Semiempirical formula for the electric field dependence of geminate ion recombination fluorescence

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Semiempirical formula for the electric field dependence of geminate ion recombination fluorescence[a)]

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A semiempirical formula is derived which governs the electric field dependence of the fluorescence produced upon recombination of geminate ions. The formula is applied to some new data on the fluorescence which follows the ultraviolet irradiation of solutions of N,N,N',N'-tetramethylparaphenylenediamine (TMPD) in tetramethylsilane and 2,2-dimethylbutane. From the two-parameter-least-squares lines which result from the application of the formula, we determine a number of derived quantities. Among these are Φ_{ip} the quantum yield for photoionization of TMPD, and $P(0,0)$ the probability of dissociation of the electron–ion pair produced by the photoionization. The values of $P(0,0)$ are found to be nearly equal to the ratio $G_{fi}/(G_{gi} + G_{fi})$ where G_{fi} and G_{gi} are the free ion and geminate ion yields, respectively, obtained in ^{60}Co γ irradiations of the pure solvents. The product of Φ_{ip} and $P(0,0)$ is Φ_e^0, the free electron quantum yield. The values of Φ_e^0 obtained from the fluorescence measurements are compared with those obtained from separate measurements of the photocurrent. Other quantities derived from the semiempirical formula include the first three moments of a function related to the distribution of electron–ion pair distances in the liquid.

I. INTRODUCTION

When a molecule in a liquid absorbs a quantum $h\nu_{ex}$ which is greater than its ionization potential, an electron-ion pair can be produced. The difference between the excitation energy $h\nu_{ex}$ and the ionization potential may appear as internal energy of the ion or as relative kinetic energy of the electron-ion pair. In the process of dissipating the kinetic energy in collisions with molecules of the liquid, the electron and its parent ion became separated by a distance r. In an ensemble of such pairs, there is a distribution $\sigma(r)$ of these separations r. By the time $\sigma(r)$ is established, the electron and ion velocities are in thermal equilibrium with the fluid. Thereafter, the electron-ion pair executes a Brownian motion governed by the Smoluchowski equation. The distribution $\sigma(r)$ forms an initial condition for this equation. Information, however, on the functional form of $\sigma(r)$ is fragmentary.

Because of its low ionization potential, N,N,N',N'-tetramethylparaphenylenediamine (TMPD) can be photooxidized to an electron-ion pair by exposing its solutions to ultraviolet radiation.[1-7] The presence of the electron-ion pair in these solutions has been indicated by the observation of three effects: (1) the photocurrent produced by the dissociation of the pair[1-3,5]; (2) quenching of the electron-ion pair recombination fluorescence by the action of an external electric field[4,5]; and (3) quenching of the recombination fluorescence by the presence of an electron scavenger.[5] Among these observations, quench-

ing data taken at low-field and small scavenger concentration have particular significance because the theory of electron-ion pair recombination is known in closed form in this regime.[8] In the case of TMPD dissolved in 2,2,4-trimethylpentane, the required data[5] are available and have been shown to be in quantitative agreement with the theory.[9]

We report herein some new measurements of the photocurrent and fluorescence which result from the ultraviolet irradiation of solutions of N,N,N',N'-tetramethylparaphenylenediamine in tetramethylsilane and 2,2-dimethylbutane. The photocurrent and fluorescence are measured as functions of the magnitude of an applied external electric field. Our scheme for photoionization/fluorescence of TMPD is shown in Fig. 1.[20] The fluorescence quantum is $h\nu_{fl}$. A molecule of TMPD in an excited state leading to ionization is M^{**}, the first excited singlet state is M^*, the ground state is M, and the electron-ion pair is $[M^+, e^-]$. The quantum yields for electron-ion pair formation and for fluorescence are Φ_{ip} and Φ_{fl}, respectively. The probability for geminate ion recombination in the presence of an applied uniform electric field E and electron scavenger A in concentration c_s is $Q(c_s, E)$.

The photocurrent which can be drawn from the liquid at zero scavenger concentration depends linearly upon $[1 - Q(0,E)]$. For a large enough range of E, data involving $Q(0,E)$ can be used to determine the form of $\sigma(r)$.[10] In previous work,[6-7] we have fitted our photocurrent data with various representations $\sigma(r, \lambda)$ of the distribution $\sigma(r)$ using the variable λ as an adjustable parameter. Due to the limited range of the electric field which could be applied in these experiments, the photo-
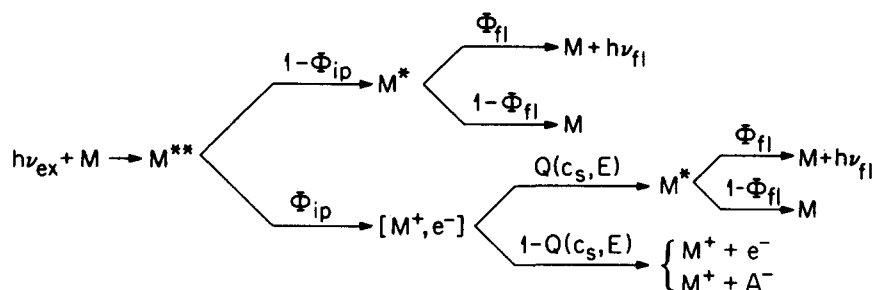
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FIG. 1. Photoionization/fluorescence scheme.

current data could be fitted with equal precision to either an exponential or a Gaussian form of $\sigma(r, \lambda)$.

In this report, we bypass the difficulties associated with the selection of $\sigma(r, \lambda)$ and, instead, fit our data directly to a semiempirical function of E. Our choice of function is deduced from the one used by Rzad, Infelta, Warman, and Schuler to analyze data on the scavenging of electron-ion pairs produced by ^{60}CO γ radiolysis.[11] In Sec. II, we derive our function. Our method depends upon the replacement of a certain dimensionless group involving $c_s^{1/2}$ by another dimensionless group involving E. Because of the difficult analyses, the theory[8] of $Q(c_s, E)$ has been obtained in closed form only through terms linear in $c_s^{1/2}$ and E. Our semiempirical function is made to be in rigorous agreement with these terms. In Sec. III, we analyze our fluorescence quenching data in terms of this function. By a simple linear regression on two parameters, we estimate Φ_{ip}, the dissociation probability $P(0, 0) = 1 - Q(0, 0)$ of the electron-ion pair, and the first three moments of a distribution related to $\sigma(r)$. The dependence of these quantities upon $h\nu_{ex}$ is also determined. In Sec. IV, we examine the implications of the higher-order terms in our semiempirical function and form our conclusions.

II. THEORY

A. Basis for analysis of previous experimental results

An analysis of the scheme shown in Fig. 1 shows that the fluorescence intensity F is given by $F \propto (1 - \Phi_{ip}) \Phi_{fl} + \Phi_{ip} Q(c_s, E) \Phi_{fl}$. If F^0 is the intensity of fluorescence when $E = 0$, and $\Delta F = F^0 - F$, we find

$$\Delta F/F^0 = \Phi_{ip} [Q(c_s, 0) - Q(c_s, E)]/[(1 - \Phi_{ip}) + \Phi_{ip} Q(c_s, 0)] .$$
(2.1)

For small enough c_s and E, there is a theoretically derived closed form expression for $Q(c_s, E)$, which reads[8]

$$Q(c_s, E) = Q(0, 0) - P(0, 0)(W^2 + V^2)^{1/2} ,$$
(2.2)

where the dimensionless groups W and V are given by

$$W = r_c \gamma E ,$$
(2.3)

$$V = (k_s c_s r_c^2/D)^{1/2} ,$$
(2.4)

with

$$r_c = e^2/\epsilon k_B T ,$$
(2.5)

$$\gamma = e/2 k_B T .$$
(2.6)

Here, e is the magnitude of the electron charge, D is

the electron diffusion coefficient, k_B is Boltzmann's constant, T is the absolute temperature, ϵ is the liquid dielectric constant, and k_s is the rate constant for electron capture by the scavenger. For $W = V = 0$, the probability of dissociation of the electron-ion pair is $P(0, 0)$. In the absence of scavenger $(V = 0)$, conservation of probability is expressed by

$$P(0, E) + Q(0, E) = 1 .$$
(2.7)

In our previous work,[9] Eq. (2.2) served to divide our fluorescence quenching data into two parts. A low-field part occurred when $W \ll V \lesssim 1$. Under this condition, combination of Eqs. (2.1) and (2.2) together with the appropriate binomial expansion of the latter led to the expression $\Delta F/F^0 = c_1 W^2$, where c_1 was a positive constant. An intermediate-field part occurred when $V \ll W \lesssim 1$, and an appropriate expansion led to the result $\Delta F/F^0 = c_2 W - c_3$, where c_2 and c_3 were other positive constants.

When there was no scavenger present, the low-field region disappeared. The ratio $\Delta F/F^0$ was proportional to W for $W \lesssim 1$ and departed from linearity when $W \gtrsim 1$. We shall refer to the regime $W \gtrsim 1$ as the high-field region.

We have shown[5] that if i and i^0 are photocurrents measured in the presence and absence, respectively, of the field E, then

$$\Delta F/F^0 = \frac{\Phi_e^0}{1 - \Phi_e^0}((i/i^0) - 1) ,$$
(2.8)

where Φ_e^0 is the free electron quantum yield defined by

$$\Phi_e^0 = \Phi_{ip} P(0, 0) .$$
(2.9)

The ratio of photocurrents is given by

$$i/i^0 = P(0, E)/P(0, 0) .$$
(2.10)

Previously,[6] to calculate $P(0, E)$ we used the expression

$$P(0, E) = 4\pi \int_0^\infty dr\, r^2 \sigma(r, \lambda)\, \phi(2\gamma E r, r_c/r) ,$$
(2.11)

where[12]

$$\phi(2\gamma E r, r_c/r) = \exp(-r_c/r)$$
$$\times \left[1 + \exp(-2\gamma E r) \sum_{n=1}^\infty \frac{(2\gamma E r)^n}{(n+1)!} \sum_{j=0}^{n-1} (n-j) \frac{(r_c/r)^{j+1}}{(j+1)!}\right]$$
(2.12)

is the Onsager escape probability[13] for an electron located at a distance r from its parent cation. To represent $\sigma(r, \lambda)$, the functional forms

$$\sigma(r, b) = (4\pi b r^2)^{-1} \exp[-(r-a)/b] H(r-a) , \qquad (2.13)$$

$$\sigma(r, r_m) = (8 r_m^3)^{-1} \exp[-\pi r^2/4 r_m^2] , \qquad (2.14)$$

were both tried. In Eq. (2.13), a is the effective radius of M^+, and $H(r-a)$ is the Heaviside step function. The parameters b or r_m, as was the case, were adjusted in order to bring $P(0,E)/P(0,0)$ into equality with the experimental value of i/i^0. For Eq. (2.13), the results were found to be insensitive to the value of a. Moreover, since i/i^0 could be fit equally well with either Eqs. (2.13) or (2.14), it was clear that our experiments failed to probe enough of the high-field region to establish accurately the form of $\sigma(r)$.

B. Power series development of theoretical forms of $Q(0,E)$ and $Q(c_s,0)$

The theory of $Q(c_s, E)$ is best summarized in the work of Hong and Noolandi[14] and Friauf, Noolandi, and Hong.[15] In solving the Smoluchowski equation for $E \neq 0$ and $c_s \neq 0$, they find a representation for $Q(c_s, E)$ in terms of a doubly infinite series of Bessel function products. A few terms from this series applicable to special cases have been known previously.[12,16] When $c_s = 0$, the result is computed from Eqs. (2.11) and (2.12). This can be arranged into a series in powers of E, which when carried out to fourth order reads[21]

$$Q(0,E) = Q(0,0) - r_c \gamma P(0,0)E - \tfrac{2}{3}(\tfrac{1}{2} r_c^2 - r_c \langle r \rangle) \gamma^2 P(0,0)E^2$$
$$- \tfrac{1}{3}(\tfrac{1}{6} r_c^3 - r_c^2 \langle r \rangle + r_c \langle r^2 \rangle) \gamma^3 P(0,0)E^3$$
$$- \tfrac{4}{15}(\tfrac{1}{48} r_c^4 - \tfrac{1}{4} r_c^3 \langle r \rangle + \tfrac{3}{4} r_c^2 \langle r^2 \rangle - \tfrac{1}{2} r_c \langle r^3 \rangle) \gamma^4 P(0,0)E^4 .$$
$$(2.15)$$

In obtaining Eq. (2.15), we have used Eq. (2.7) and defined the moments $\langle r^n \rangle$ according to

$$\langle r^n \rangle = \frac{4\pi \int_0^\infty dr\, r^2 \sigma(r) \exp(-r_c/r) r^n}{4\pi \int_0^\infty dr\, r^2 \sigma(r) \exp(-r_c/r)}$$
$$= \frac{4\pi}{P(0,0)} \int_0^\infty dr\, r^2 \sigma(r) \exp\left(\frac{-r_c}{r}\right) r^n . \qquad (2.16)$$

On the other hand, when $E = 0$ the expansion in powers of $c_s^{1/2}$ is known[16,17]:

$$Q(c_s, 0) = Q(0,0) - (k_s r_c^2/D)^{1/2} P(0,0) c_s^{1/2}$$
$$+ (k_s r_c^2/D) \langle g(r) \rangle c_s \cdots , \qquad (2.17)$$

but only through c_s. Here $g(r)$ is a complicated function of r whose complete specification can be found in Refs. 8 and 16. Its mean value $\langle g(r) \rangle$ is defined by

$$\langle g(r) \rangle = \frac{4\pi \int_0^\infty dr\, r^2 \sigma(r) g(r)}{4\pi \int_0^\infty dr\, r^2 \sigma(r)} . \qquad (2.18)$$

In the general case where neither c_s nor E is zero, the only known terms are those shown in Eq. (2.2).

C. Derivation of semiempirical function

Because the range of our data permitted us to obtain only limited information concerning the form of $\sigma(r)$, we have chosen in this paper to avoid the numerical integration implicit in the evaluation of Eq. (2.11) and to fit our data instead to a semiempirical function of E. In constructing this function, we begin by noting the success of the empirical formula

$$G(P) = G_{fi} + G_{gi}(\alpha_s c_s)^{1/2}[1 + (\alpha_s c_s)^{1/2}]^{-1} , \qquad (2.19)$$

which has been used to represent the yield $G(P)$ of scavenged electrons observed in ^{60}CO γ radiolysis of liquid alkanes.[11] Here G_{fi} and G_{gi} are, respectively, the yield of free ions (dissociated electron-ion pairs) and geminate ions (recombined electron-ion pairs) observed in the absence of scavenger and with zero-applied electric field. The concentration scale factor α_s is determined by fitting $G(P)$ data to Eq. (2.19). In terms of G_{fi} and G_{gi}

$$P(0,0) = G_{fi}/G_t , \qquad (2.20)$$

$$Q(0,0) = G_{gi}/G_t , \qquad (2.21)$$

where

$$G_t = G_{fi} + G_{gi} . \qquad (2.22)$$

The geminate ion recombination probability $Q(C_s, 0)$ is

$$Q(c_s, 0) = 1 - G(P)/G_t . \qquad (2.23)$$

With these identifications, Eq. (2.19) can be rearranged to read

$$Q(c_s, 0) = Q(0,0)[1 + (\alpha_s c_s)^{1/2}]^{-1} . \qquad (2.24)$$

Now Eq. (2.24) applies empirically only when $E = 0$. To handle the case where neither c_s nor E is zero, we refer to Eq. (2.2). Because Eq. (2.2) depends upon c_s and E solely through the combination $(W^2 + V^2)^{1/2}$, we are motivated to replace $(\alpha_s c_s)^{1/2}$ in Eq. (2.24) by the product $\beta(W^2 + V^2)^{1/2}$ so that

$$Q(c_s, E) = Q(0,0)[1 + \beta(W^2 + V^2)^{1/2}]^{-1} , \qquad (2.25)$$

where β is a new (dimensionless) empirical parameter.

For $\beta(W^2 + V^2)^{1/2} < 1$, Eq. (2.25) has the power series expansion

$$Q(c_s, E) = Q(0,0) - Q(0,0)\beta(W^2 + V^2)^{1/2} + Q(0,0)\beta^2(W^2 + V^2)$$
$$- Q(0,0)\beta^3(W^2 + V^2)^{3/2} + Q(0,0)\beta^4(W^2 + V^2)^2 - \cdots .$$
$$(2.26)$$

Note that the coefficient of each power of $(W^2 + V^2)$ is just $-\beta$ times the coefficient of the previous power. In applying our semiempirical approach to the case $V = 0$, we are assuming that the form of $\sigma(r)$ is such that Eqs. (2.15) and (2.26) are identical term by term. We will have more to say about this in Sec. IV.

To make Eq. (2.26) consistent with the theoretically exact limiting form expressed in Eq. (2.2), we must have

$$\beta = P(0,0)/Q(0,0) , \qquad (2.27)$$

which suffices to give β a meaning in terms of quantities having a physical interpretation. Through Eqs. (2.7) and (2.11), $P(0,0)$ and $Q(0,0)$ depend upon the integral of $\sigma(r, \lambda)$. They will, consequently, be functions of the parameter λ, which in turn will depend upon the energy of the excitation and the nature of the solvent. Hence, in general we can expect β also to depend upon the excitation energy and the solvent.

To analyze our data, which were taken in the absence of added scavenger, we set $V = 0$ in Eq. (2.25) and substitute the result into Eq. (2.1) to obtain
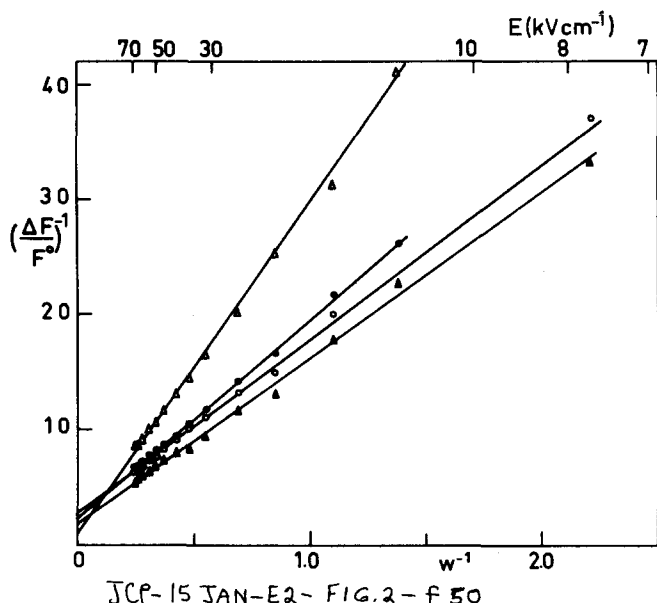
JCP- 15 JAN-E2- FIG.2- f 50

FIG. 2. Data plotted according to Eq. (3.1) for TMPD in tetra-
methylsilane. ($\bullet$) $h\nu_{ex} = 6.05$ eV, $I = 2.359$, $S = 17.17$, $\tilde{r} = 0.999$.
(o) $h\nu_{ex} = 5.90$ eV, $I = 2.810$, $S = 14.98$, $\tilde{r} = 0.999$. ($\blacktriangle$) $h\nu_{ex}$
$= 5.61$ eV, $I = 1.835$, $S = 14.40$, $\tilde{r} = 0.998$. ($\triangle$) $h\nu_{ex} = 5.39$ eV,
$I = 1.121$, $S = 28.62$, $\tilde{r} = 0.999$.

$$\frac{\Delta F}{F^0} = \frac{\Phi_{ip}Q(0,0)}{(1 - \Phi_{ip}) + \Phi_{ip}Q(0,0)} \left(\frac{\beta W}{1 + \beta W}\right) . \qquad (2.28)$$

Equation (2.28) is our semiempirical formula. For
$W \sim 0$, Eq. (2.28) is linear as is required by the data.
For $W \sim \infty$, Eq. (2.28) saturates as is logically required.

III. RESULTS

In order to make convenient use of Eq. (2.28), we
write it in the linear form

$$(\Delta F/F^0)^{-1} = I + SW^{-1} , \qquad (3.1)$$

with two adjustable parameters S and I. From the val-
ues of S and I, we may calculate β, $P(0,0)$, and Φ_{ip} ac-
cording to

$$\beta = I/S , \qquad (3.2)$$

$$P(0,0) = I/(I + S) , \qquad (3.3)$$

$$\Phi_{ip} = (I + S)/[I(S + 1)] , \qquad (3.4)$$

$$\Phi_e^0 = 1/(S + 1) . \qquad (3.5)$$

In accord with Eq. (3.1), we have plotted $(\Delta F/F^0)^{-1}$
as a function of W^{-1} using some fluorescence quenching
data obtain in $\sim 2 \times 10^{-5}$ M solutions of TMPD in tetra-
methylsilane and 2,2-dimethylbutane irradiated at 292
K with photons of various energies. Experimental de-
tails have been published previously.[4,5] The measure-
ments were carried out with fields in the 0 – 70 kV/cm
range. In Figs. 2 and 3, we show our results. As can
be seen, quite good straight lines with excellent corre-
lation coefficients $\tilde{r}$ were obtained in the $7 \lesssim E \lesssim 70$ kV/
cm range for tetramethylsilane solutions and in the 20
$\lesssim E \lesssim 70$ kV/cm range for 2,2-dimethylbutane. From the
least-squares determinations of I and S, the quantities

β, $P(0,0)$, and Φ_{ip} were calculated; the results are
shown in columns 3 and 5 of Table I and column 5 of
Table II. We estimate the fractional error to be 5% in
β, 2% in Φ_{ip}, and 5% in $P(0,0)$.

In column 10 of Table I, we have formed the ratio $G_{fi}/$
G_t for comparison with our calculation of $P(0,0)$. Al-
though in the ^{60}CO γ radiolysis, about 25 eV is expended
in producing an electron-ion pair, we find that G_{fi}/G_t
compares favorably with our values of $P(0,0)$ wherein
the pair is produced with 5 to 6 eV of energy. It would
appear from the general agreement that the ranges of
the electrons produced in the photoionizations and in the
radiolyses are not very different. This confirms what
has been previously found.[3,7]

In tetramethylsilane below 7 kV/cm and in 2,2-di-
methylbutane below 20 kV/cm, departures from Eq.
(3.1) were found. Typical examples are shown in Fig.
4. The behavior of the experimental data in Fig. 4 is
not totally unexpected when it is realized that at low
fields, a small concentration of scavenger may compete
with the electric field to prevent electron-ion recom-
bination fluorescence. Since we started these studies,
we have repeatedly observed a dramatic effect of minute
traces of impurities on $\Delta F/F^0$. In particular in the case of
2,2,4-trimethylpentane solvent, electron scavenging in
aerated solutions was demonstrated[5] and used to calcu-
late the rate constant for electron attachment to O_2.[9]
In general, the effect of electron attaching impuri-
ties is to reduce ΔF. This causes $(\Delta F/F^0)^{-1}$ to be
larger than predicted by Eq. (2.28) for electric
field quenching alone. Figure 4 shows that this is what
we have observed. Moreover, in experiments on a given
sample, we have noted a gradual decrease of $\Delta F/F^0$ with
time, indicating perhaps the slow dissolution of impuri-
ties absorbed on the walls of the cell.

Although we made measurements of recombination
fluorescence of TMPD dissolved in 2,2,4-trimethylpen-
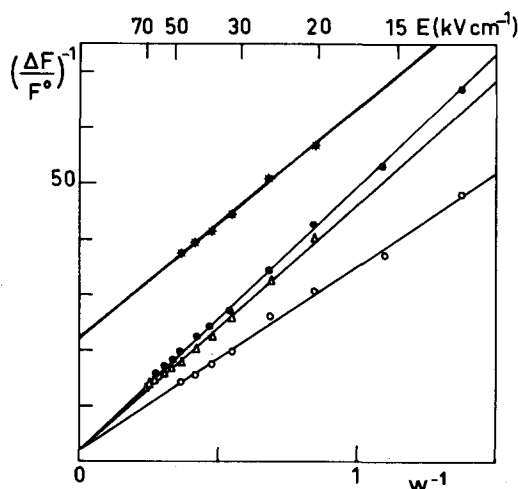
FIG. 3. Data plotted according to Eq. (3.1) for TMPD in 2,2-
dimethylbutane. (o) $h\nu_{ex} = 6.20$ eV, $I = 1.951$, $S = 33.24$, $\tilde{r}$
$= 0.997$. ($\triangle$) $h\nu_{ex} = 6.05$ eV, $I = 2.389$, $S = 43.67$, $\tilde{r} = 0.999$. ($\bullet$)
$h\nu_{ex} = 5.90$ eV, $I = 2.083$, $S = 47.42$, $\tilde{r} = 0.999$. (*) $h\nu_{ex} = 5.77$
eV, $I = 2.155$, $S = 40.67$, $\tilde{r} = 0.999$; for the sake of clarity the
line has been shifted by 20 units in $(\Delta F/F^0)^{-1}$ upwards.

TABLE I. Comparison of semiempirical, Onsager, and high-energy escape probabilities.

| Solvent | $h\nu_{ex}$ (eV) | Semiempirical | | | Onsager theory | | High energy data | | |
		β Eq. (3.2)	$\langle g(r) \rangle$ ($\times 10^3$)	$P(0,0)$ Eq. (3.3)	$P(0,0)$ (expt.)	$P(0,0)$ (Gauss)	G_{fi}	G_{gi}	G_{fi}/G_t
Tetramethylsilane	6.05	0.14	17	0.12	0.16	0.27			
	5.90	0.18	27	0.15	0.14	0.25			
	5.61	0.13	15	0.11	0.13	0.24	0.74[a]	3.6[b]	0.17
	5.39	0.073	5	0.068	0.14	0.24			
2,2-Dimethylbutane	6.20	0.059	3	0.056	0.049	0.13			
	6.05	0.055	3	0.052	0.057	0.14			
	5.90	0.053	3	0.051	0.043	0.12	0.304[a]	4.00[b]	0.071
	5.77	0.053	3	0.050	0.087	0.19			

[a]Reference 18.
[b]Assuming that G_t is close to 4.3 as suggested in Ref. 19.

tane, we could not achieve electric fields much beyond 30 kV/cm because of the electrical breakdown of the vapor phase above the liquid. Indeed, the achievable values of W were so low that the term βW in the denominator of Eq. (2.28) had no significance, so that β could not be determined from a plot of Eq. (3.1).

We have shown previously[6] how Eqs. (2.11)–(2.14) can be used to determine $P(0,0)$. Because of the two possible choices for $\sigma(r, \lambda)$ corresponding to Eqs. (2.13) and (2.14), respectively, two values, $P(0,0)$ (expt) and $P(0,0)$ (Gauss), were obtained. These are shown in columns 6 and 7 of Table I.

The free electron quantum yield Φ_e^0 is determined by plotting data according to Eq. (2.8). We have found this equation to be obeyed in all tested cases. Values of Φ_e^0 are tabulated in column 3 of Table II. When Φ_e^0 is combined with $P(0,0)$ (expt) and $P(0,0)$ (Gauss) according to Eq. (2.9), the associated quantum yields Φ_{ip} (expt) and Φ_{ip} (Gauss) may be calculated. A comparison of these values with Φ_{ip} computed from Eq. (3.4) is shown in Table II.

By use of Eq. (3.5), we can determine Φ_e^0 in a fashion entirely independent of the measurement of the photocurrent. The results are listed in column 4 of Table II. If our semiempirical formula were completely correct and/ or impurities did not intervene, columns 3 and 4 of Table II would be identical.

IV. DISCUSSION

In the work of Onsager,[13] which is summarized by Eqs. (2.7), (2.11), and (2.12), we have a formally complete theory of $Q(0,E)$. When $V = 0$, we note that the series form of the semiempirical formula given by Eq. (2.26) must be identical to the series representation of the Onsager theory given by Eq. (2.15). A term by term comparison of Eqs. (2.15) and (2.26) gives in zero order the identity $Q(0,0) = Q(0,0)$; in first order, $\beta = P(0,0)/Q(0,0)$, which is the condition expressed by Eq. (2.27); and in second, third, and fourth orders, the equations

$$\langle r \rangle = \tfrac{1}{2}(1 + 3\beta) r_c , \tag{4.1}$$

$$\langle r^2 \rangle = 3(\tfrac{1}{9} + \tfrac{1}{2}\beta + \beta^2) r_c^2 , \tag{4.2}$$

$$\langle r^3 \rangle = \tfrac{1}{2}(\tfrac{7}{12} + 3\beta + 9\beta^2 + 15\beta^3) r_c^3 , \tag{4.3}$$

respectively. As previously noted, each coefficient in the series given by Eq. (2.26) is just $-\beta$ times the coefficient of the previous term. This fact has led us to the special relations satisfied by the moments $\langle r^n \rangle$ expressed by Eqs. (4.1)–(4.3).

We may summarize as follows: In our previous work,[6] we calculated $Q(0,E)$ by choosing a form for $\sigma(r)$. In our present work, we have assumed a closed form for $Q(0,E)$ and computed the moments $\langle r^n \rangle$. Should the data conform for all values of E to our choice of $Q(0,E)$, we could use the moments to work back to a unique determination of $\sigma(r)$.

TABLE II. Comparison of semiempirical and Onsager quantum yields.

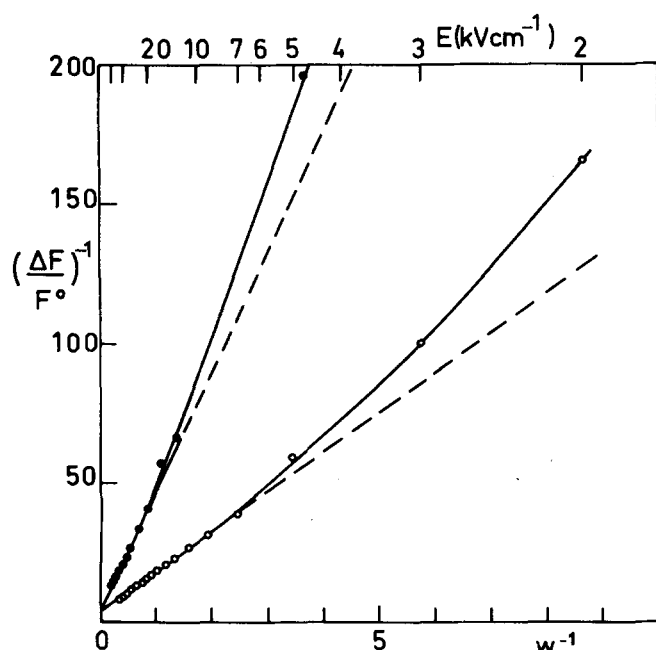| Solvent | $h\nu_{ex}$ (eV) | Φ_e^0 Eq. (2.8) | Semiempirical | | Onsager theory | |
			Φ_e^0 Eq. (3.5)	Φ_{ip} Eq. (3.4)	Φ_{ip} (expt)	Φ_{ip} (Gauss)
Tetramethylsilane	6.05	0.077	0.056	0.46	0.50	0.28
	5.90	0.075	0.062	0.41	0.53	0.30
	5.61	0.081	0.064	0.57	0.65	0.35
	5.39	0.055	0.036	0.53	0.40	0.23
2,2-Dimethylbutane	6.20	0.039	0.030	0.53	0.35	0.18
	6.05	0.030	0.024	0.43	0.46	0.19
	5.90	0.023	0.021	0.41	0.52	0.19
	5.77	0.030	0.024	0.47	0.34	0.16

FIG. 4. Deviations from Eq. (3.1). (●) TMPD in 2,2-di-methylbutane, $h\nu_{ex} = 6.05$ eV. (○) TMPD in tetramethylsilane, $h\nu_{ex} = 5.90$ eV.

Since we determined β by our experiments, we used Eqs. (4.1)–(4.3) to compute moments through $\langle r^3 \rangle$. The results are summarized in Tables III and IV. For comparison, we have included moments calculated from Eq. (2.16) and the previously assumed forms for $\sigma(r)$ expressed by Eqs. (2.13) and (2.14), respectively. The escape probabilities $P(0,0)$, $P(0,0)$ (expt), and $P(0,0)$ (Gauss) given in columns 5, 6, and 7, respectively, of Table I function as estimates of the zeroth moment $\langle r^0 \rangle$. It is apparent that the moments calculated semiempirically favor neither the exponential nor the Gaussian form of $\sigma(r)$.

TABLE III. Moments for tetramethylsilane from Eqs. (4.1)–(4.3). All lengths are in units of r_c, which for TMSI at 292 K is 296 Å. At 6.05 eV, parameters for the exponential representation of $\sigma(r,\lambda)$ were $a = 5$ Å, $b = 159.3$ Å, and, for the Gaussian representation, $r_m = 185.2$ Å. At 5.90 eV, $a = 5$ Å, $b = 158.6$ Å, $r_m = 172.3$ Å. At 5.61 eV, $a = 5$ Å, $b = 141.8$ Å, $r_m = 168.2$ Å. At 5.39 eV, $a = 5$ Å, $b = 153$ Å, $r_m = 170.5$ Å.

$h\nu_{ex}$ (eV)	Moment	Semiempirical Eqs. (4.1)–(4.3)	Onsager theory (expt)	(Gauss)
	$\langle r \rangle$	0.707	1.166	0.908
6.05	$\langle r^2 \rangle$	0.597	1.793	0.889
	$\langle r^3 \rangle$	0.604	3.494	0.923
	$\langle r \rangle$	0.768	1.163	0.851
5.90	$\langle r^2 \rangle$	0.698	1.781	0.780
	$\langle r^3 \rangle$	0.747	3.459	0.760
	$\langle r \rangle$	0.692	1.075	0.834
5.61	$\langle r^2 \rangle$	0.574	1.505	0.747
	$\langle r^3 \rangle$	0.573	2.660	0.709
	$\langle r \rangle$	0.609	1.136	0.844
5.39	$\langle r^2 \rangle$	0.459	1.689	0.766
	$\langle r^3 \rangle$	0.428	3.179	0.736

TABLE IV. Moments for 2,2-dimethylbutane computed from Eqs. (4.1)–(4.3). At 292 K, $r_c = 295$ Å. At 6.20 eV, $a = 5$ Å, $b = 70.3$ Å, $r_m = 110.9$ Å. At 6.05 eV, $a = 5$ Å, $b = 76$ Å, $r_m = 114$ Å. At 5.90 eV, $a = 5$ Å, $b = 66$ Å, $r_m = 106$ Å. At 5.77 eV, $a = 5$ Å, $b = 101$ Å, $r_m = 140$ Å.

$h\nu_{ex}$ (eV)	Moment	Semiempirical Eqs. (4.1)–(4.3)	Onsager theory (expt)	(Gauss)
	$\langle r \rangle$	0.588	0.675	0.580
6.20	$\langle r^2 \rangle$	0.432	0.556	0.356
	$\langle r^3 \rangle$	0.397	0.549	0.229
	$\langle r \rangle$	0.582	0.708	0.593
6.05	$\langle r^2 \rangle$	0.425	0.619	0.373
	$\langle r^3 \rangle$	0.389	0.650	0.247
	$\langle r \rangle$	0.579	0.647	0.556
5.90	$\langle r^2 \rangle$	0.421	0.510	0.329
	$\langle r^3 \rangle$	0.385	0.479	0.203
	$\langle r \rangle$	0.579	0.854	0.708
5.77	$\langle r^2 \rangle$	0.421	0.923	0.538
	$\langle r^3 \rangle$	0.385	1.223	0.428

It is also of interest to discuss Eq. (2.25) for the case $W = 0$. A series expansion for the semiempirical formula is obtained for this case from Eq. (2.26). The relevant theoretical expansion is given by Eq. (2.17). A term by term comparison leads in zeroth order to the identity $Q(0,0) = Q(0,0)$; in first order to $\beta = P(0,0)/Q(0,0)$; and in second order to

$$\langle g(r) \rangle = \beta^2 Q(0,0) = I^2/[S(I+S)] \ , \qquad (4.4)$$

where we have used Eqs. (2.7), (3.2), and (3.3) to express $\langle g(r) \rangle$ in terms of S and I. The results obtained for $\langle g(r) \rangle$ are summarized in column 4 of Table I. Because the range of $g(r)$ has both positive and negative regions,[16] we cannot determine the sign of $\langle g(r) \rangle$ from Eq. (2.16) without a priori knowledge of $\sigma(r)$. Analysis[17] of the ^{60}CO γ radiolysis scavenger data, however, indicates that $\langle g(r) \rangle$ should be positive, which is in agreement with Eq. (4.4) and Table I.

It has been our presumption from the start that $Q(c_s, E)$ is de facto a function of only the one variable $W^2 + V^2$. We can examine this hypothesis by following Friauf, Noolandi, and Hong.[15] We write[22]

$$Q(c_s, E) = 4\pi \int_0^\infty dr\, r^2 \sigma(r)\, \tilde{R}(r, W, V) \ , \qquad (4.5)$$

where

$$\tilde{R}(r, W, V) = \frac{4}{r} \sum_{l=0}^\infty \{a_{l0}^2(W)/N_l\, [W, (W^2+V^2)^{1/2}]\}$$

$$\times y_{1l}(r, W)\, y_{2l}\, [r, W, (W^2+V^2)^{1/2}] \ . \qquad (4.6)$$

The notation in Eq. (4.6) summarizes an elaborate analytic structure. Hong and Noolandi[14] give expressions for the functions y_{1l} and y_{2l}, which are doubly infinite series of Bessel function products. The Wronskian N_l is calculated from y_{1l} and y_{2l}, while the coefficients a_{l0} are determined from a three-term recursion relation. Nonetheless, a careful study in Ref. 14 of Eq. (2.21), Eqs. (2.23)–(2.27), and Eq. (A4) reveals the separate dependence upon W and $(W^2 + V^2)$ indicated above. The

fact is, however, that W enters through the combination $(W^2 + V^2)^{1/2}$ wherever V occurs. To this extent, the electric field and the scavenger must give similar information about the nature of the distribution $\sigma(r)$. This is the basis for the success we have achieved in starting our analysis from Eq. (2.19). The additional dependence upon W indicated by Eq. (4.6) suggests an interesting comparison of experiments. If it were not for this dependence, $G(P)/G_{fi}$ and i/i^0 would be the same when $W = V$. The difference between $G(P)/G_{fi}$ and i/i^0 is thus sensitive to the separate dependence upon W indicated in Eq. (4.6). *The maximum value of W in our experiments was* 4.3. Inasmuch as the scavenger experiments achieve larger values of V than this, it is clearly of interest to attempt to increase W, so that when $W = V$ the difference between $G(P)/G_{fi}$ and i/i^0 is accentuated.

We conclude that the introduction of our semiempirical formula has done two things. First, it has permitted the rapid graphical reduction of fluorescence data without recourse to statistical techniques more complex than linear regression. Second, it has suggested the hypothesis that the electric field and scavenger experiments test the distribution $\sigma(r)$ in similar ways and has indicated a procedure for assessing the difference.

ACKNOWLEDGMENT

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[21]We have corrected a sign error in the term in E^4 which appears in Eq. (7) of Ref. 12.

[22]Friauf, Noolandi, and Hong (see Refs. 14 and 15) take lengths to have the units of $r_c/2$. Hence, r in Eqs. (4.5) and (4.6) is a dimensionless variable.