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G. Ascarelli

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*J. Chem. Phys.* **84**, 3199 (1986); 10.1063/1.450249

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# Electric field dependence of the capture rate constant of electrons by SF<sub>6</sub> and O<sub>2</sub> dissolved in either liquid Ar or Xe<sup>a)</sup>

G. Ascarelli

Department of Physics, Purdue University, West Lafayette, Indiana 47907  
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Bakale *et al.*<sup>1</sup> measured the capture rate  $k$  of electrons by SF<sub>6</sub> and O<sub>2</sub> in liquid Ar and Xe near the triple point. They interpreted the dependence of  $k$  on the electric field  $F$  using hot electrons. We will show that this is unnecessary.

The kinetics for the capture of an electron by an impurity is determined by the trapping in its excited state.<sup>2-4</sup> This should be valid<sup>1</sup> for electrons captured by O<sub>2</sub> or SF<sub>6</sub> dissolved in Ar or Xe. This state will have a binding energy  $\epsilon$ , a probability of capturing an electron per unit time  $\alpha$ , that of re-emission into the conduction band  $\beta$ , and that of making a transition to the ground state  $\gamma$ . Call  $N$  the impurity density,  $n_1$  the density of electrons in the conduction band,  $n_2$  those in the excited state, and  $n_3$  those in the ground state.

We can then write

$$\begin{aligned}\frac{dn_1}{dt} &= -\alpha N n_1 + \beta n_2, & \frac{dn_2}{dt} &= \alpha N n_1 - (\beta + \gamma) n_2, \\ \frac{dn_3}{dt} &= \gamma n_2.\end{aligned}\quad (1)$$

These equations have a solution  $n_1 = n_1^0 \exp -kt$ , where

$$k = \frac{1}{2}(\alpha N + \beta + \gamma) \left\{ 1 \pm \left[ 1 - 4 \frac{\alpha N \gamma}{(\alpha N + \beta + \gamma)^2} \right]^{1/2} \right\}. \quad (2)$$

Since we know that when  $\alpha \rightarrow 0$ ,  $k \rightarrow 0$ , the minus sign is chosen. Expanding the radical, we write

$$k = \alpha N \gamma / (\alpha N + \beta + \gamma).$$

For a Maxwellian electron distribution, we have<sup>2,5</sup>

$$\beta / \alpha = (2\pi m_0 m^* k_B T / h^2)^{3/2} \exp - \epsilon(F) / k_B T.$$

When the electron is bound in a hydrogenic orbit, the Schrödinger equation can be separated in parabolic coordinates  $(\eta, \xi)$  and the quantity (in atomic units)<sup>6,7</sup>  $\phi(\eta) = -(E/2) + (\rho_1/\eta K) - (m^2 - 1)/4m^* \eta^2 + (F\eta/4)$  plays the role

role of the potential.<sup>7</sup> Here  $m^*$ ,  $K$ ,  $m$ , and  $\rho_1$ , are, respectively, the electron effective mass in units of  $m_0$ , the relative dielectric constant, the azimuthal quantum number, and one of the parabolic quantum numbers. The extremum of  $\phi(\eta)$  is at  $\eta_m$ . Because large  $\eta$  are important, the third term in  $\phi(\eta)$  is neglected. The binding energy is  $\epsilon = E/2 - 2(\rho_1 F/K)^{1/2}$ , and

$$\begin{aligned}\frac{1}{k} &= \left( \frac{1}{\gamma} + \frac{1}{\alpha N} \right) + \left[ \frac{1}{N\gamma} \left( \frac{2\pi m_0 m^* k_B T}{h^2} \right)^{3/2} \exp \left( - \frac{E}{2k_B T} \right) \right] \\ &\times \exp \frac{2}{k_B T} \sqrt{\frac{\rho_1 F}{K}} = B + A \exp c \sqrt{F}.\end{aligned}$$

A least squares analysis determines  $A$ ,  $B$ , and  $c$ . We find  $B < 0$ , and we assign this artifact to the approximation done in going from Eq. (3) to Eq. (3a) in Reference 1. The values of  $c$  are compared with the H atom theory in Table I. When  $n = 2$ , the possible values of  $\rho_1$  are<sup>7</sup>  $\frac{3}{4}$ ,  $\frac{1}{2}$ , and  $\frac{1}{4}$ , for states that transform as  $(S - z)$ ,  $x$  or  $y$ , and  $(S + z)$ , respectively. For a quantum number  $n$ ,  $\rho_1$  varies between  $(n - 1)/2n$  and  $1/2n$ .

No model for the excited states of SF<sub>6</sub><sup>-</sup> and O<sub>2</sub><sup>-</sup> in Ar or Xe exists. In the gas the electron affinity of O<sub>2</sub> is<sup>9</sup>  $\sim 0.45$  eV. There are no known excited states. That of SF<sub>6</sub> is between<sup>10</sup> 1.1 and 1.5 eV.

In SF<sub>6</sub><sup>-</sup> the electron can only be bound if it approaches the six F nuclei. When  $K$  increases, the extra electron density near the F decreases and  $c$  decreases more rapidly than as  $K^{-1/2}$ . The charge density in O<sub>2</sub><sup>-</sup> ground state is rather localized between the atoms<sup>11,12</sup> and the extra electron that approaches an O sees an effective charge  $> e$ ; accordingly,  $c$  is larger than for H. Excited states of O<sub>2</sub><sup>-</sup> in Ar or Xe should have a similar behavior; this is necessary to explain the observed values of  $c$ .

We have shown that the electric field dependence of the capture of electrons by SF<sub>6</sub> or O<sub>2</sub> in Ar and Xe is explained without reference to hot electrons. The line

TABLE I. Comparison of the experimental and the calculated values of the coefficient  $c$  multiplying  $\sqrt{F}$ . The theoretical values are calculated for a hydrogenic state with either principal quantum number 2 or larger, whose symmetry is given in the rightmost column.  $K$  is calculated from the polarizability<sup>8</sup> using the Clausius-Mosotti equation.

Solvent	Dopant	$c_{\text{exp}}$	$c_{\text{th}} (n = 2)$	$c_{\text{th}} (n \text{ large})$	Symmetry
Ar	SF <sub>6</sub>	$3.65 \times 10^{-3} \pm 1 \times 10^{-4}$	$4.06 \times 10^{-3}$	$8.12 \times 10^{-3}/n$	$(S + z)$
			$5.74 \times 10^{-3}$		$x, y$
	O <sub>2</sub>	$1.74 \times 10^{-2} \pm 1 \times 10^{-3}$	$7 \times 10^{-3}$	$8.12 \times 10^{-3}$	$(S - z)$
Xe	SF <sub>6</sub>	$1.07 \times 10^{-4} \pm 1 \times 10^{-5}$	$1.58 \times 10^{-3}$	$3.16 \times 10^{-3}/n$	$(S + z)$
			$2.23 \times 10^{-3}$		$x, y$
	O <sub>2</sub>	$8.15 \times 10^{-3} \pm 1 \times 10^{-4}$	$2.74 \times 10^{-3}$	$3.16 \times 10^{-3}$	$(S - z)$

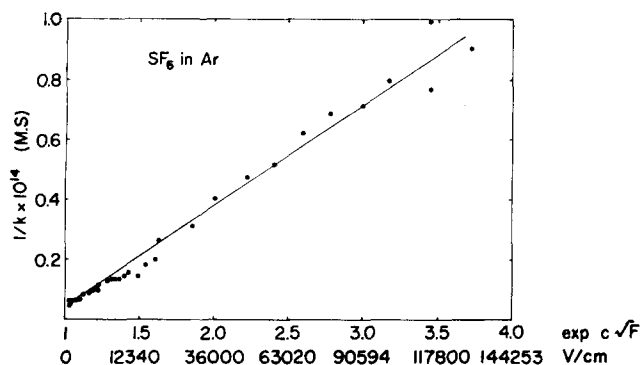


FIG. 1. Experimental dependence of the inverse of the trapping rate constant of electrons by  $\text{SF}_6$  in Ar as a function of  $\exp c \sqrt{F}$ . The value of  $c$  is given in Table I.

in Fig. 1 is very sensitive to the parameter  $c$  whose value agrees embarrassingly well with what is expected from a theory of the Schottky ionization of an excited state of an H like impurity.

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## ERRATA

### Erratum: Dynamics of fluctuations and spinodal decomposition in polymer blends [*J. Chem. Phys.* **72**, 4756 (1980)]

P. G. de Gennes

Collège de France, 75231 Paris Cedex 05, France

The structure of the mobility coefficient  $\Lambda(q)$  described in this paper is wrong at large wave vectors  $q$ . A direct calculation of the coherent scattering function  $S_q(t)$  (for one labeled chain in a homopolymer melt) shows that (for  $qR_0 > 1$ )  $S_q(t)$  splits into *two* parts: one associated with the local distribution of kinks (fast relaxation) and one associated with the overall drift of the chain in its tube (slow relaxation). In the paper a single relaxation time was introduced, while two times are required in reality. The corrected  $S_q(t)$  is analyzed in a paper submitted to *Journal de Physique* (Paris).