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Dissociative Electron Capture in Water Vapor

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An electron swarm experiment has been conducted to study the process of negative-ion formation in water vapor by dissociative electron capture. Assuming that electrons are captured in a single process at one well-defined energy, the present results are consistent with a beam experiment reported by Buchel'nikova. It was found that the capture cross section, (due to the formation of H^-), when integrated over energy, was 7.7×10^{-18} cm^2 ev, which is consistent with the electron beam results of 6.5×10^{-18} cm^2 ev. The energy at which the process peaks was found to be 6.4 ev, which agrees quite well with the peak energy found by Buchel'nikova, but in general disagrees with other values obtained by mass spectroscopy.

I. INTRODUCTION

FORMATION of negative ions by electron capture is an important phenomenon in many fields of current interest, e.g., atmospheric physics, radiation physics, radiation chemistry, and radiation biology. Electron interactions with water molecules are certainly an important elementary process in radiation chemistry and radiation biology; for example, the determination of the magnitude of electron capture in dissociating water will help in deciding the basic mechanisms involved in the radiolysis of water.[1]

Several studies[2–4] of negative-ion formation due to electron impact in water vapor have been carried out with the mass spectrograph. These studies identify the types of negative ions formed and give the range of electron energy over which the dissociative capture processes are important, but provide little information on the magnitude of the cross section for formation. Thus, in the case of the formation of H^- the first peak is observed by Lozier to be at 6.6 ev, by Mann, Hustrulid, and Tate at 7.1 ev, and by Cottin at 6.0 ev, and in no case is the magnitude of the cross section estimated. Bradbury's studies[5] of electron attachment using a swarm method were not interpreted in terms of the specific processes involved, and hence cross sections at given electron energies were not derived.

A recent publication[6] reported cross sections for formation of H^- using a beam method in which the energy spread of the electron beam was reported to be 0.2 or 0.3 ev. Beam experiments often lead to systematic errors in the determination of the absolute electron energy scale and in the normalization of the absolute cross section. It is therefore useful to perform an experiment by a totally independent method which can be tested for consistency with the beam experiment. In the present experiment the process of electron capture in water vapor was investigated by means of a swarm method in which small amounts of water vapor were added to pure argon. By extrapolating the results to zero water concentration, it is possible to measure the cross section for electron capture in water averaged over the energy distribution characteristic of argon and a given value of E/P[v cm^{-1} (mm Hg)$^{-1}$]. Using the general form of the cross section observed by Buchel'nikova as a guide, we find our results consistent with the beam experiment. This gives us added confidence in the results reported by Buchel'nikova, and in the values used in our interpretation for the electron energy distribution in argon.

II. METHOD

It has been shown[7] that the time-dependent change in potential $V(t)$ of the collector plate of a plane ionization chamber of separation d cm, due to free electrons moving through the chamber, is given by

$$g(t)=(A/f)[1-\exp(-ft/\tau_0)], \tag{1}$$

where A is a constant, τ_0 is the collection time of free electrons and $f=\alpha f_1Pd$. In this expression α is the attachment coefficient for electrons defined by

$$dN=-\alpha Nf_1Pdx, \tag{2}$$

where $-dN/N$ is the fraction of electrons captured in moving dx in the field direction and f_1P is the pressure of the attaching gas, referred to a standard temperature of 25°C. If the pulse is examined with a pulse amplifier of equal differentiating and integrating time constants (both equal to t_1), the output pulse of such an amplifier is given by

$$V(\tau)=\int_0^\tau \frac{dg(t)}{dt}\frac{(\tau-t)}{t_1}e^{-(\tau-t)/t_1}dt, \tag{3}$$

where $t/t_1e^{-t/t_1}$ is the response of the amplifier to a step function.

Using Eq. (1) for $g(t)$, the expression given in Eq. (3) for $V(\tau)$ becomes for $\tau\leq\tau_0$

$$V(\tau)=\frac{Ae^{-\tau/t_1}}{(\tau_0-t_1f)}\left[\frac{\exp(u\tau)}{u}-\tau-\frac{1}{u}\right], \tag{4a}$$

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* Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

[1] R. L. Platzman (private communication).

[2] W. W. Lozier, Phys. Rev. **36**, 1417 (1930).

[3] M. M. Mann, A. Hustrulid, and J. T. Tate, Phys. Rev. **58**, 340 (1940).

[4] M. Cottin, J. Chim. phys. **56**, 1024 (1959).

[5] N. E. Bradbury, J. Chem. Phys. **2**, 827 (1934); N. E. Bradbury and H. Tatel, *ibid.* **2**, 835 (1934).

[6] I. S. Buchel'nikova, Soviet Phys.—JETP 35(8), 783 (1959).

[7] T. E. Bortner and G. S. Hurst, Health Phys. **1**, 39 (1958).

and for $\tau \geq \tau_0$,

$$V(\tau)=\frac{A\exp(-\tau/t_1)}{(\tau_0-t_1f)}\left[\{\exp(u\tau_0)-1\}\tau - \exp(u\tau_0)\left(\tau_0-\frac{1}{u}\right)-\frac{1}{u}\right], \quad (4b)$$

where $u=(\tau_0-t_1f)/t_1\tau_0$. Equations (4a) and (4b) have been evaluated to find the "pulse height," i.e., the maximum value of $V(\tau)$ for $\tau_0/t_1=0$, 1, 2, 3, 4, and 5 as a function of f.[8] With experimental values for τ_0 and the pulse height, f and hence α may then be calculated.

In the present experiment the apparatus and general procedure were essentially the same as previously described.[7,9] Water, contained in a small trap, was pumped periodically for several days to remove dissolved oxygen before the water vapor was admitted to the chamber. The argon was obtained from a commercial cylinder of highly purified gas and was further purified by drying with magnesium perchlorate and by fractional distillation from a trap cooled with liquid nitrogen. Later, a resin[10] to remove dissolved oxygen was put into the water trap, and the results were the same.

III. RESULTS

Figures 1, 2, and 3 show the pulse-height data obtained when various amounts of water vapor were mixed with Ar at 400, 800, and 1800 mm Hg, respectively. Drift velocity data for mixtures of Ar and water are shown in Fig. 4. From these data the attachment coefficients α were calculated and are shown in Fig. 5. In this figure, α for various E/P values is plotted as a function of the ratio of water pressure, f_1P, to Ar pressure, f_2P.

From Fig. 5 it is seen that α is, within experimental error, independent of total pressure but depends strongly on the ratio f_1P/f_2P. This suggests that the electron energy distribution in Ar is influenced by water, and that an increase in f_1P/f_2P decreases the number of electrons in the range where dissociative capture takes place. It seems reasonable to expect that the limiting values of α as f_1P/f_2P approaches zero, α_0, are to be associated with the electron energy distribution of pure Ar. Thus we can write α_0 in terms of the capture cross section, $\sigma_c(\epsilon)$, at energy ϵ as follows:

$$\alpha_0\left(\frac{E}{P}\right)=\frac{N_0(2/m)^{\frac{1}{2}}}{w(E/P)}\int_0^\infty \epsilon^{\frac{1}{2}}\sigma_c(\epsilon)f\left(\epsilon,\frac{E}{P}\right)d\epsilon, \quad (5)$$

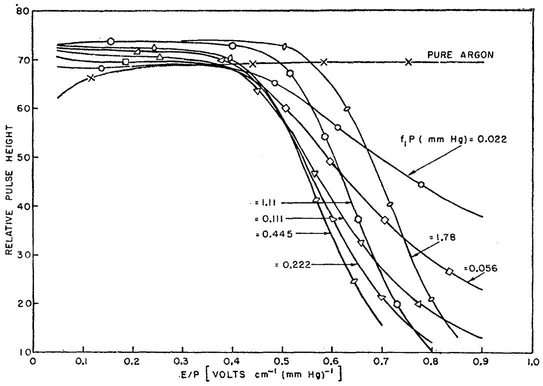

FIG. 1. Pulse height vs E/P for H_2O-Ar mixtures (400 mm Hg).

where $f(\epsilon,E/P)$ is the normalized energy distribution function for electrons in pure Ar, $w(E/P)$ is the electron drift velocity in Ar, m is the electron mass, and N_0 is the number of water molecules per cm^3 at 1 mm Hg.

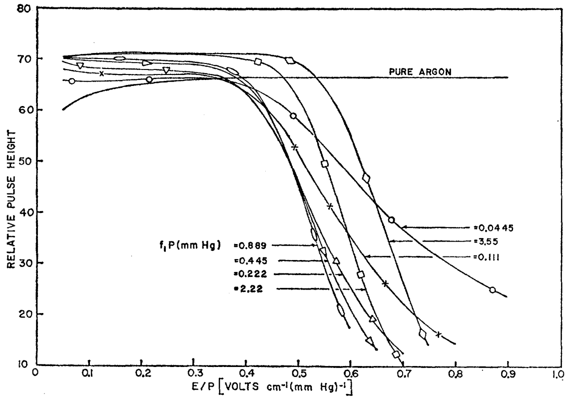

FIG. 2. Pulse height vs E/P for H_2O-Ar mixtures (800 mm Hg).

Considering the fact that the mass spectrograph data[2–4] and the beam experiment[6] show a fairly narrow peak for the formation of H^- and that in all such experiments the electron beam has an appreciable spread in

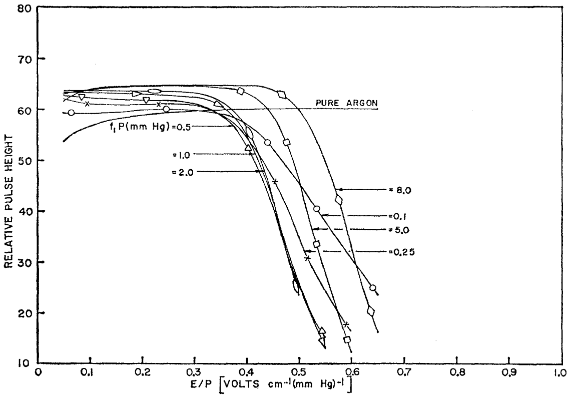

FIG. 3. Pulse height vs E/P for H_2O-Ar mixtures (1800 mm Hg).

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[8] The original publication (reference 7) contained errors for $\tau_0/t_1 \geq 2$ which have subsequently been corrected and reported by H. B. Eldridge, Oak Ridge National Laboratory Report ORNL-3090 (unpublished). This report contains a detailed tabulation of the pulse height as a function of f for various values of τ_0/t_1.

[9] G. S. Hurst and T. E. Bortner, Phys. Rev. **114**, 116 (1959).

[10] The resin used was Duolite S-10 provided by the Chemical Process Company, Redwood City, California.

TABLE I. Evaluation of the ratio $w\alpha_0/f(\epsilon_1)$ for various values of ϵ_1. An (E/P)-independent ratio indicates a solution to Eq. (6).

E/P	α_0 cm^{-1} (mm Hg)$^{-1}$	$w\alpha_0\times10^{-6}$ sec^{-1} (mm Hg)$^{-1}$	Electron energy (ev) 6.3 $f(\epsilon_1)$	6.3 $w\alpha_0/f(\epsilon_1)$	6.4 $f(\epsilon_1)$	6.4 $w\alpha_0/f(\epsilon_1)$	6.5 $f(\epsilon_1)$	6.5 $w\alpha_0/f(\epsilon_1)$	6.6 $f(\epsilon_1)$	6.6 $w\alpha_0/f(\epsilon_1)$
0.40	0.18	0.058	0.00224	25.9×10^6	0.00161	36.0×10^6	0.00114	50.9×10^6	0.000793	73.1×10^6
0.45	0.57	0.185	0.00615	30.1×10^6	0.00472	39.2×10^6	0.00358	51.7×10^6	0.00269	68.8×10^6
0.50	1.20	0.396	0.0126	31.4×10^6	0.0102	38.8×10^6	0.00813	48.7×10^6	0.00643	61.6×10^6
0.55	2.0	0.670	0.0213	31.5×10^6	0.0179	37.4×10^6	0.0149	45.0×10^6	0.0122	54.9×10^6
0.60	3.0	1.02	0.0317	32.2×10^6	0.0273	37.4×10^6	0.0233	43.8×10^6	0.0198	51.5×10^6
0.65	4.1	1.41	0.0428	32.9×10^6	0.0377	37.4×10^6	0.0330	42.7×10^6	0.0287	49.1×10^6
0.70	5.3	1.86	0.0540	34.4×10^6	0.0484	38.4×10^6	0.0432	43.1×10^6	0.0383	48.6×10^6
0.75	6.6	2.34	0.0647	36.2×10^6	0.0589	39.7×10^6	0.0533	43.9×10^6	0.0481	48.6×10^6

energy, it is reasonable to select a strongly peaked function as a trial solution for $\sigma_c(\epsilon)$ in Eq. (5). Hence,

$$\alpha_0\left(\frac{E}{P}\right)=\frac{N_0(2/m)^{\frac{1}{2}}}{w(E/P)}\epsilon_1^{\frac{1}{2}}f\left(\epsilon_1,\frac{E}{P}\right)\int_0^\infty\sigma_c(\epsilon)d\epsilon,\qquad(6)$$

where ϵ_1 is the energy at which the capture cross section peaks. Since the various observers are not in agreement on the energy at which the cross section peaks, we consider ϵ_1 as a variable and find a value which satisfies Eq. (6) for the experimental range of E/P. Tabulations of $w\alpha_0/f(\epsilon)$ for various electron energies ϵ_1 are shown in Table I. In these tabulations the drift velocity w for Ar was taken from Bortner, Hurst, and Stone.[11] The values of the electron energy distribution function for Ar were based on the solution of the Blotzmann transport equation following the procedure of Barbiere[12] and Bowe,[13] and are conveniently tabulated[14] for future reference. It is seen from Table I that if we let $\epsilon_1=6.4$ ev, a good solution to Eq. (6) is found, while for values of $\epsilon_1=6.3$ or 6.5, the fit to Eq. (6) is less accurate. The magnitude of the cross section integral

$$A=\int_0^\infty\sigma_c(\epsilon)d\epsilon,$$

corresponding to $\epsilon_1=6.4$ ev, is 7.7×10^{-18} cm^2 ev. The magnitude of A and the energy where the cross section is a maximum, ϵ_1, derived in this way compared favorably with the results obtained by Buchel'nikova.[6] From the curve published by Buchel'nikova, one may estimate $\epsilon_1=6.4$ ev and $A=6.5\times10^{-18}$ cm^2 ev. The statistical errors for α_0 are not believed to be larger than ±5%, and

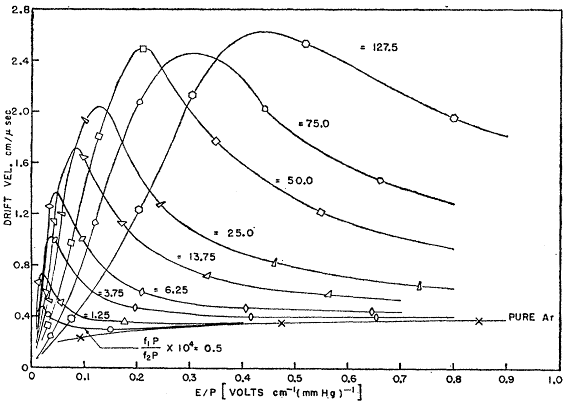

FIG. 4. Electron drift velocity in H_2O-Ar mixtures (400 mm Hg).

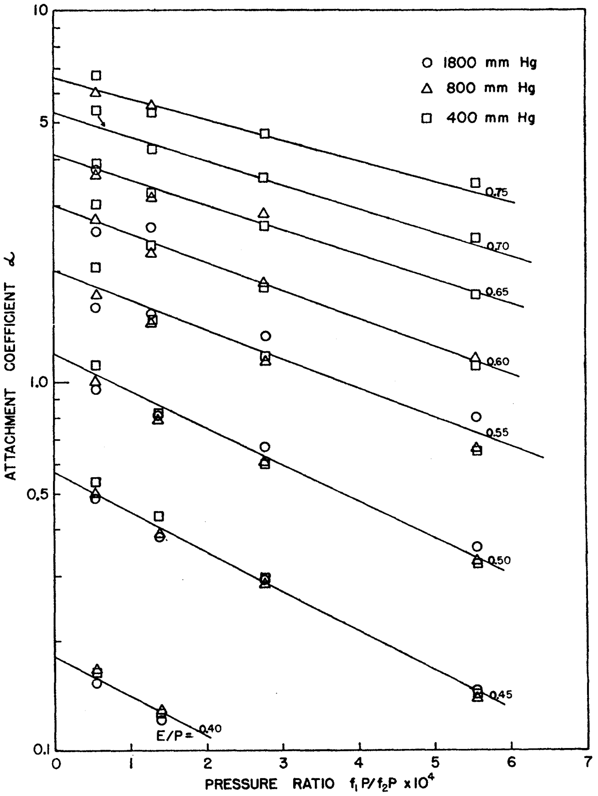

FIG. 5. Attachment coefficient α as a function of the ratio of H_2O pressure to Ar pressure for various values of E/P.

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[11] T. E. Bortner, G. S. Hurst, and W. G. Stone, Rev. Sci. Instr. **28**, 103 (1957).

[12] D. Barbiere, Phys. Rev. **84**, 653 (1951).

[13] J. C. Bowe, Phys. Rev. **117**, 1416 (1960).

[14] R. H. Ritchie and G. E. Whitesides, Oak Ridge National Laboratory Report ORNL-3081, June 2, 1961.

statistical errors for w are approximately $\pm 2\%$. These errors, as seen from Table I, would not change appreciably the values quoted above for ϵ_1 and A. However, the significance of the consistency between the results of the beam experiment and the present swarm experiment is closely related to the validity of the electron energy distribution function used in the analysis of the swarm experiment. In support of the distribution function, we note that Bowe[13] has shown that for Ar the calculated distribution function gave values for the electron drift velocity which agree well with experiment.

The present method of analysis of the swarm data in terms of a strongly peaked function for the cross sections does not provide a unique assignment of the width of the capture region, e.g., in Table I it is seen that a solution to Eq. (5) could be expressed in terms of the sum of three strongly peaked functions taken at 6.3, 6.4, and 6.5 ev. This would, however, leave unchanged the peak energy and the magnitude of the total cross-section integral A. It is likely that the true width of the capture region is less than that reported by Buchel'nikova. Unfortunately, the potential energy curves[15] for H_2O are not well established; therefore, the width of the capture region cannot be realistically estimated.[16]

A further consistency check using the electron energy distribution functions in argon was made by comparing the swarm results for electron capture in Ar-O_2 mixtures reported in reference 7 with the beam experiment reported in reference 6. Even though the check involved only a small fraction of the total number of electrons in the high-energy tail, both the magnitude and the dependence of α (for O_2) on E/P were in very good agreement with the beam experiment.

In summary, we have found no evidence of internal inconsistency between the swarm experiments and the beam experiments for electron capture in both H_2O and O_2, provided that the swarm experiments are conducted in mixtures with argon for which the electron energy bistribution is established from independent considerations. This suggests the swarm method as a means of establishing the energy scale and absolute cross section for various electron capture reactions, provided that the swarm experiments are performed under conditions where good information is available on the electron energy distribution.

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[15] K. L. Laidler, J. Chem. Phys. 22, 1740 (1954).

[16] A basis for estimating the width of capture regions has been outlined by H. D. Hagstrum, Revs. Modern Phys. 23, 185 (1951).

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Wave Functions for the Free Electron. II. The Inclusion of Polarization and Exchange*

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The effect of the polarization of the atomic core by the free electron on the free-electron wave function and the effect of the exchange of the free electron with the bound orbitals on this wave function are treated by perturbation theory. Polarization must be considered first. Its effect on the atomic charge cloud is introduced through an expansion over the bound wave functions for the atom in terms of the free-electron separation as a parameter. This parametric treatment of electron separation means we cannot accept the solution at small separations from the nucleus although this is not a serious restriction. From this wave function we obtain a polarized Coulomb potential from which a solution for the free-electron function may be obtained using our old programs. Having solved the free-electron wave equation with the exchange potential terms supposed zero, we use this solution to compute the exchange integrals. The equation including these integrals is then solved to obtain approximate wave functions for free electrons containing both exchange and polarization.

I. INTRODUCTION

IN a previous paper we have detailed the programs developed by us[1] for the determination of the wave function for an electron in the field of a neutral atom where the atom is supposed to give rise only to a Coulomb potential. In that paper we deliberately neglected the effects of (1) the polarization of the atomic charge cloud by the free electron and (2) the exchange of the free electron with the various bound electrons in the atomic charge cloud. In what is to follow we shall discuss the inclusion of these effects.

In recent years several methods for the inclusion of polarization and exchange have been used, and we shall touch briefly on a few of them. First we remark

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* Based on work performed under the auspices of the U. S. Air Force Ballistic Missiles Division.

† Consultant: 48 Maple Avenue, Centerville 59, Ohio.

[1] R. G. Breene, Jr., and Maria C. Nardone, Phys. Rev. 115, 93 (1959).