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LINKING THE GASEOUS AND THE CONDENSED PHASES OF MATTER: THE SLOW ELECTRON AND ITS INTERACTIONS¹

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ABSTRACT

The interfacing of the gaseous and the condensed phases of matter as effected by interphase and cluster studies on the behavior of key reactions involving slow electrons either as reacting initial particles or as products of the reactions themselves is discussed. Emphasis is placed on the measurement of both the cross sections and the energetics involved, although most of the available information to date is on the latter. The discussion is selectively focussed on electron scattering (especially the role of negative ion states in gases, clusters, and dense matter), ionization, electron attachment and photodetachment. The dominant role of the electric polarization of the medium is emphasized.

INTRODUCTION

Interphase and Cluster Studies

The interfacing of the gaseous and the condensed phases of matter requires multidisciplinary and systematic investigations as to how the microscopic and the macroscopic properties of materials and the elementary processes involving electrons, photons, ions, and neutral particles change as one makes the transition from a low pressure gas (isolated-particle behavior) to the condensed phase. There have been two complementary approaches in this endeavor: (i) interphase physics/chemistry and (ii) clusters. In the former approach, a given reaction (or property) is studied as a function of the density and the nature of the medium in which it occurs from the low-pressure gas to the liquid or the solid. Actually, traditionally such studies begin at either end of the density range: from the liquid (solid) density to progressively lower densities and from a low density gas (binary collisions)

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to progressively higher densities (multiple scattering regime), and to the condensed phase. Both bridge the density gap between low pressure gases and condensed matter (e.g., see Refs. 1-5 and references therein). In the latter approach, the properties and reactions of a given species (atom or molecule) are studied as a function of its size (increased gradually by clustering), cluster² shape and cluster composition. A unique feature of clusters is that they allow studies of the transition from large finite clusters to the bulk and thus determination of the minimum cluster size beyond which the cluster properties no longer vary with size but are essentially similar to those of a macroscopic sample of the material (e.g., see Ref. 6 (and references cited therein) and Refs. 7-12).

Why Slow Electrons?

Slow electrons are abundant and reactive species in all phases of matter¹³. They are generated in gaseous and condensed matter by a multiplicity of mechanisms: energy transfer from high-energy particles to atoms and molecules; absorption of light by neutrals or negative ions; collisions of excited and unexcited atoms, negative ions with neutrals, electrons with neutrals or ions; injection from surfaces. They lose their energy and slow-down in matter in elastic and a multiplicity of inelastic collisions¹⁴. They interact before they are thermalized (i.e., during their slowing down) and also after they have reached thermal equilibrium or steady-state conditions (when an applied electric field E is superimposed on the medium). This distinction is significant since the interactions of slow electrons in a dense medium depend on the "state" of the electron itself.

For a low-pressure gas, the electrons are normally free and the collision (interaction) mean free path l is much longer than the electron de-Broglie wavelength. In a dense medium (high pressure gas, liquid or solid) l is smaller than the de-Broglie wavelength and as the medium density increases the electrons become localized or delocalized into conduction bands. In the former case, their mobilities are low and their kinetic energies are thermal and in the latter case their mobilities are high and their kinetic energies (under an applied electric field) can exceed considerably thermal energies³.

The reactions of slow electrons in dense matter often differ greatly from those in a low-pressure gas. They are unique in that they help us unravel the structure of atoms and molecules, probe the structural and dynamical changes with the density and the nature of matter, and quantify the energetics and dynamics of basic reactions in matter.

This Lecture

In this lecture we discuss the behavior of key reactions--as studied by interphase and cluster researches--involving slow electrons either as reacting initial particles or as products of the interactions themselves. We emphasize measurement of both cross sections and energetics, although most of the available information to date is on the latter. We selectively focus on electron scattering (especially the role of negative ion states in gases, clusters, and dense matter), ionization, electron attachment and photodetachment and emphasize the dominant role of the electric polarization of the medium on the reaction energetics. The comparison between the gaseous and the liquid phase measurements is restricted to dielectric

²Normally the term cluster is used to describe finite aggregates of 2 to 10⁴ particles (atoms or molecules).

liquids with conduction bands³ where the excess electrons are quasi-free--not localized as, say, in polar media--and the connection between the electron behavior in the two phases is more apparent. Finally, the general nature of this lecture unavoidably touches on aspects of the theme of this meeting that will be covered by subsequent lecturers. We hope that it will enhance the value of and the anticipation for these upcoming and in-depth lectures.

DIRECT AND INDIRECT ELECTRON COLLISIONS

Slow electrons lose their energy and slow down in matter in elastic and (a multiplicity of) inelastic collisions. Such collisions are either direct or indirect (Fig. 1). In a direct - glancing - collision the electron is scattered at a distance from the target, the duration of the collision is short, and the cross section for the collision--whether elastic or inelastic--is appreciable over a broad range of incident electron energies. In contrast, in indirect collisions the electron is temporarily captured by the target forming a transient anion whose

Figure 1. Schematic pictures depicting direct and indirect electron-molecule collisions; M^{-*} indicates a transient negative ion with excess energy denoted by the asterisk.

³These are dense media whose $V_0 < 0$ eV; V_0 is the energy of the excess electron at the bottom of the conduction band. It is defined as $V_0 = W_M - W_{vac}$ where W_M and W_{vac} are, respectively, the work functions of a metal immersed in the dense medium and in vacuum.

lifetime can vary from $\sim 10^{-15}$ to $> 10^{-3}$ s (Refs. 13-15). Such collisions are resonant, i.e., they occur over a limited energy range--where empty orbitals exist for electrons to enter into and be temporarily retained. Subsequent to its formation the transient anion M^* is destroyed by autodetachment (i.e., indirect elastic or inelastic electron scattering) or by "permanent" negative ion formation: fragment anions by dissociation and parent anions by stabilization. These processes are of general occurrence in nature. An example of an indirect collision leading only to elastic and inelastic scattering is shown in Fig. 2 for N_2 (no permanent N_2^- or N^- ions are formed since the electron affinities of N_2 and N are negative). The pronounced peak in the momentum transfer cross section σ_m and in the total vibrational cross section at ~ 2.3 eV--pointed to by the arrows in Fig. 2--is due, respectively, to the elastic and the inelastic scattering of electrons via the decay of the transient anion N_2^{*-} formed by the temporary capture by N_2 molecules of ~ 2.3 eV electrons. Examples of the formation of "permanent" fragment negative ions via indirect (resonant) collisions are shown in Fig. 3. Clearly, these negative ion resonances occur abundantly in the energy range below ~ 20 eV and their cross sections increase as their energy positions are lowered.

Figure 2. Cross sections for various electron scattering processes in N_2 as a function of electron energy (see the text) (based on Fig. 51 of Ref. 14, Vol. 2, p. 194).

Figure 3. Dissociative electron attachment cross sections as a function of electron energy for a number of molecules (from Ref. 14, Vol. 1, p. 559).

Indirect collisions forming transient anions occur in condensed matter as well, but as we shall see their "isolated species" properties, energetics, and effects on other processes involving slow electrons are modified in dense matter by the nature and the density of the medium in which they occur. We shall try to understand some of these changes by considering knowledge from selected investigations on condensed phase and clusters.

ELECTRON SCATTERING

In Table 1 are listed examples of the effects of phase on various electron energy loss processes and cross sections (see also Refs. 16,17). Let us illustrate some of these by examining the effect of phase on the differential oscillator strength distribution $f(\epsilon)$ of water shown in Fig. 4. Clearly one sees a general loss of structure and a shift of $f(\epsilon)$ to higher energies in going from the vapor to the condensed phase. Interestingly, the main difference is between the vapor and the condensed matter and not between the various forms (liquid, hexagonal ice, amorphous ice) of the latter. These phase effects seem to diminish with excitation energy. Important as this information is, it is still largely indirect^{18,19} and limited. It should be noted in this connection that total inelastic cross sections estimated²⁰ for slow (1-20 eV) electron scattering in amorphous ice compare in magnitude (they are, actually,

Table 1. Examples of Condensed Phase Effects on the Oscillator Strength Spectrum

Shift of oscillator strength to higher energies (occurs over wide ranges of excitation energy)

Excitation of special modes of motion (plasmons in metals and excitons in molecular and ionic crystals; occur at specific energies)

Intermolecular vibrations (vibrational and translational phonons)

High Rydberg states (normally absent)

Negative Ion Resonances (exist as in single molecules but perturbed by the medium, e.g., their symmetries, lifetimes, selection rules, energetics)

Ejected electrons undergo further interactions

Scattering affected by correlation (medium structure) effects, nuclear/electronic excitation mode coupling, screening of interaction potential

Dissociation processes influenced by fast radiationless transitions and changes in energetics

Figure 4. Differential oscillator strength distribution, $f(\epsilon)$, of water vapor (A), liquid water (B), hexagonal ice (C), and amorphous ice (D) (Refs. 18 and 19).

slightly larger) and general trend with gas phase data (see discussion in Ref. 20); this conclusion, however, requires further scrutiny.

Let us now look at a system, namely xenon, for which scattering cross sections for slow electrons are well-known in the gas^{13,14,21} and electron drift velocities as a function of the density, N , reduced electric field E , E/N , have been measured in the low pressure gas^{13,14,21}, the high pressure gas^{2,22}, the liquid^{2,23}, and the solid^{2,23}. From the liquid phase electron transport data Sakai et al.²⁴ deduced two types of scattering cross sections, namely, a cross section for elastic energy loss (energy transfer to acoustic phonons which is independent of the liquid structure)

$$\sigma_0(\epsilon) = 2\pi \int_0^\pi (1 - \cos \theta) \sigma(\epsilon, \theta) \sin \theta d\theta, \quad (1)$$

and a cross section for elastic momentum transfer which depends on the liquid structure through the structure factor $S(K)$

$$\sigma_1(\epsilon) = 2\pi \int_0^\pi (1 - \cos \theta) \sigma(\epsilon, \theta) S(K) \sin \theta d\theta \quad (2)$$

where $\sigma(\epsilon, \theta)$ is the differential scattering cross section, θ is the scattering angle and ϵ is the electron energy. These are compared with the low-pressure gas momentum transfer cross section σ_m in Fig. 5. Both $\sigma_0(\epsilon)$ and $\sigma_1(\epsilon)$ exhibit a displaced and shallower (relative to the low pressure gas) Ramsauer-Townsend minimum and are much lower in magnitude than $\sigma_m(\epsilon)$ especially at low ϵ . As ϵ increases, $S(K) \rightarrow 1$ and the gas and liquid cross sections converge. A quantitative determination of the scattering cross section in the liquid is still lacking although the lowering of its magnitude in the condensed phase clearly is due to the screening of the scattering potential by the medium.

The indicated changes in the energy dependence and the magnitude of the scattering cross section in going from the low-pressure gas to the liquid explain nicely the much higher drift velocities, w , of slow electrons in gaseous compared to liquid xenon (Fig. 6). At a fixed E/N the $w(E/N)$ of slow electrons in solid xenon are about twice those in liquid xenon²². While this is consistent with the lower values of the total electron scattering cross section in solid xenon (σ_s) deduced by Bader et al.²⁵ (Fig. 7), the behavior of σ_s (Fig. 7) is different at high energy from that of σ_1 or σ_0 (Fig. 5) in the liquid, probably indicating different scattering processes.

A behavior similar to that in xenon has been reported²⁶ for the $w(E/N)$ of room temperature liquids with conduction bands [eg. see, Fig. 8]⁴.

⁴See Stephens²⁷ for a possible relationship between the mobilities of thermal electrons in different pentane isomers and their respective structure functions.

Figure 5. Cross sections $\sigma_0(E)$ and $\sigma_1(E)$ for liquid xenon and $\sigma_m(E)$ for gaseous xenon (see the text and Refs. 3 and 24).

Figure 6. Electron drift velocity w as a function of E/N for liquid²³ and gaseous²¹ Xe at the indicated temperatures.

Figure 7. Comparison of the total electron scattering cross section for gaseous, σ_g , Xe and for solid, σ_s , Xe (17 K deposition on Pt.) plotted as a function of the electron energy (note that the zero energy in the solid is shifted by the V_o value of the solid) (from Ref. 25).

Figure 8. w vs E/N for gaseous and liquid tetramethylsilane ($T = 300$ K) (based on Ref. 26).

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The cross sections in Figs. 5 and 7 are due to direct electron scattering. In condensed matter--as in low pressure gases--indirect scattering of slow electrons occurs abundantly. It manifests itself through a strong enhancement in the scattering cross section over limited energy regions where the negative ion states (NISs) are located. A prototypical example is shown in Fig. 9 for solid films of N_2 . The cross section function for excitation of the N_2 molecule in solid N_2 films in the first ($v = 1$) vibrational level via its lowest, $N_2^{\cdot-}$ ($^2\Pi_g$), negative ion state has--as in the isolated-molecule case--distinct structure which originates from the vibrational levels of the transient $N_2^{\cdot-}$ ($^2\Pi_g$) state. The position of the first peak in Fig. 9 (first broken vertical line) lies ~ 0.7 eV lower than the corresponding position in the low pressure gas (first solid vertical line in Fig. 9). This lowering of the energy position of the $N_2^{\cdot-}$ ($^2\Pi_g$) state is a general characteristic of the changes in the energetics of the NISs of atoms and molecules embedded in dense matter and is due to the polarization of the medium which surrounds the temporarily localized electron on the molecule. The cross section functions for excitation of N_2 in the $v = 2, 3$, etc. levels exhibit similar behavior¹⁶. Interestingly, however, while in the solid--as in the isolated molecule--the vibrational excitation increased by ~ 2 orders of magnitude in the region of the resonance, Sanche et al.¹⁶ observed no such enhancement in the elastic scattering channel in the N_2 solid film. This is in sharp contrast to the gas where indirect elastic electron scattering is profoundly enhanced. The formation of the NIS in the condensed phase--as in gases--is localized in space and is dominated by the short-range forces. For this reason in the solid--as in the gas--the formation of a NIS leads to intramolecular changes that enhance excitation of individual vibrational levels of the molecular constituents. The decay of the NIS in the condensed phase, however, should differ from that in the gas because it is affected by the medium due to polarization. The intermolecular changes lead to continuous acoustic excitations (phonons) which in essence replace the (low pressure) elastic scattering. This process is very probable due to the large number of such low frequency vibrations (see Refs. 2,16,17,28, and 29). It, thus, seems that the formation of negative ion states in dense matter enhances intramolecular vibrational excitation and intermolecular excitation of phonon modes of the lattice. A theoretical understanding of slow electron interactions in condensed matter in a manner analogous to gases, is, however, still lacking.

The electrons that have been slowed down via the NISs cause (see later) profound changes in the observed electron attachment properties of molecules in dense matter and in clusters.

Figure 9. Relative cross section for indirect scattering of slow electrons via the $N_2^- (^2\Pi_-)$ negative ion state of N_2 in solid N_2 film leaving N_2 excited in the $v = 1$ vibrational level. Note that the position of the first peak in the cross section function for the solid lies ~ 0.7 eV lower than for the corresponding gas (see the text) (based on Fig. 13b in Ref. 16).

IONIZATION IN DENSE MATTER AND IN CLUSTERS

Electron Impact Ionization

In spite of its basic and applied significance, there appears to be no direct measurement of the electron impact ionization cross section as a function of the electron energy $\sigma_{ei}(\epsilon)$ for any system. There is, however, some limited information on the effective ionization cross section of H_2 in H_2 clusters as a function of the cluster size (Fig. 10) which indicates that the $\sigma_{ei}(\epsilon)$ for closely packed and interacting H_2 molecules is smaller than that for the isolated H_2 molecules³⁰. There exists, also, some indirect information on media with $V_0 < 0$ eV such as xenon. For this medium the electron impact ionization coefficient $\alpha(E/N)$ does not scale with the density N in going from the gas to the liquid³¹. In Table 2 are compared: the total electron yield $G_w(e, \gamma, x)$ for electrons, γ -rays and x-rays; the energy to produce an electron-ion pair for β particles, W_β ; and the ionization threshold energy for the low pressure gas, I_G , and the liquid, I_L . The lowering of W_β (increase in G_w) for the liquid can be attributed to the lowering of I in the liquid compared to the gas (see below). Due to the lower I_L , electronic states that would have led to inelastic scattering in the gas lead to ionization in the liquid.

Figure 10. Effective electron impact ionization cross section of cluster beams of H_2 as a function of the mean cluster size N for 500 eV. The solid point shows the value, σ_u , of the cross section for uncondensed H_2 at the same electron energy³⁰.

Table 2. Comparison of $G_{ie}(e, \gamma, x)$, W_β and I for gaseous and liquid xenon¹

Quantity	Liquid	Gas
$G_{ie}(e, \gamma, x)$	6.4	4.6 (electrons/100 eV)
W_β	~16	21.9 (eV/i.p.)
I	~9.0	12.13 eV

¹See the text and Ref. 1.

Single and Multiphoton Ionization of Molecules in Fluids

Here again absolute cross section measurements are scarced. However, many studies on pure liquids and solutions quantified the effect of the medium on the energetics of the reaction

where F stands for the fluid medium in which the molecule M is embedded and the reaction takes place. If we neglect the small broadening of the valence electron levels in the fluid due to condensation, for liquids (F = L) the measurements showed^{1,2,32,33} that

$$I_L = I_G + V_o + P^* \quad (4)$$

In Eq. (4), P^* is the polarization energy of the positive ion M_F^+ and is normally represented by the Born expression

$$P^* = - \frac{e^2}{2R} \left[1 - \frac{1}{\epsilon_{opt}} \right] \quad (5)$$

where R is the effective radius of the positive ion cavity and ϵ_{opt} is the optical dielectric constant of the medium. For a number of organic molecules in nonpolar liquids³, $I_L - I_G (= V_o + P^*) \sim -1$ to -3 eV and $\langle R \rangle \sim 2.7$ Å. A major uncertainty in the determination of P^* remains the lack of accurate knowledge of R.

The validity of (4) can indeed be seen from measurements (see Ref. 34, Table 3) of I_L of a certain molecule (azulene) in a number of dielectric liquids with different V_o values. Since in this case we are dealing with the same positive ion, P^* may be regarded as constant for these nonpolar liquids and, hence, the I_L should correlate with the V_o of the liquids. Indeed, the linear dependence of I_L on V_o implied under such conditions by Eq. (4) is exhibited by the measurements in Table 3 (see Fig. 11).

Table 3: I_L and I_G for Azulene in Dielectric Liquids With Various V_o Values³⁴

Liquid	I_L (eV)	I_G (eV)	V_o (eV)
Tetramethyltin (TMT) ¹	5.33	7.42	-0.75
Tetramethylsilane (TMS) ¹	5.45		-0.55
2,2,4,4-Tetramethylpentane (TMP) ¹	5.70		-0.36
n-Pentane (n-Pt) ¹	6.12		+0.01
n-Tridecane	6.28		+0.21

¹Abbreviations used in Fig. 11.

Similarly, for a fluid of number density N the ionization threshold, $I_F(N)$, of a molecule (atom) embedded in the fluid has been found (e.g., Refs. 35,36) to be related to its isolated-molecule value, I_G , by

Figure 11. I_L vs V_o for the azulene molecule, M , ionized by two photon absorption ($2 h\nu + M_L \rightarrow M_L^+ + e_L$) in a number of nonpolar liquids (Ref. 34; see Table 3).

$$I_F(N) = I_G + P^*(N) + V_o(N) \quad (6)$$

i.e., by the N -dependence of P^* and V_o ; the N -dependence of P^* is dominated by the N -dependence of ϵ_{opt} while the N -dependence of V_o is more complicated. The $V_o(N)$ has been calculated in a few cases using the Springett, Jortner, and Cohen (SJC) model³⁵⁻³⁷. In Fig. 12 is plotted the I_F of the molecule TMPD (N,N,N',N' -tetramethyl- p -phenylenediamine) in ethane as a function of the ethane density $\rho(M/I)$ from the dilute gas to the liquid. The effect of increasing medium density on I_F is a continuous gradual decrease and a smooth transition to the liquid. The solid lines represent the dependence of I_F on N for the indicated values of the "hard core" radius $\langle \bar{a} \rangle$ as predicted by the SJC model.

From the experimental investigations to date it appears that the energetics of ionization in dense matter are modified from their values in dilute gases by the charge induced medium polarization energies. The energetics of the process for nonpolar fluids is reasonably well understood and needs to be extended to polar media.

Photoionization Energetics in Clusters

Many studies have been devoted recently to this topic and subsequent lectures will deal with the subject in more detail. Here we merely lay down a few aspects of the energetics of the process as a background for the other lectures and, also, to integrate our discussion on the kind of knowledge obtained by the two complementary approaches we mentioned in the Introduction. Let us first refer to Fig. 13 which shows schematically⁶ the dependence on the cluster size of a cluster property $x(n)$; n is the number of the cluster constituents. For small n , $x(n)$ exhibits specific cluster size effects (e.g., shell closure effects). For large n , Jortner⁶ expressed $x(n)$ as

Figure 12. Ionization threshold of TMPD (N,N,N',N'-tetramethyl-p-phenylenediamine) in ethane as a function of the ethane density from a dilute gas to the liquid at the indicated temperatures. The data points ■ are measurements made in liquid ethane at 295 K. The solid lines represent the dependence of I_F on N for the indicated values of the "hard core" radius $\langle \bar{a} \rangle$ as predicted by the Springett-Jortner-Cohen (SJC) model^{35,37}.

$$x(n) = \chi(\infty) + An^{-\beta} \quad (7)$$

namely, in terms of the corresponding bulk value $x(\infty)$ and a correction term $An^{-\beta}$ ($0 \leq \beta \leq 1$) which accounts for the modification of the bulk value in the cluster due to the "excluded volume" outside of it. Expressing Eq. (7) in terms of the cluster radius R_c (taken equal to $R_0 n^{1/3}$ where R_0 is the effective single particle radius determined from the molecular (atomic) volume using the bulk medium density) we have

$$\chi(R_c) = \chi(\infty) + (A R_0^{3\beta}) R_c^{-3\beta} \quad (8)$$

This "cluster-size equation" attempts to provide a quantitative description of the "smooth" cluster size dependence of $x(n)$ for large clusters and it interpolates to the corresponding bulk value $x(\infty)$ in much the same way as Eqs. (4) and (6) we have discussed earlier.

Let us apply (7) and (8) to the case of the ionization potential $I(n)$ of clusters. We can write

$$I(n) = I_A + P^*(R_c) = I_A + P^*(\infty) + C(R_c) = I(\infty) + C(R_c) \quad (9)$$

where I_A is the ionization potential of the isolated species A, $P^*(\infty)$ is the bulk polarization energy and $C(R_c)$ is the correction for the finite cluster size (i.e., the long-range electrostatic

Figure 13. Schematic representation of the cluster size dependence of a cluster property $x(n)$ on the number, n , of the cluster constituents (from Ref. 6; see the text).

interaction of the generated charge with the "excluded region"). If we use for $C(R_c)$ the classical electrostatic expression which gives the energy required to remove an electron from a uniformly conducting sphere having the same dimensions as the cluster, namely,

$$C(R_c) = (e^2/2R_c)(1 - 1/\epsilon_{opt}) = (e^2/2R_c)(1 - 1/\epsilon_{opt})n^{-1/3} \quad (10)$$

we have

$$I(n) = I(\infty) + (e^2/2R_c)(1 - 1/\epsilon_{opt})n^{-1/3} \quad (11)$$

In Eq. (11), $I(\infty) = I_A + P^*(\infty)$ is the bulk photoelectric threshold for molecular clusters, the top of the bulk valence energy for semiconductor clusters, or the bulk metal work function for metallic clusters.

The validity of Eq. (11) is illustrated in Fig. 14 for the rare gas and mercury clusters⁸. The results of Rademann et al.⁸ for mercury clusters show in addition the gradual transition from van der Waals-type to metallic properties; on the basis of their data in Fig. 14 this transition occurs in the cluster size range of ~ 70 atoms. In cluster energetics as in interphase studies energetics a major uncertainty in applying relations such as Eqs. (4), (5), and (11) is the proper knowledge of R .

Figure 14. Ionization potential (in eV) vs $n^{-1/3}$ for Ar, Kr, Xe, and Hg clusters (from Ref. 8) (see the text).

ELECTRON ATTACHMENT

Subsequent lectures will--most assuredly--discuss the effect of the state and the nature of the medium on the attachment of slow electrons to molecules. We, also, elaborated on interphase studies of electron attachment and the relevance of electron attachment processes in gases to those in the condensed phase earlier (e.g., Refs. 1-3). We shall, thus, be brief. In Fig. 15, the rate constant for the dissociative electron attachment reaction

as measured in gaseous argon, $(k_a)_G$, and in liquid argon, $(k_a)_L$, is plotted as a function of respective values of the mean electron energy, $\langle \epsilon \rangle_G$ in gaseous argon and $\langle \epsilon \rangle_L$ in liquid argon. In spite of the large uncertainty in $\langle \epsilon \rangle_L$, the comparison of $(k_a)_G$ ($\langle \epsilon \rangle_G$) with $(k_a)_L$ ($\langle \epsilon \rangle_L$) in Fig. 15 shows three rather distinct features: (i) the dissociative attachment resonant reaction (12) occurs in liquid argon as it occurs in the argon buffer gas, (ii) the position of the dissociative attachment resonance shifts to lower energy as a result of the polarization of the medium around the transient N_2O^{*-} , and (iii) the rate constant for the reaction is higher in the liquid than in the gas largely because of the lowering of the energy of the negative ion state.

Figure 15. Electron attachment rate constant for N_2O in gaseous ($(k_a)_G$) and liquid ($(k_a)_L$) argon plotted as a function of the respective, $\langle \epsilon \rangle_G$ and $\langle \epsilon \rangle_L$, mean electron energies (the data for liquid argon are from Ref. 38).

Studies of electron attachment to molecules in clusters and in solid films generally showed similar changes: the perturbation from the isolated-molecule case of the formation of the transient anion and its decay channels by the medium. Thus, as is shown in Fig. 16a, the negative ion resonance that produces O^- from O_2 and peaks at ~ 6.7 eV in the gas exists in solid films of mixtures of O_2 in Ar, but it is shifted to lower energies by ~ 0.7 eV. Additionally, the yield of O^- from O_2 from the solid shows (Fig. 16a)--in contrast to the isolated O_2 case--enhanced O^- production at ~ 8 and ~ 14 eV. These enhancements ("peaks") in the O^- yield have been attributed by Sanche and collaborators (e.g., see Ref. 16) to the transitions

and

which are symmetry forbidden in the isolated molecule case, but become allowed in the solid because of the perturbation by the medium. Observation of O^- via dissociative electron attachment to O_2 in O_2 clusters as a function of cluster size showed similar evidence. This is indicated by the enhancement in the O^- yield around 8 and 14 eV in Fig. 16c with increasing stagnation pressure from 1 to 3.5 bar (the cluster size distribution increases with increasing stagnation pressure).

From these rather limited studies it can be inferred that in going from the gaseous to the condensed phase additional negative ion states contribute to indirect energy loss and dissociative electron attachment processes.

Figure 16. a. O^- from O_2 in O_2 gas (upper curve) and O_2/Ar (1/10 mixture), solid film. b. Schematic potential energy curves for $O_2(^1\Sigma_g^-)$ (---) and O_2^- ($^1\Pi_g$, $^3\Pi_g$, $^3\Sigma_g^-$, $^3\Sigma_u^-$) (—). c. Yield of O^- from O_2 clusters at 1, 2, and 3.5 bar stagnation pressure normalized at the lowest maximum to the yield of O^- from O_2 at low pressure (effusive —). (a and b from Ref. 16; c from 39).

Besides these changes, the proximity of collision partners within the condensed medium or the cluster will enhance the production of parent negative ions (e.g., O_2^-). Furthermore, the negative ion properties of single molecules or clusters with strong "zero" or "near-zero" nondissociative electron attachment resonances are strongly influenced by inelastic electron scattering by the cluster constituents. This is beautifully illustrated in Fig. 17 where the production of $(\text{O}_2)_2^-$ in O_2/N_2 mixed clusters is strongly influenced by the inelastic electron scattering by N_2 , especially by the inelastic electron scattering via the 2.3 eV negative ion resonance $\text{N}_2^{*-} (^2\Pi_g)$. The yield of this ion exhibits a strong resonance at ~ 2.3 eV in the case of the O_2/N_2 clusters (Fig. 17b) which is absent in the homogeneous clusters of O_2 (Fig. 17a). The profound effect of inelastic electron scattering (especially via NIRs) by the cluster constituents on the intensity and energy dependence of the anions formed in clusters by the capture of "near-zero" energy electrons indicates that such processes can be employed to probe electronic and negative ion states of molecules in clusters.

Figure 17. Yield of $(\text{O}_2)_2^-$ from (a) pure O_2 clusters and (b) O_2/N_2 clusters (O_2/N_2 gas mixture ratio 1/10). The stagnation pressure was 4 bar⁴⁰. The pronounced additional resonance in (b) at ~ 2.3 eV is due to the formation of $(\text{O}_2)_2^-$ by capture of electrons inelastically scattered to near-zero energy via the 2.3 eV $\text{N}_2^{*-} (^2\Pi_g)$ resonance of N_2 .

PHOTODETACHMENT IN GASES, LIQUIDS, AND CLUSTERS

The photodetachment of electrons from negative ions in low-pressure gases is well-understood and the relation of the photodetachment threshold E_{th} to the electron affinity, EA, of the electron attaching species is well-established (e.g., see Ref. 13). Near threshold, the photodetachment cross section, σ_{pd} , is predicted^{41,42} to vary as

$$\sigma_{pd}(E) = BE(E - E_{th})^{(2l+1)/2} \alpha k^{2l+1}, \quad (15)$$

where B is a constant, $E = h\nu$ is the photon energy, and k and l are the linear and angular momenta of the ejected electron. For atoms, A , the value of the E_{th} for the process

is equal to the electron affinity $EA(A)$ of A , which in turn, is equal to the "vertical detachment energy" (VDE). For molecules, M , the relation of E_{th} for the process

to the electron affinity, $EA(M)$, of M and the VDE is complicated by possible differences in the structural parameters of M and M^- . If we define the VDE for (17) as the minimum energy required to eject the electron from the negative ion in its ground electronic and molecular state without changing the internuclear separations, then the VDE is related to the EA and E_{th} by

$$E_{th} = VDE = EA + \Delta E, \quad (18)$$

i.e., the VDE for (17) exceeds the EA by ΔE ; the magnitude of ΔE depends on the relative positions of the potential energy curves (surfaces) of M and M^- .

The photodetachment of electrons from negative ions in dense gases, liquids and clusters has been studied--and the energetics of the process have been related to their gas-phase values--for only a limited number of cases (e.g., see Refs. 43-46). Even more limited seem to be the measurements of the photodetachment cross sections. Experimental studies are in progress at the author's laboratory to determine the photodetachment energetics and cross sections as a function of medium density from a low-pressure gas to the liquid. Establishing the energetics and the cross sections for photodetachment as a function of the nature and density of the medium is significant because it gives a direct measure of the stability of the anion in dense matter and because it provides a basic input for understanding electron transfer mechanisms in dense matter.

In dense gases, liquids and clusters, the photodetachment process for molecular negative ions is complicated by the effect of the medium on E_{th} and the potential energy curve (surface) of M^- . Rewriting reaction (17) for, say, the liquid as

$$M_L^- + h\nu \rightarrow M_L + e_L \quad (19)$$

and assuming that $(EA)_L = (EA)_G + V_o - P^-$ (Refs. 1,44) we have

$$\begin{aligned} (E_{ph})_L &= (VDE)_L = (EA)_L + (\Delta E)_L \\ &= (EA)_G + V_o - P^- + (\Delta E)_L \end{aligned} \quad (20)$$

where V_o and P^- are the polarization energies of the electron and the negative ion in the medium, and $(EA)_L$ and $(EA)_G$ are the values of the electron affinity of M in the liquid and the gas phase.

Among the few studies of photodetachment of negative ions in liquids is that on $C_6F_6^-$ (Refs. 43,44). Let us, then, by way of example, refer to the method of Faidas et al. [44] which utilizes a two-laser photoconductivity technique suitable for photodetachment studies in dense fluids and the results they obtained on $C_6F_6^-$ photodetachment in liquid TMS using this method. A schematic of their experimental arrangement and an outlay of the principle of their technique is shown in Fig. 18. A cell--with appropriate light windows and feedthroughs--contains the molecule (C_6F_6) under study dissolved in the liquid (TMS) at an appropriate concentration. Two counter-propagating coaxial laser beams traverse the interaction volume in the liquid cell with a time delay of $\sim 5 \mu s$. The first laser beam from

Figure 18. Schematics of the two laser photodetachment technique and an oscillogram of the conductivity signal (see the text and Ref. 44).

an excimer laser ($\lambda = 308$ nm; $fwhm = 15$ ns) ionizes biphotonically the liquid and produces electrons which give rise to a fast signal (initial drop in Fig. 18b identified by $\downarrow$ and the process $nh\nu + X \rightarrow X^+ + e$). These electrons quickly (within < 1 ns) attach to C_6F_6 forming $C_6F_6^-$ (process $e + M \rightarrow M^-$ in Fig. 18b); the slow falling portion of the signal (indicated by M^- in Fig. 18b) after the initial steep fall is due to these slow-moving anions. At the preset time delay (~ 5 μ s), the second laser pulse (tunable dye laser, $fwhm = 0.6$ ns) detaches the electron from $C_6F_6^-$ (when $h\nu > (E_{th})_L$) and produces a second transient signal (step drop in Fig. 18b identified with $\downarrow$ and $h\nu + M^- \rightarrow M + e$), followed by a slow drop when the detached electrons attach to C_6F_6 again forming slow moving $C_6F_6^-$.

The basis for determining the photodetachment cross section $\sigma_{pd}(E)$ as a function of the photon energy E can be seen by referring to Fig. 19. The first (excimer) laser pulse has an essentially flat intensity profile $I_e(r)$ for distances $r < \alpha$ where α is the radius of the cross sectional area of the interaction volume (Fig. 19a). This pulse generates electrons uniformly in the interaction volume with a density distribution $n_e(r) \propto I_e^2(r)$. Under the experimental conditions employed by Faidas et al. all these electrons were captured by C_6F_6 within 1 ns and the resultant negative ions $C_6F_6^-$ were essentially stationary with an ion density distribution $n_i(r) = n_e(r) \propto I_e^2(r)$ when the second (tunable dye) laser pulse arrived ~ 5 μ s later. The intensity profile $I_d(r)$ of the dye laser pulse was Gaussian and lay well within α (Fig. 19c). The density distribution, $n_{ed}(r)$, of the photodetached electrons is

$$n_{ed}(r) = \sigma_{pd}(E) n_i(r) I_d(r) \quad (21)$$

Under the experimental conditions employed, $n_{ed}(r) \ll n_i(r)$, the $I_e(r)$, $n_i(r)$, and $I_d(r)$ were virtually constant along the axis of the interaction volume, and

$$\sigma_{pd}(E) = \frac{N_{ed}}{N_i} \frac{\pi \alpha^2}{I_d} \quad (22)$$

Thus, $\sigma_{pd}(E)$ can be determined from a measurement of the ratio N_{ed}/N_i of the total number of photodetached electrons, N_{ed} , to the total number of negative ions N_i , a measurement of the total number of photons in the dye laser pulse I_d and a knowledge of α and the intensity profiles of the two laser beams.

In Fig. 20 is shown the $\sigma_{pd}(E)$ for $C_6F_6^-$ in TMS ($T = 298$ K) determined by this technique. The cross section $\sigma_{pd}(E)$ exhibits two well-defined maxima at 2.58 and 3.15 eV due presumably to excited negative ion states of $C_6F_6^-$. The photodetachment threshold $(E_{th})_L$ was determined by fitting the experimental measurements near threshold to

$$(\sigma_{pd}/E)^{1/n} = B[E - (E_{th})_L] \quad (23)$$

with $n = 1/2(2l+1)$. The best fit was obtained for $n = 3/2$ (i.e., $l = 1$, see Eqs. (15) and (23)) and $(E_{th})_L = 1.51$ eV. Using this value, Eq. (20), and literature values of $(EA)_G$ Faidas et al. concluded that the electron affinity of C_6F_6 is lowered in liquid TMS by ~ 0.4 eV compared to its isolated-molecule value.

Finally, photodetachment studies on a number of cluster negative ions aided considerably our understanding of the energetics of the process. Experimental studies on the vertical values of EA (photodetachment thresholds; e.g., see Refs. 45,46) revealed the existence of the expected (Fig. 13, and Refs. 6 and 11) specific size variations and the smooth (increase) transition to the bulk property as the cluster size is increased. This is clearly shown in Fig.

Figure 19. Schematics of the photodetachment technique illustrating: (a) the laser interaction region, (b) the type of signal measured, and (c) the laser intensity and negative ion density profiles (see the text and Ref. 44).

Figure 20. The absolute photodetachment cross section $\sigma_{pd}(E)$ (right-hand side Y axis) of $C_6F_6^-$ in tetramethylsilane as a function of the photon energy, E , and a linear least squares fit of $(\sigma_{pd}/E)^{2/3}$ (left-hand side Y axis) for $E < 1.95 \text{ eV}$. The intercept with the X axis gives a threshold energy E_{th} of 1.51 eV (Ref. 44).

21 where the measured EA values of Cu_n clusters are plotted as a function of cluster size⁴⁵. Odd copper clusters are seen to have substantially lower EA than adjacent even clusters and this continues at least through Cu_{17} . It was pointed out⁴⁵ that the LUMO (lowest unoccupied molecular orbital) of the even clusters would be expected to be strongly antibonding and the corresponding negative ion more weakly bound than if the electron were to be placed in the half-filled nonbinding HOMO of an odd cluster.⁵

The electron affinity, $\text{EA}(n)$, of the larger clusters would be predicted to increase as [e.g., see Ref. 6)

$$\text{EA}(n) = \text{EA}(R_c) = \text{EA}(\infty) - a \frac{e^2}{R_c} \quad (24)$$

where $\text{EA}(\infty)$ is the bulk band energy and $a = 1/2$ for the polarization and $a = 5/8$ for the metal droplet model of negative metal clusters. The predictions of (24)--as in the case of (5), (10), and (20) we have seen earlier--depend on the accuracy of R_c .

Figure 21. Experimental electron affinities for Cu_n compared with predictions of the classical spherical drop model ■ (Ref. 45); I (Ref. 47); --- and — predicted using Eq. (24) and $a = 5/8$, $\text{EA}(\infty) = 4.65$ eV, $R = n^{1/3} r_0$ (---) and $R = n^{1/3} r_0 + \Delta r$ (—) with r_0 (half the average distance between the atoms in the bulk) = 1.41 Å and Δr (correction for orbital overlap among bounded atoms) = 0.53 Å (from Ref. 45).

⁵An opposite alternation is exhibited by the ionization threshold energy I (i.e., $I_{\text{odd}} < I_{\text{even}}$) (e.g., see Ref. 11).

REFERENCES

1. Christophorou, L. G., and Siomos, K., Interphase Physics: Linking Knowledge on Electron-Molecule Interactions in Gases to Knowledge on Such Processes in Condensed Matter, in "Electron-Molecule Interactions and Their Applications," Christophorou, L.G., Ed., *Academic Press*, Orlando, 1984, Vol. 2, Chapt. 4.
2. Christophorou, L. G., Gas/Liquid Transition: Interphase Physics, in "The Liquid State and Its Electrical Properties," Kunhardt, E. E., Christophorou, L. G., and Luessen, L. H., (Eds.), *Plenum Press*, New York, 1988, pp. 283-316.
3. Christophorou, L. G., Radiation Interactions in High-Pressure Gases, in "Physical and Chemical Mechanisms in Molecular Radiation Biology," Glass, W. A. and Varma, N. M., Eds., *Plenum Press*, New York, 1991, pp. 183-230.
4. Kunhardt, E. E., Christophorou, L. G., and Luessen, L. H., (Eds.), "The Liquid State and Its Electrical Properties," *Plenum Press*, New York, 1988.
5. Freeman, G. R., (Ed.), "Kinetics of Nonhomogeneous Processes," *Wiley-Interscience*, New York, 1987.
6. Jortner, J., Cluster Size Effects, *Z. Phys. D* 24:247 (1992).
7. Kappes, M. M., Schär, M., Radi, P., and Schumacher, E., On the Manifestation of Electronic Structure Effects in Metal Clusters, *J. Chem. Phys.* 84:1863 (1986).
8. Rademann, K., Reactivity and Electron Structures of Isolated Clusters, *Ber. Bunsenges. Phys. Chem.* 94:1295 (1990); Photoelectron Spectroscopy and UV/VIS-Photoabsorption Spectroscopy of Isolated Clusters, *Z. Phys. D* 19:161 (1991).
9. Leopold, D. G., Ho, J., and Lineberger, W. C., Photoelectron Spectroscopy of Mass-Selected Metal Cluster Anions. I. Cu_n^- , $n = 1-10$, *J. Chem. Phys.* 86:1715 (1987).
10. Märk, T. D., Free Electron Attachment to van der Waals Clusters, *Intern. J. Mass Spectr. Ion Proc.* 107:143 (1991).
11. Bonačić-Koutecký, V., Fantucci, P., and Koutecký, J., Quantum Chemistry of Small Clusters of Elements of Groups Ia, Ib, and IIa: Fundamental Concepts, Predictions, and Interpretation of Experiments, *Chem. Rev.* 91:1035 (1991).
12. Illenberger, E., Electron Attachment Reactions in Molecular Clusters, *Chem. Rev.* 92:1589 (1992).
13. Christophorou, L. G., "Atomic and Molecular Radiation Physics," *Wiley-Interscience*, New York, 1971.
14. Christophorou, L. G. (Ed.), "Electron-Molecule Interactions and Their Applications," *Academic Press*, Orlando, 1984, Vols. 1 and 2.
15. Christophorou, L. G., The Lifetimes of Metastable Negative Ions, *Adv. Electr. Electron Phys.* 46:55 (1978).
16. Sanche, L., Primary Interactions of Low Energy Electrons in Condensed Matter, in "Excess Electrons in Dielectric Media," Ferradini, C., and Jay-Gerin, J.-P., Eds., *CRC Press*, Boca Raton, 1991, pp. 1-42.
17. Inokuti, M., How is Radiation Energy Absorption Different Between the Condensed Phase and the Gas Phase?, in "Radiation Effects and Defects in Solids," Gordon and Breach, U.K., 117, (1991), pp. 143-162.

18. LaVerne, J. A. and Mozumder, A., Effect of Phase on the Stopping and Range Distribution of Low-Energy Electrons in Water, *J. Phys. Chem.* 90:3242 (1986).
19. Ashley, J. C., Stopping Power of Liquid Water for Low-Energy Electrons, *Rad. Research* 89:25 (1982).
20. Michaud, M. and Sanche, L., Total Cross Sections for Slow-Electron (1-20 eV) Scattering in Solid H₂O, *Phys. Rev. A* 36:4672 (1987).
21. Hunter, S. R., Carter, J. G., and Christophorou, L. G., Low-Energy Electron Drift and Scattering in Krypton and Xenon, *Phys. Rev. A* 38:5539 (1988).
22. Dmitrenko, V. V., Romanyuk, A. S., Suchkov, S. I. and Uteshev, Z. M., Electron Mobility in Dense Xenon Gas, *Sov. Phys. Tech. Phys.* 28:1440 (1983).
23. Miller, L. S., Howe, S. and Spear, W. E., Charge Transport in Solid and Liquid Ar, Kr, and Xe, *Phys. Rev.* 166:871 (1968).
24. Sakai, Y., Nakamura, S., and Tagashira, H., Drift Velocity of Hot Electrons in Liquid Ar, Kr, and Xe, *IEEE Trans. Electr. Insul.*, EI-20:133 (1985).
25. Bader, G., Perluzzo, G., Caron, L. G., and Sanche, L., Elastic and Inelastic Mean-Free Path Determination in Solid Xenon from Electron Transmission Experiments, *Phys. Rev. B*, 26:6019 (1992).
26. Faidas, H., Christophorou, L. G., McCorkle, D. L., and Carter, J. G., Electron Drift Velocities and Electron Mobilities in Fast Room-Temperature Dielectric Liquids and Their Corresponding Vapors, *Nucl. Instr. Meth. Phys. Res.* A294:575 (1990).
27. Stephens, J. A., Comment on Electron Mobility in the Liquid Isomeric Pentanes, *J. Chem. Phys.* 84:4721 (1986).
28. Fano, U., Studies of Slow Electron Action on Condensed Media, *Radiat. Phys. Chem.* 32:95 (1988); Short- and Long-Range Interactions of Slow Electrons in Condensed Matter: Effects of Reflection and Transmission, *Phys. Rev. B* 36:1929 (1987).
29. Mills, D. L., Resonant Scattering of Slow Electrons in Molecular Solids: Suppression of the Elastic Beam, *Phys. Rev. B* 45:36 (1992); Resonant Scattering of Electrons in the Presence of Coupling to Phonons, *Phys. Rev. B* 45:13221 (1992).
30. Henkes, W. and Mikosch, F., The Effective Cross Section for Ionization by Electrons of Molecules in Hydrogen Clusters, *Int. J. Mass Spectr. Ion Phys.* 13:151 (1974).
31. Derenzo, S.E., Mast, T. S., Zaklad, H., and Müller, R.A., Electron Avalanche in Liquid Xenon, *Phys. Rev. A* 9:2582 (1974).
32. Schmidt, W. F., Electron Conduction Processes in Dielectric Liquids, *IEEE Trans. Electr. Insul.* EI-19:389 (1984).
33. Raz, B. and Jortner, J., Energy of Quasi-Free Electron State in Liquid and Solid Rare Gases, *Chem. Phys. Lett.* 4:155 (1969).
34. Faidas, H. and Christophorou, L. G., Laser Multiphoton Ionization of Aromatic Molecules in Nonpolar Liquids, *Rad. Phys. Chem.* 32:433 (1988).
35. Faidas, H., Christophorou, L. G., Datskos, P. G., and McCorkle, D. L., The Ionization Threshold of N, N, N', N'-Tetramethyl-p-phenylenediamine in Dense Fluid Ethane; Effects of Fluid Density and Temperature, *J. Chem. Phys.* 90:6619 (1989).

36. Steinberger, I. T., Photoconductivity, Conduction Electron Energies, and Excitons in Simple Fluids, in Ref. 4, p. 235.
37. Springett, B. E., Jormer, J., and Cohen, M. H., Stability Criterion for the Localization of an Excess Electron in a Nonpolar Fluid, *J. Chem. Phys.* 48:2720 (1968).
38. Bakale, G., Sowada, U., and Schmidt, W. F., Effect of an Electric Field on Electron Attachment to SF_6 , N_2O , and O_2 in Liquid Argon and Xenon, *J. Phys. Chem.* 80:2556 (1976).
39. Jaffke, T., Hashemi, R., Christophorou, L. G., and Illenberger, E., Mechanisms of Anion Formation in O_2 , O_2/Ar , and O_2/Ne Clusters; the Role of Inelastic Electron Scattering, *Z. Phys. D* 25:77 (1992).
40. Hashemi, R., Jaffke, T., Christophorou, L. G., and Illenberger, E., Role of Inelastic Electron Scattering by N_2 in the Formation of $(\text{O}_2)_n^-$ Anions in Mixed O_2/N_2 Clusters, *J. Phys. Chem.* 96:10605 (1992).
41. Christophorou, L. G., Electron Attachment and Detachment Processes in Electronegative Gases, *Contrib. Plasma Physics* 27:237 (1987).
42. Geltman, S., Theory of Threshold Energy Dependence of Photodetachment of Diatomic Molecular Negative Ions, *Phys. Rev.* 112:176 (1958).
43. Sowada, U., and Holroyd, R. A., Laser Photodetachment Spectra of C_6F_6^- in Nonpolar Liquids, *J. Phys. Chem.* 84:1150 (1980).
44. Faidas, H., Christophorou, L. G., and McCorkle, D. L., Laser Photodetachment in Liquids: C_6F_6^- in Tetramethylsilane, *Chem. Phys.* 193:487 (1992).
45. Leopold, D. G., Ho, J., and Lineberger, W. C., Photoelectron Spectroscopy of Mass-Selected Metal Cluster Anions I. Cu_n^- , $n=1-10$, *J. Chem. Phys.* 86:1715 (1987).
46. DeLuca, M. J., Han, C.-C., and Johnson, M. A., Photoabsorption of Negative Cluster Ions Near the Electron Detachment Threshold: A Study of the $(\text{O}_2)_n^-$ System, *J. Chem. Phys.* 93:268 (1990).
47. Zheng, L.-S., Karner, C. M., Brucat, P. J., Yang, S. H., Pettiette, C. L., Craycraft, M. J., and Smalley, R. E., Photodetachment Studies of Metal Clusters: Electron Affinity Measurements for Cu_n , *J. Chem. Phys.* 85:1681 (1986).

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