DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Final Performance Report for

DOE DE-FG05-85ER60356

**Interaction of Slow Electrons with High-Pressure Gases ('Quasi-liquids');
Synthesis of Our Knowledge on Slow Electron-Molecule Interactions**

Contract Year Ending August 14, 1987

D. L. McCorkle and L. G. Christophorou, Principal Investigators

Department of Physics and Astronomy
The University of Tennessee
Knoxville, Tennessee 37796-1200

D. L. McCorkle
Research Assistant Professor

RECEIVED

MAR 23 1994

OSTI

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

I. Publications

- DOE/ER/60356-2 "Electron Attachment to F₂," D. L. McCorkle, L. G. Christophorou, A. A. Christodoulides, and L. Pichiarella, J. Chem. Phys. 85, 1966-1970 (1986).
- DOE/ER/60356-3 "The Ionization Threshold of N, N, N', N'-tetramethyl-*p*-phenylenediamine in Dense Fluid Ethane: Effects of Fluid Density and Temperature," H. Faidas, L. G. Christophorou, P. G. Datskos, and D. L. McCorkle, J. Chem. Phys. 90, 6619-6626 (1989).
- DOE/ER/60356-4 Final Progress Report (March 15, 1986 - August 14, 1987).

II. Importance and Scope

A crucial step in our efforts to develop not only a coherent picture of radiation interaction with matter, but also to understand radiation effects and mechanisms, as well as the effects of chemical pollutants and toxic compounds, is to relate the often abundant knowledge on isolated molecules (low pressure gases) to that on liquids or solids. To understand the roles of the physics and chemical properties of molecules in biological reactions, we must know how these "isolated-molecule" properties change as molecules are embedded in gradually thicker and thicker (denser and denser) gaseous and, finally, liquid environments.

The work initiated by us both at the Physics Department of The University of Tennessee and at the Oak Ridge National Laboratory addresses itself to this question. At both places, high pressure (40 to ~8000 kPa) electron swarm experiments are currently in operation yielding information as to the effects of the density and nature of the environment on fundamental electron-molecule interaction processes at densities intermediate to those corresponding to low pressure gases and liquids, and the gradual transition from "isolated molecule" to "condensed phase" behavior.

Additionally, there is a pressing need for basic physical data on the electronic states of atmospheric halocarbons in general, and of polycyclic aromatic hydrocarbons in particular. Such data are of special significance because of the occurrence of these molecules in the atmosphere, and are presently lacking. We have seen that low energy electrons are very disruptive for many halocarbons and perfluorocarbon compounds, and the fragmentation products released are potentially hazardous for the environment. Halocarbons are usually photochemically reactive and some of their fragments might attach the

atmospheric ozone (O_3). Also the role of electron attachment to hydrated and dimer molecules at low gas temperature is essential for the modelling of reaction pathways in the upper atmosphere. We attempt to obtain such knowledge experimentally at high and low temperature.

We have concentrated our efforts for the past several years on the effects of changes of the gaseous density on fundamental physical properties of molecules in an effort to relate gaseous and liquid electron interaction mechanisms. So far we have studied the effects of density on electron mobility, electron attachment, and electron scattering at low energy. Another important physical process that is expected to be affected profoundly in going from gas to liquid is photionization and its energetics. We have initiated a joint study with Oak Ridge National Laboratory of the effects of gas density on the photoionization process.

II. Final Performance Report

A. Electron Attachment to F_2

The rate constant for electron attachment to F_2 was measured at 233 K, 298 K and 373 K in the buffer gas nitrogen over the mean energy range 0.04-0.75 eV and in the buffer gas argon at 298 K over the mean energy range 0.4 - 2.95 eV. The rate constant function attains a maximum value at ~ 0.04 eV and decreases monotonically with increasing mean energy above thermal energy; the magnitude of the rate constant increases only slightly with increasing temperature.

The electron attachment rate constant for F_2 is quite large at low energy; it is much larger than that of the heavier halogens for mean electron energy less than 1 eV. The measured rate constants for F_2 were compared with those of others both experimental and theoretical and found to be in good general agreement.

The cross section for electron attachment to F_2 was unfolded from the measured rate constant and shows a main maximum at ~ 0.0 eV; a shoulder at ~ 0.5 eV and a weak maximum at ~ 1.1 eV. Our swarm-unfolded cross sections generally show good agreement with electron-beam determined cross sections when both techniques probe the same processes. However, due to the large uncertainty in the present rate constant measurements, due to the difficulty in the measurement of the F_2 concentration, the swarm-unfolded cross sections are approximate and may lack uniqueness. It is clear that the cross section maximizes at ~ 0.0 eV and decreases sharply with increasing energy above thermal. The shoulder at ~ 0.5 eV and the weak maximum at ~ 1.1 eV are less certain.

The unfolded cross section was also compared with those obtained from semi-empirical and *ab initio* calculations. The theoretical calculations predicted correctly the

small increase in the rate constants with temperature we observed. Also good several agreement is found in the overall magnitude and energy dependence of the present cross section and those obtained by theory. However, the theory does not indicate the presence of the strong "zero" energy process; the existence of which is firmly established by both the present swarm and earlier beam studies.

B. The Ionization Threshold of N, N, N', N'-tetramethyl-*p*-phenylenediamine in Dense Fluid Ethane

We measured the ionization threshold of N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD) in ethane over the density range 0.15-13.3 M/l and over the temperature range 295-413 K using a multiphoton ionization conductivity technique. A new ionization cell was built and used in the present experiments, that could be pressurized to 150 atm at 423 K. It consists of a six-way solid stainless steel cube with two sapphire windows and electrical feedthroughs. The electrodes are two parallel plates 3 cm in diameter at a distance of 0.5 cm apart. The applied electric fields were relatively high (typically 4-8 kV/cm) to avoid space charge effects. Because of the high values of the applied electric fields, the ethane pressure was kept $>\sim 3$ atm to avoid charge amplification and breakdown. Also, because of the low vapor pressure of TMPD (melting point = 323 K; vapor pressure ≈ 3 Torr at 373 K), the gas-phase measurements were carried out at $T \geq 323$ K. A pair of thermocouples were mounted onto the cell and permitted measurement and control of the temperature to within ± 1 K. The ethane density was calculated to an accuracy of $\pm 3\%$ from the measured pressure and temperature and literature PVT (pressure-volume-temperature) data.

The TMPD (Aldrich; 99% pure) was purified further with successive fractional distillations and the ethane (Alphagaz; 99% pure) was degassed with freeze-pump-thaw cycles without further treatment.

The ionization threshold I_F was determined with the multiphoton ionization conductivity technique as follows: The photoionization signal I_s was measured as a function of the laser intensity I_l at 5 nm intervals in the wavelength region where the two-photon ionization onset of TMPD is expected to lie (300-500 nm depending on the temperature and density of ethane). From these measurements the slope $S = d \log I_s / d \log I_l$ was determined as a function of the laser wavelength. The two-photon ionization (TPI) onset was identified with the wavelength at which the two- and three-photon ionization processes contribute, respectively, 10% and 90% of the measured photoconductivity signal. The uncertainty in the determination of the onset (and thus I_F) was ~ 0.05 eV. The ratio of the three-photon ionization signal just above the TPI onset to the two-photon ionization signal just below the onset was $\sim 10^{-3}$. The measurements were carried out at laser intensities, signal levels, and applied electric field values such that they were free from the effects of laser volume saturation and space charge formation.

The I_F was found to be a function of both density and temperature in the ranges studied. At fixed temperature (≈ 373 K), I_F was found first to decrease with increasing density and then to level off at densities of ~ 10 M/ ℓ and temperature, $T = 295$ K, the I_F was found to increase with increasing density. At constant density ($\rho = 5.90$ M/ ℓ) I_F decreased with increasing T between 323 and 413 K.

The ionization threshold of a molecule in the liquid phase (I_L) or, more generally, in a dense fluid (I_F) is usually given by

$$I_L(\text{or } I_F) = I_G + P^* + V_0 \quad (1)$$

where I_G is the adiabatic ionization threshold in the gas phase (low density limit), P^* is the polarization energy of the positive ion, and V_0 is the energy of the quasifree electron at the bottom of the conduction band of the fluid medium.

Generally, one would expect both P^* and V_0 and through these I_F to depend on the density and temperature of the fluid medium.

We obtained calculated V_0 values for ethane by numerically solving the appropriate Schrödinger equation using an effective potential in which we assume a local screening of the electron and neglect the Coulomb and exchange interaction of the excess electron with the molecules around the Wigner-Seitz cavity. We used the Born formula to estimate P^* , assuming that the positive ion (created by the photoionization process) resides at the center of a spherical cavity and is motionless.

The calculated V_0 values for ethane and the estimated values of P^* were used to determine the ionization threshold I_F of TMPD as a function of the ethane density, ρ . In this exercise we used $I_G = 5.90$ eV. The calculated values of the I_F as a function of ρ for various hard core radii $\langle \bar{a} \rangle$ were compared with the experimental data. We saw that the predicted values for I_F using hard-core radii values $\langle \bar{a} \rangle = 1.38\text{-}1.42$ Å describe reasonably well the experimental values of I_F at $T = 373$ K. Additionally, by assuming that V_0 varies with T through the dependence of $\langle \bar{a} \rangle$ on T (P^* was taken to be T independent) we obtained a dependence of I_F on T . We saw that the prediction of the present analysis is consistent with the observed dependence of I_F on T .

*budget + reprints removed,
cb*

DATE

FILMED

4 / 15 / 94

END