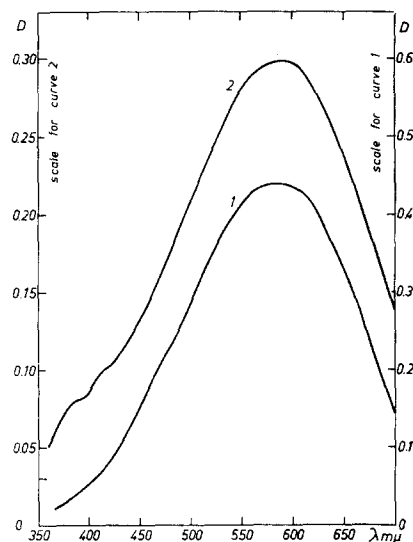


Fig. 1. Absorption spectra of glasses prepared from 5N KOH+5N NaOH aqueous solution at 77°K: (1) glass irradiated by 200-kV x rays; (2) glass containing 10^{-3} M phenol irradiated with 254- $m\mu$ Hg line.

1200 $m\mu$ in metal ammonia glasses at 20°K.¹⁰ It is somewhat difficult to provide a satisfactory explanation for the shift of the solvated electron band to 586 $m\mu$ in frozen aqueous solutions, compared to solid ammonia. It should be pointed out that γ -irradiated ice at 77°K just gives rise to a uv band at $\lambda_{\max}=280 m\mu$.¹¹ Thus the role of the alkali hydroxide is crucial for the formation of this trapping center. In these glasses the electron may be trapped in an expanded orbital in the field of an alkali cation. Such a trapping center due to cation-electron interaction^{12,13} was observed in metal ammonia solutions, characterized by an absorption band $\lambda_{\max}=800 m\mu$ at 240°K,^{13,14} while in Na-NH₃ glasses at 20°K an absorption band at $\lambda_{\max}=595 m\mu$ ¹⁰ is probably due to this center. The 586- $m\mu$ band ob-

served in our work may be due to the same type of trapping center in frozen aqueous solutions.

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Hartree-Fock Perturbation Method*

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A PERTURBATION method for the Fock-Dirac density matrix in the finite matrix representation of the Hartree-Fock (H-F) approximation has been developed. Application of the method requires no knowledge of the eigenvalues and eigenvectors of the unoccupied orbitals. It is applicable to closed shell systems in the restricted H-F approximation and to any system in the unrestricted H-F approximation. The method has been formulated so that once one has evaluated the first-order change in the density matrix due to a perturbation, all of the other changes may be evaluated by simple matrix algebra. The derivation takes advantage of some conditions on the Fock-Dirac density matrix recently given by McWeeny in deriving his perturbation method.¹ The present method differs from McWeeny's in that it requires only a finite number of operations to calculate each order in perturbation theory, whereas McWeeny's requires, in principle, an infinite number. We outline in this note the derivation of the formulas.²

The unperturbed H-F effective Hamiltonian is the M by M matrix $\mathbf{F}^{(0)}$. (We assume in what follows that an orthonormal basis set is used. One can easily generalize this to the nonorthonormal case.³) Its orthonormalized eigenvectors are the column matrices \mathbf{U}_k , its eigenvalues, E_k . The unperturbed Fock-Dirac density matrix is $\mathbf{p}^{(0)} = \sum_k^{\text{occ}} \mathbf{U}_k \mathbf{U}_k^\dagger$, where the summa-

tion is over the N occupied orbitals. The perturbation is $\lambda \Delta$, where λ is the expansion parameter. We write $\mathbf{p} = \sum_{n=0}^{\infty} \lambda^n \mathbf{p}^{(n)}$ for the density matrix of the perturbed system. McWeeny¹ has shown that since \mathbf{p} must be idempotent, the $\mathbf{p}^{(n)}$ have restrictions placed on them. (We write $\mathbf{1}$ for the unit matrix.) In particular he has shown that $\mathbf{p}_{11}^{(n)} = \mathbf{p}^{(0)} \mathbf{p}^{(n)} \mathbf{p}^{(0)}$ and $\mathbf{p}_{22}^{(n)} = (\mathbf{1} - \mathbf{p}^{(0)}) \mathbf{p}^{(n)} (\mathbf{1} - \mathbf{p}^{(0)})$ are completely determined by the matrices of order $n-1$ and lower. Thus by perturbation theory one has to determine only $\mathbf{p}_{12}^{(n)} = \mathbf{p}^{(0)} \mathbf{p}^{(n)} (\mathbf{1} - \mathbf{p}^{(0)})$.

The formula from which we derive our perturbation method is

$$\mathbf{p}_{12}^{(n)} = - \sum_k^{\text{occ}} \sum_l^{\text{un}} (E_k - E_l)^{-1} \mathbf{P}_k (\Delta \mathbf{p}^{(n-1)} - \mathbf{p}^{(n-1)} \Delta) \mathbf{P}_l, \quad (1)$$

where $\mathbf{P}_k = \mathbf{U}_k \mathbf{U}_k^\dagger$ and \sum^{un} indicates summation over the unoccupied orbitals. The formula may be derived from $\mathbf{Fp} - \mathbf{pF} = 0$.² Equation (1) and McWeeny's conditions on $\mathbf{p}_{11}^{(n)}$ and $\mathbf{p}_{22}^{(n)}$, are equivalent to the Schrödinger formula when there is only one occupied orbital. One may derive McWeeny's perturbation method from (1) by assuming that the magnitude of the ratio of the eigenvalues of any unoccupied orbital to that of any occupied orbital is less than unity, then expanding $(E_k - E_l)^{-1}$ in a power series and noting that $\mathbf{F}^m = \sum_k (E_k)^m \mathbf{P}_k$. We derive our method from (1) by using a mathematical trick.

We define $\mathbf{F}_K = \mathbf{F}^{(0)} - E_K \mathbf{1} + \omega \mathbf{p}^{(0)}$, where E_K is the eigenvalue of any occupied orbital and ω is an arbitrary, nonzero real number. If there is no degeneracy between occupied and unoccupied levels, then \mathbf{F}_K^{-1} exists. Furthermore, we have the relation

$$(\mathbf{1} - \mathbf{p}^{(0)}) \mathbf{F}_K^{-1} = \sum_k^{\text{un}} (E_k - E_K)^{-1} \mathbf{P}_k. \quad (2)$$

Multiplying $\mathbf{p}_{12}^{(n)}$ in (1) from the left by \mathbf{P}_K , and combining this expression with (2), we see that

$$\mathbf{P}_K \mathbf{p}_{12}^{(n)} = \mathbf{P}_K (\Delta \mathbf{p}^{(n-1)} - \mathbf{p}^{(n-1)} \Delta) (\mathbf{1} - \mathbf{p}^{(0)}) \mathbf{F}_K^{-1}. \quad (3)$$

The complete n th-order correction is

$$\mathbf{p}_{12}^{(n)} = \sum_K^{\text{occ}} \mathbf{P}_K \mathbf{p}_{12}^{(n)}.$$

If several occupied orbitals are degenerate, \mathbf{P}_K in (3) may be replaced by the sum of the \mathbf{P}_k 's for the degenerate levels. This is why it is advantageous to develop our method for the Fock-Dirac density matrix rather than for the orbitals. Equation (3) is the formula we wished to derive. In order to use our method one must know the eigenvalues and eigenvectors of the occupied orbitals and one must invert one matrix \mathbf{F}_K for every different E_k of the occupied levels. The number ω may be chosen arbitrarily, but in practice one would want to choose ω so that \mathbf{F}_K^{-1} may be accurately and rapidly calculated by an electronic computer.