Negative ion photodetachment and the electron effective mass in liquids

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The electron photodetachment cross section for a negative ion in the gas phase is compared with the photodetachment cross section for the same ion when it is dissolved in a liquid supporting "free" electron propagation. The ratio of the amplitudes of these two cross sections near threshold is found to depend upon the effective mass m^* of an electron in the conduction band of the liquid. We apply this result to electron photodetachment from O_2^-. In terms of the electron's free mass m, we find for liquid argon at 87 K ($m^* = 0.26$ m), 2,2-dimethylbutane at 296 K ($m^* = 0.27$ m), 2,2,4-trimethylpentane at 296 K ($m^* = 0.27$ m), and tetramethylsilane at 296 K ($m^* = 0.27$ m). At 200 K, the effective mass in tetramethylsilane decreases to $m^* = 0.21$ m. In the case of liquid argon, the effective mass calculated herein agrees qualitatively with values which can be estimated from measurements of the electron mobility and exciton spectrum.

I. INTRODUCTION

Cross section data for the process $h\nu + A^- \rightarrow A + e^-$ for many molecular negative ions A^- in the gas phase has been rapidly accumulating in recent years.[1] The dependence of the cross section $\sigma(G)$ on photon energy E near the gas phase electron photodetachment threshold $E(G)$ has been shown to have its origin in the spatial symmetry of the highest occupied molecular orbital (HOMO) of the ion.[2,3] For the case where A^- is O_2^-, for example, $\sigma(G)$ is known to vary near threshold as

$$\sigma(G) = B(G)E[E - E(G)]^{3/2} , \tag{I.1}$$

where $B(G)$ is a constant.[4] The exponent on the factor $E - E(G)$ depends in general upon the symmetry of the HOMO and is in this case consistent with a Π_g state for O_2^-.[2]

Recent photoconductivity experiments have demonstrated that the photodetachment reaction can also be observed when A^- is in solution.[5-7] Figure 1 shows an energy level diagram for O_2^- dissolved in a liquid whose bulk electron affinity, symbolized by $-V_0$, is positive. The dissolved negative ion forms an electron trap, which lies at an energy $E(L)$ below the bottom of the conduction band of the liquid. The figure indicates the relationship of $E(L)$ to $-V_0$ and to E_g, the band gap of the liquid. Some liquids with positive bulk electron affinities are argon, tetramethylsilane, 2,2-dimethylbutane, and 2,2,4-trimethylpentane.

When O_2^- is dissolved in any of these four liquids, the electron photodetachment cross section has been observed to exhibit the threshold behavior

$$\sigma(L) = B(L)E[E - E(L)]^{3/2} \tag{I.2}$$

which is the analog of Eq. (I.1).[6] The liquid phase threshold $E(L)$ is blue shifted with respect to $E(G)$ by the amount $E(L) - E(G) = V_0 - P_-$, where P_- is the solvation

energy of O_2^-.[5,6] Because of this result and the close similarity between Eqs. (I.1) and (I.2), the only remaining major question is the relationship between $B(L)$ and $B(G)$.

It is the intent of this paper to derive an expression for the ratio $B(L)/B(G)$. Our principal assumption will be that the final state of the photodetached electron lies in the conduction band of the liquid where the density of states can be calculated in the free electron approximation using an effective mass m^*. This is not an unreasonable assumption, since for the liquids we shall consider the electron mobilities are high (>5 cm^2 V^{-1} s^{-1}), and their relative temperature independence indicates an absence of traps. This is evidence for a more or less
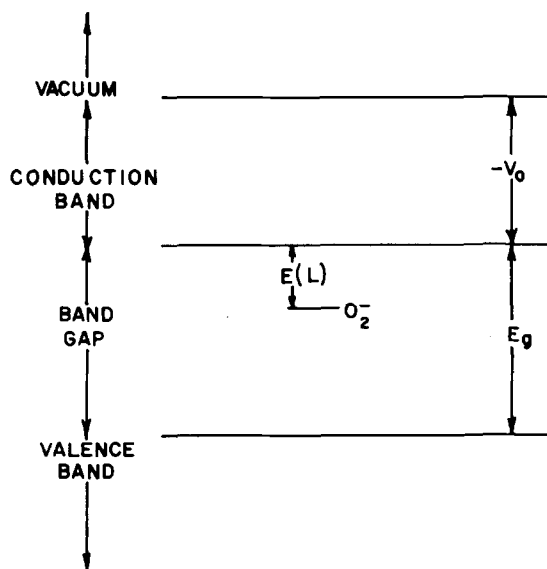
FIG. 1. Schematic energy level diagram for a liquid containing dissolved O_2^-. The valence band of the liquid is separated from the conduction band by the band gap energy E_g, while the conduction band is separated from the vacuum by the liquid electron affinity $-V_0$. The state of O_2^- is separated from the conduction band by the threshold energy $E(L)$. The drawing is not to scale.

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TABLE I. Electron effective mass in various liquids. Values of T, ϵ, and $B(L)$ taken from Ref. 6.

Liquid	$T(°K)$	ϵ	$B(L)$ $(10^{-19}$ cm^2 $eV^{-5/2})$	m^*/m
Argon	87	1.516	1.07	0.26
2,2-Dimethylbutane	297	1.777	1.17	0.27
2,2,4-Trimethylpentane	296	1.936	1.24	0.27
Tetramethylsilane	296	1.84	1.17	0.27
Tetramethylsilane	200	2.04	0.68	0.21

unhindered electron propagation through the conduction band. We will use our result for $B(L)/B(G)$ to calculate m^* for four different liquids.

II. THEORY

In the Appendix, we derive the equation

$$\sigma = \frac{8e^2}{3\hbar^2 c} \left(\frac{F_0^2}{nE_0^2}\right) m^* \nu \kappa \int d\Omega_\kappa \left| \int d^3r\, \psi(\mathbf{r})\, \mathbf{r}\, \exp(-i\mathbf{\kappa} \cdot \mathbf{r}) \right|^2 \quad \text{(II.1)}$$

for the condensed phase cross section. Here c is the speed of light in vacuum, e is the electron charge, $\hbar$ is Planck's constant divided by 2π, F_0 is the local electric field of the light, E_0 is the Maxwell field, n is the refractive index of the medium, m^* is the electron effective mass, ν is the frequency of the light, $\psi(\mathbf{r})$ is the wave function of the electron in the HOMO of the negative ion, $\mathbf{r}$ is the electron coordinate, κ is the wave number of the electron in the conduction band of the medium, and $d\Omega_\kappa$ is the differential solid angle associated with κ.

An evaluation of Eq. (II.1) in absolute terms requires a scrupulously accurate representation of the wave function $\psi(\mathbf{r})$. Fortunately, such an evaluation is unnecessary here, since we are interested only in finding a scale factor. We may, therefore, exclude from consideration all quantities unaffected by the presence of the liquid. We consequently confine our attention to the local electric field, and to the electron effective mass and wave number.

For the local electric field, we take the Lorentz expression[8]

$$F_0 = \left(\frac{n^2 + 2}{3}\right) E_0 . \quad \text{(II.2)}$$

From Eq. (II.2) can be derived the Lorentz–Lorenz equation for the density dependence of the refractive index, which has been shown to be in good agreement with optical data for the liquids which we shall consider.[9]

In Eq. (II.1), the factors following m^* depend upon the electron wave number. It has been shown[2,3] that in the limit of small κ,

$$\nu \kappa \int d\Omega_\kappa \left| \int d^3r\, \psi(\mathbf{r})\, \mathbf{r}\, \exp(-i\mathbf{\kappa} \cdot \mathbf{r}) \right|^2 \propto \nu \kappa^{2l+1} , \quad \text{(II.3)}$$

where l is an integer.

If we use the relations $E = h\nu$ and $E - E(L) = h^2\kappa^2/2m^*$, we can combine Eqs. (II.1)–(II.3) to obtain

$$\sigma(L) \propto \frac{(n^2 + 2)^2}{9n} (m^*)^{(2l+3)/2} E[E - E(L)]^{(2l+1)/2} . \quad \text{(II.4)}$$

Because of the tie between the empirical equations (I.1) and (I.2), we presume that Eq. (II.4) should also apply to the gas phase if $E(L)$ is replaced by $E(G)$, m^* is replaced by the rest mass m of the electron, and n is set equal to unity. Accordingly,

$$\sigma(G) \propto (m)^{(2l+3)/2} E[E - E(G)]^{(2l+1)/2} . \quad \text{(II.5)}$$

From Eqs. (II.4) and (II.5), we conclude

$$\frac{B(L)}{B(G)} = \frac{(n^2 + 2)^2}{9n} \left(\frac{m^*}{m}\right)^{(2l+3)/2} . \quad \text{(II.6)}$$

For determination of m^*, Eq. (II.6) can be rewritten as

$$\frac{m^*}{m} = \left[\frac{9n}{(n^2 + 2)^2} \frac{B(L)}{B(G)}\right]^{2/(2l+3)} . \quad \text{(II.7)}$$

This is our principal result.

III. CALCULATION OF m^*

We have applied Eq. (II.7) to the calculation of m^* for liquid argon, tetramethylsilane, 2,2-dimethylbutane, and 2,2,4-trimethylpentane. The solute species was O_2^-, for which it has been shown that $l = 1$.[4,6]

To use Eq. (II.7), however, it was first necessary to determine a statistically reliable value for $B(G)$. To this end, we wrote Eq. (I.1) in the form $[\sigma(G)/E]^{2/3} = [B(G)]^{2/3} E - [B(G)]^{2/3} E(G)$, and fitted it by linear regression to the gas phase photodetachment data of Burch, Smith, and Branscomb.[4] From their Table I, we selected for linear regression treatment the cross section values associated with the five lowest photon energies. These data covered the range 0.531 to 1.653 eV over which the reported cross section varied from 0.35×10^{-18} to 8.23×10^{-18} cm^2. We found $E(G) = 0.13$ eV and $B(G) = 2.7 \times 10^{-18}$ cm^2 $eV^{-5/2}$. The correlation coefficient was 0.9994. When data for energies higher than this were included in the linear regression routine, the correlation coefficient declined.

For O_2^- dissolved in liquid argon, tetramethylsilane, 2,2-dimethylbutane, and 2,2,4-trimethylpentane, $B(L)$ has been determined experimentally by Sowada and Holroyd.[6] They also tabulated values of the dielectric constant ϵ from which we calculated the refractive index using the Maxwell relation $n^2 = \epsilon$.

Combining the values of $B(L)$ and n with the values of $B(G)$ estimated above, we computed values of m^*. The results are shown in Table I.

IV. DISCUSSION

From Table I it can be seen that the electron effective mass varies little from liquid to liquid. As a material

expands, however, one would expect the effective mass
to approach the free mass in the limit of zero density.
We note that as liquid tetramethylsilane warms, m^*
increases in accordance with expectation. Despite this
useful correlation, two experimental difficulties in-
tervene to make a broad interpretation of the other
results in Table I difficult.

First, it has been suggested[1] that the measurements
of Burch, Smith, and Branscomb overestimate the gas
phase cross section by about 20%. In their experiment,
the O_2^- was prepared in an ion source. Because of the
high energy nature of the source, we should expect the
O_2^- to have been produced in a variety of excited vibra-
tional states to which the electron was relatively weakly
bound compared with the ground state. The presence
of these weakly bound states would have enhanced the
apparent value of $B(G)$. If $B(G)$ were to be corrected
downward, all our values of m^* would be increased.

Second, Sowada and Holroyd have pointed out that
photodetachment from O_4^- may have interfered with
their measurements of the O_2^- cross section in the
liquid phase.[6] They speculate that the O_4^- was introduced
by way of the reaction $O_2^- + O_2 \rightarrow O_4^-$.

These provisos notwithstanding, it is interesting to
compare m^* calculated herein with values obtainable
from the analysis of other experiments. For example,
the extensive data on the electron drift mobility in
liquid argon have been compared with the predictions of
Boltzman transport theory.[10,11] Unfortunately, theory
and experiment are in agreement only in the region of
the phase diagram near the triple point. This difficulty
aside, the transport theory predicts an effective mass of
0.75 m in the liquid at 87 K.[11]

Also for liquid argon doped with xenon, Messing et al.
have searched for a Wannier exciton spectrum associated
with Rydberg states of the Xe atom.[12] They were able to
make a clear identification of the $n = 2$ state of Xe, but
other transitions were broad, and the assignment of
higher Rydberg states was problematical. Nonethe-
less, on the basis of a tentative assignment of the $n = 3$
state, they concluded that $m^* = 0.42$ m.

Both of the above values of m^* for liquid argon ex-
ceed the value given in Table I. However, if $B(G)$ were
corrected downward, as we have suggested, closer
agreement would result.

Sowada and Holroyd have shown that Eq. (I.2) also
applies to electron photodetachment from $C_6F_6^-$ dis-
solved in tetramethylsilane, 2,2,4-trimethylpentane,
and four other liquids.[7] Unfortunately, Eq. (I.1) has
yet to be established in the gas phase for C_6F_6. Once
this has been done, however, we should be able to
check and extend Table I.

The electromagnetic factor F_0^2/nE_0^2 in Eq. (II.1) also
occurs in the theory of electron bound-bound transitions
in condensed matter.[13] It can be evaluated on the basis
of both quantum mechanical and classical models. For
a cylindrically symmetric molecule, evaluation of the
quantum mechanical model requires a knowledge of the
radius and length of the molecule.[14] For O_2^-, it is dif-

ficult to establish either of these with certainty. Sever-
al classical calculations of the electromagnetic factor
have been carried out with differing results.[15] Of these,
the Lorentz model, for which $F_0^2/nE_0^2 = (n^2 + 2)^2/9n$, pre-
dicts the strongest dependence upon n. Nevertheless,
in the region $1.2 \leq n \leq 1.4$, which applies to Table I,
all the classical calculations agree with one another
within 10%, so that for our purposes the choice is im-
material.

Despite the fact that there is room for improvement
in both the experiments and the calculations of the elec-
tromagnetic factor, we conclude that we have in Eq.
(II.6) a simple closed result for the ratio $B(L)/B(G)$.
We have shown how this formula can be employed to
make an estimate of the electron effective mass in free
electron liquids and have indicated how this information
should be useful in the theory of the electron drift
mobility and the analysis of Wannier exciton spectra.

Note added in proof: After this paper was submitted
for publication Dr. Sowada and Dr. Holroyd informed
the author they had repeated the experiment on the
photodetachment of O_2^- in liquid argon at 87 K and had
satisfactorily corrected the data for interference by O_4^-.
The corrected result they report is $B(L) = 0.427 \times 10^{-19}$
$cm^2 eV^{5/2}$. Upon substitution of this value into Eq. (II.7),
we obtain $m^* = 0.18$ m. This value of m^* is again
smaller than those suggested for liquid argon by trans-
port theory and by exciton spectroscopy.

ACKNOWLEDGMENTS

APPENDIX

Consider a two component system made up of solute
and solvent. Let the molecules of the solute be in quan-
tum state E_m. We are interested in the cross section σ
for optical transitions from E_m to some final state E_n.
If w is the transition rate and S_p is the flux of photons
resonant with the transition, we have

$$\sigma = w/S_p . \tag{A1}$$

To evaluate the right-hand side of Eq. (A1), we com-
pute S_p from Poynting's vector and w from Fermi's
Golden Rule.

1. Calculation of S_p

Consider the electric field $\mathbf{E}(\mathbf{R}, t)$ of a light wave at
some point $\mathbf{R}$ and time t in the solution

$$\mathbf{E}(\mathbf{R}, t) = \mathbf{E}_0 \sin(\omega t - \mathbf{k} \cdot \mathbf{R}) , \tag{A2}$$

where $\mathbf{E}_0$ is the amplitude, ω is the angular frequency,
and $\mathbf{k}$ is the wave vector. According to Maxwell's equa-
tions, the magnetic field $\mathbf{H}(\mathbf{R}, t)$ associated with Eq. (A2)
is

$$\mathbf{H}(\mathbf{R}, t) = \frac{c}{\omega\mu} [\mathbf{k} \times \mathbf{E}(\mathbf{R}, t)] , \tag{A3}$$

where μ is the magnetic permeability of the solution.
The Poynting vector $\mathbf{S}(\mathbf{R}, t)$ is

$$S(\mathbf{R}, t) = \frac{c}{4\pi} \left[\mathbf{E}(\mathbf{R}, t) \times \mathbf{H}(\mathbf{R}, t) \right] , \tag{A4}$$

where c is the speed of light in vacuum. If we substitute Eqs. (A2) and (A3) into Eq. (A4) and use the vector identity for the triple cross product, we obtain

$$S(\mathbf{R}, t) = \frac{c^2 [\mathbf{E}(\mathbf{R}, t) \cdot \mathbf{E}(\mathbf{R}, t)]}{4\pi \mu \omega} \mathbf{k} . \tag{A5}$$

An average of Eq. (A5) over one time cycle yields a vector of magnitude

$$\langle S \rangle = \frac{c^2 E_0^2}{8\pi \mu \omega} k . \tag{A6}$$

In the solution, the speed of light $v = \omega/k$ is less than c. Specifically, $c/v = n = \sqrt{\epsilon \mu}$, where n and ϵ are the refractive index and dielectric constant, respectively, for the angular frequency ω. For a nonmagnetic material $\mu = 1$, so that Eq. (A6) can be written as

$$\langle S \rangle = \frac{c E_0^2 n}{8\pi} . \tag{A7}$$

Since each photon carries energy $h\nu(\nu = \omega/2\pi)$, the photon flux is

$$\langle S_p \rangle = \frac{\langle S \rangle}{h\nu} = \frac{c n E_0^2}{8\pi h\nu} . \tag{A8}$$

2. Calculation of w

Consider a solute molecule located at $\mathbf{R} = 0$. The local optical electric field $\mathbf{F}(0, t)$ at this point is

$$\mathbf{F}(0, t) = \mathbf{F}_0 \sin \omega t . \tag{A9}$$

The local field can be shown to consist of two parts: (1) the direct field $\mathbf{E}(0, t)$ of the light, and (2) the indirect field calculated by summing the fields produced by the dipoles induced by the light in all other molecules in the solution. The amplitude $\mathbf{F}_0$ can be calculated on this basis from E_0 using various models for the liquid structure.[8]

The local field produces a perturbation $V(t)$,

$$V(t) = e\mathbf{r} \cdot \mathbf{F}_0 \sin \omega t = V \sin \omega t \tag{A10}$$

in the orbit of an electron in the solute molecule. Here, $\mathbf{r}$ is the electron coordinate, and e is its charge. Fermi's Golden Rule states that the rate of transition w from state E_m to state E_n for this electron is

$$w = \frac{\pi}{2\hbar} \sum_n |V_{mn}|^2 \rho(E_n) , \tag{A11}$$

where $\rho(E_n)$ is the density of states with energy E_n and V_{mn} is the matrix element of the transition

$$|V_{mn}|^2 = e^2 |\mathbf{r}_{mn} \cdot \mathbf{F}_0|^2 . \tag{A12}$$

The inner product can be expanded as

$$|\mathbf{r}_{mn} \cdot \mathbf{F}_0|^2 = |X_{mn}|^2 F_{0x}^2 + |Y_{mn}|^2 F_{0y}^2 + |Z_{mn}|^2 F_{0z}^2$$
$$+ 2 \operatorname{Re}(X_{mn}^* Y_{mn}) F_{0x} F_{0y} + 2 \operatorname{Re}(X_{mn}^* Z_{mn}) F_{0x} F_{0y}$$
$$+ 2 \operatorname{Re}(Y_{mn}^* Z_{mn}) F_{0y} F_{0z} , \tag{A13}$$

where F_{0x}, F_{0y}, and F_{0z} are the components of $\mathbf{F}_0$, and Re stands for the real part of the complex number in parentheses. We take $\cos \alpha$, $\cos \beta$, and $\cos \gamma$ to be the

direction cosines of $\mathbf{r}_{mn}$ with respect to F_{0x}, F_{0y}, and F_{0z}, respectively. In the absence of special conditions, the solute molecules will be oriented at all angles with respect to $\mathbf{F}_0$. For a diagonal term such as $|X_{mn}|^2 F_{0x}^2 = |X_{mn}|^2 F_0^2 \cos^2 \alpha$ and a uniform distribution of α, the average value of $\cos^2$ is $1/3$. For an off diagonal term such as $\operatorname{Re}(X_{mn}^* Y_{mn}) F_{0x} F_{0y} = \operatorname{Re}(X_{mn} Y_{mn}) F_0^2 \cos \alpha \cos \beta$, the average value of the direction cosines is zero. Hence, following averages over all direction cosines, Eq. (A13) becomes

$$|\mathbf{r}_{mn} \cdot \mathbf{F}_0|^2 = \tfrac{1}{3} |\mathbf{r}_{mn}|^2 F_0^2 . \tag{A14}$$

Putting Eqs. (A12) and (A14) into Eq. (A11), we find the result

$$w = (\pi/2\hbar)(e^2 F_0^2/3) \sum_n |\mathbf{r}_{mn}|^2 \rho(E_n) . \tag{A15}$$

Equation (A15) applies to any allowed electric dipole transition.

3. Calculation of σ

Substituting Eqs. (A8) and (A15) into Eq. (A1) gives

$$\sigma = \frac{8\pi^3 e^2 \nu}{3c} \left(\frac{F_0^2}{n E_0^2} \right) \sum_n |\mathbf{r}_{mn}|^2 \rho(E_n) . \tag{A16}$$

To specialize Eq. (A16) to photodetachment, we take the state E_n to lie in the continuum. We can consider, for example, a free electron confined to a potential box of side L. For such an electron having wave vector κ, the density of states within solid angle $d\Omega_\kappa$ is

$$(L^3/\pi^3)\kappa^2 . \tag{A17}$$

Measured from the bottom of the conduction band, the electron energy $E(\kappa)$ is

$$E(\kappa) = E - E(L) = \frac{\hbar^2 \kappa^2}{2m^*} , \tag{A18}$$

where E is the photon energy, $E(L)$ is the photodetachment threshold energy, and m^* is the electron effective mass. The density of states per unit electron energy lying within $d\Omega_\kappa$ is gotten from Eq. (A17) by multiplying by $[dE(\kappa)/d\kappa]^{-1}$. The result is

$$\rho[E(\kappa)] = \frac{L^3 m^* \kappa}{\pi^3 \hbar^2} d\Omega_\kappa . \tag{A19}$$

A wave function for the continuum state consistent with Eqs. (A18) and (A19) is

$$\phi(\mathbf{r}) = L^{-3/2} \exp(i\boldsymbol{\kappa} \cdot \mathbf{r}) . \tag{A20}$$

Geltman has shown that this wave function is sufficient to calculate the correct cross section near threshold for diatomic molecular negative ions.[2] Wave functions with higher order corrections, such as the partially orthogonalized plane waves of Reed et al.,[3] would give a set of eigenvalues different from Eq. (A18) and a different density of states. Because of the short range of the molecular potential field, however, we would not expect the differences to be great.

Taking $\psi(\mathbf{r})$ to be the wave function of the electron in the negative ion and Eq. (A20) for the continuum state, we can use Eqs. (A16) and (A19) to write

$$\sigma = \frac{8e^2}{3\hbar^2 c}\left(\frac{F_0^2}{nE_0^2}\right)m^*\nu\kappa\int d\Omega_\kappa \left|\int d^3r\,\psi(\mathbf{r})\,\mathbf{r}\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r})\right|^2,$$

$$(A21)$$

where we have replaced the sum over final states by an integral over $d\Omega_\kappa$.

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