

## Rate of electron capture by O<sub>2</sub> calculated from geminate ion recombination fluorescence data

James K. Baird

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in the number of extrema is observed. We should also note that these finite element wave functions produce transition probabilities of comparable accuracy to close coupling results.<sup>2,3</sup> The latter calculations required 11 to 16 basis functions at 1.5 eV. It may be argued that fewer basis functions could be used since the wave function is not very oscillatory in the reaction region. However, this would result in less accurate transition probabilities. The basis functions clearly have many more extrema than actually found in the global wave function [c.f., Figs. 1(c) and 2(c)], and yet the smooth behavior of the wave function in this region makes it ideally suited to a polynomial local finite element representation.

Consideration of the figures strongly suggests that an optimum computational procedure can be developed by judiciously combining the finite element and close coupling methods. To understand this point, note that the strong interaction region is fairly localized near the reflection plane. The onset of a regular pattern in Figs. 1(b) and 2(b) indicates a weak coupling regime. The regularity of alternating + and - wave functions is apparent in Fig. 1(b), where the line labeled II is a center of symmetry for regions I-III. Similar behavior is also found in Fig. 2(b) in spite of its more complicated structure. In this outer region the number of coupled channels can be systematically reduced to ul-

timately just open channels. On the other hand, the computational effort for the finite element method is approximately independent of the region involved. Therefore, close coupling becomes increasingly efficient upon leaving the strong coupling regime. The natural conclusion from these observations is that perhaps the optimal scheme should consist of joining the finite element method in the strong interaction region with the close coupling method in the outer region.

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<sup>b)</sup>Permanent address: Bogazici University, Mathematics Department, Bebek, Istanbul, Turkey.

<sup>c)</sup>Alfred P. Sloan Fellow; Camille and Henry Dreyfus Teacher-Scholar.

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## Rate of electron capture by O<sub>2</sub> calculated from geminate ion recombination fluorescence data<sup>a)</sup>

James K. Baird<sup>b)</sup>

Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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Bullot, Cordier and Gauthier observed geminate ion recombination fluorescence when they irradiated with 5.9 eV photons a solution of *N,N,N',N'*-tetramethylparaphenylenediamine (TMPD) in 2,2,4-trimethylpentane (TMP).<sup>1</sup> They found that the fluorescence  $F(E)$  in the presence of an applied electric field  $E$  was weaker than the fluorescence  $F(0)$  in the absence of the field. They noted that according to the Onsager theory<sup>2</sup> of geminate ion recombination, a plot of  $[F(0) - F(E)]/F(0)$  vs  $E$  for small enough  $E$  should be a straight line starting from the origin. Their low field data, however, was not linear at all, but rather approached the origin in a roughly parabolic fashion. This caused their intermediate field data, which was linear in  $E$ , to extrapolate to the origin with a negative intercept. They noted that the magnitude of the intercept could be reduced by de-aerating their solutions. They suggested that in the aerated solutions the observed departure from the Onsager theory was due to electron capture by dissolved oxygen. We will show that their observations are in accord with Tachiya's form<sup>3a)</sup> of the Mozumder limiting

law<sup>3(b)</sup> for geminate ion scavenging in the presence of a uniform external electric field. We will derive therefrom the rate constant for electron capture by O<sub>2</sub>.

A slightly extended form of the photoionization/fluorescence scheme suggested by Bullot *et al.*<sup>1</sup> is shown in Fig. 1. The excitation and fluorescence quanta are  $h\nu_{ex}$  and  $h\nu_{fl}$ , respectively. A molecule of TMPD in an excited state leading to ionization is  $M^{**}$ . The first

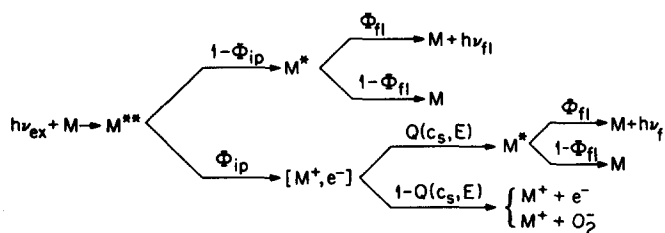


FIG. 1. Photionization/fluorescence scheme.

excited singlet state is  $M^*$ , while the geminate ion pair is represented by  $[M^*, e^-]$ .<sup>12</sup> The quantum yields for ion pair formation and for fluorescence are  $\Phi_{ip}$  and  $\Phi_{fl}$ , respectively. The probability of geminate recombination in the presence of an electric field and oxygen concentration  $c_s$  is  $Q(c_s, E)$ . Analysis of the scheme shows that  $F(E) \sim (1 - \Phi_{ip})\Phi_{fl} + \Phi_{ip}Q(c_s, E)\Phi_{fl}$ . Tachiya's limiting law<sup>3(a),13</sup> for  $Q(c_s, E)$  can be written

$$Q(c_s, E) = Q(0, 0) - r_c P(0, 0) [(e/2k_B T)^2 E^2 + (e/\mu k_B T) k_s c_s]^{1/2}, \quad (1)$$

where  $P(0, 0) = 1 - Q(0, 0)$ ,  $r_c$  is the Onsager length,  $e$  the magnitude of the electron charge,  $k_B$  Boltzmann's constant,  $T$  the absolute temperature,  $\mu$  the electron mobility, and  $k_s$  is the rate constant for electron capture by  $O_2$ . The ratio  $[F(0) - F(E)]/F(0)$  is hence

$$\frac{F(0) - F(E)}{F(0)} = \frac{\Phi_{ip} r_c P(0, 0) \{[(e/2k_B T)^2 E^2 + (e/\mu k_B T) k_s c_s]^{1/2} - (e/\mu k_B T)^{1/2} (k_s c_s)^{1/2}\}}{1 - \Phi_{ip} P(0, 0) [1 + r_c (k_B T/e\mu)^{1/2} (k_s c_s)^{1/2}]}. \quad (2)$$

For  $(e/2k_B T)^2 E^2 \ll (e/\mu k_B T) k_s c_s$ , the leading term of a binomial expansion of Eq. (2) is quadratic in  $E$ . For  $(e/2k_B T)^2 E^2 \gg (e/\mu k_B T) k_s c_s$ , Eq. (2) is of the form  $[F(0) - F(E)]/F(0) = aE - b$ . From the ratio of intercept to slope, we find the simple relation

$$k_s c_s = \frac{1}{4} \left( \frac{b}{a} \right)^2 \frac{\mu}{(k_B T/e)}. \quad (3)$$

Equation (3) may be used to compute  $k_s$  as follows: From Fig. 1 of Ref. 1, we find that  $a = 8.2 \times 10^{-7}$  cm V<sup>-1</sup> and  $b = 2.8 \times 10^{-3}$  at  $T = 292$  K. Allen, Gangwer, and Holroyd<sup>4</sup> report  $\mu = 40.8 \exp(-585/T)$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, from which we compute  $\mu = 5.5$  cm<sup>2</sup> V<sup>-1</sup> sec<sup>-1</sup>. The mole fraction  $X$  of  $O_2$  dissolved in TMP is given by Henry's law  $X = p/K$ . Kobatake and Hildebrand<sup>5</sup> report  $K^{-1} = 2.853 \times 10^{-3}$  atm.<sup>-1</sup> The partial pressure of  $O_2$  is  $p = 0.21$  atm. Noting that the solution is dilute and using the density and molecular weight of TMP, we compute  $c_s = 3.6 \times 10^{-3}$  M. With this data, we find from Eq. (3)  $k_s = 1.8 \times 10^{11}$  M<sup>-1</sup> sec<sup>-1</sup>. For comparison, the results of pulse radiolytic conductance experiments give for  $k_s$  the values  $0.42 \times 10^{11}$  M<sup>-1</sup> s<sup>-1</sup> reported by Lukin and Yakovlev,<sup>6</sup>  $2.7 \times 10^{11}$  M<sup>-1</sup> s<sup>-1</sup> reported by Baxendale *et al.*,<sup>7</sup> and  $1.4 \times 10^{11}$  M<sup>-1</sup> s<sup>-1</sup> reported by Holroyd and Gangwer.<sup>8</sup> Our result should be regarded as being in good agreement with the latter two.

It is tacitly assumed in using the photoionization/fluorescence scheme of Fig. 1 that an electron, which reacts with a molecule of  $O_2$ , is no longer able to produce fluorescence when it ultimately recombines with  $M^*$ . This assumption seems to be justified by the degree of agreement of Eq. (2) with experiment.

Finally, we note that the limiting law has been applied with similar success to the problem of scavenging of geminate ions produced in liquids by <sup>60</sup>Co radiolyses.<sup>9,10,11</sup>

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- <sup>b</sup>Also adjunct member of the faculty of the Department of Physics, University of Kansas, Lawrence, Kansas 66045.  
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<sup>13</sup>The physical model underlying the calculation of  $Q(c_s, E)$  is the Brownian motion of  $[M^*, e^-]$  in the presence of scavenger and a uniform external electric field (see Ref. 3). The Brownian motion is governed by the Smoluchowski equation. By using the method of "prescribed diffusion," Mozumder was the first to find an approximate solution to this problem [Ref. 3(b)]. From Eq. (9b) of Ref. 3(b), we find that

$$Q(c_s, E) = Q(0, 0) - r_c P(0, 0) \gamma(E) \times \{[(e/2k_B T)^2 E^2 + (e/\mu k_B T) k_s c_s]^{1/2} - (e/2k_B T) E\},$$

where  $\gamma(E)$  is a function defined on p. 782 of Ref. 3(b). This equation is to be contrasted with Eq. (1) above, which was obtained by Tachiya from the Smoluchowski equation through use of a perturbation method [Ref. 3(a)]. An exact solution of the Smoluchowski equation expressed in terms of an infinite series of Bessel function products has been derived by Hong and Noolandi (Ref. 14). Certain asymptotic results are obtainable in closed form from this series. Among these is Eq. (1) above, which may be derived by combining Eqs. (5.13), (5.16), and (B18) of Ref. 14 with the specialization that the radius,  $a$  of  $M^*$  is zero.

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