Ionization Cross Sections of F_2 and Cl_2 by Electron Impact*

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A measurement has been made of the electron impact ionization cross section of F_2 and Cl_2 over the energy range 15–100 V. Both species exhibit a maximum cross section at electron energies near 100 eV, the maximum values being approximately 1.5×10^{-16} and 7.0×10^{-16} cm² for F_2 and Cl_2, respectively. The measurement in Cl_2 fits an observed correlation between the maximum cross section and the square root of the polarizability. This correlation seems to apply to a wide variety of atomic and molecular species. Based on this correlation we estimate the polarizability of F_2 to be approximately 8×10^{-25} cm³.

INTRODUCTION

We have recently had occasion to mass analyze some gas mixtures containing molecular fluorine or chlorine dilute in argon. Unfortunately, there does not appear to be any experimental or theoretical cross section data available for electron impact ionization of the halogen molecules at low electron energies up to the peak cross section (typically 100 eV for most atomic and molecular species). As a result we have measured these cross sections using a commercial residual gas analyzer incorporating a quadrupole mass filter. Although the accuracy and energy resolution of this type of measurement are not very high, the apparatus does permit a reasonable value of the peak ionization cross section.

EXPERIMENT AND TECHNIQUE

A commercial gas analyzer[1] was used to measure ionization cross sections relative to the previously determined cross section for the ionization of Ar. The instrument incorporates a quadrupole mass filter and a low energy electron gun with the electron energy being variable from 0 to 100 V and with a probable uncertainty of several volts in the electron energy. The ion signal is detected with a 14 stage Be–Cu electron multiplier.

The basis of the experiment is the measurement of the relative ion signals for the halogen and argon obtained from ionization of a mixture of these species. The ion current is directly proportional to the ionization cross section and the electron current. Since relative measurements are made, it is only necessary to record the ion current ratio and the electron energy.

The gases were mixed in a 6 liter chamber separated from the quadrupole system by a 1/4 mm aperture. Prior to the measurements the gas chamber walls were passivated with fluorine over a period of several hours. During this process, the metal oxide surfaces are replaced by fluorides. After passivation this chamber could be filled with fluorine to the desired pressure which then remained essentially constant whereas before passivation the pressure would rapidly decrease due to absorption at the walls. The pressure was measured with a capacitance monometer,[2] and we worked with mixture pressures typically in the range of 1 torr

in the chamber. This resulted in pressures of the order of 10^{-5} torr in the mass spectrometer system which was continuously pumped by a cold trapped, oil diffusion pump.

The experimental technique was verified by measurements in Ne/Ar mixtures by comparing the experimental ion signal ratios of the singly charged ions with the previously measured cross sections of these species.[3] Because Ne^+ and Ar^{2+} have the same mass to charge ratio, it was necessary to correct for the excitation of Ar^{2+} and this was done by separate measurements in pure argon. These experimental results were in agreement to within 15% of the published data after applying a 3 V shift to the energy scale. This correction was required to account for the voltage drop across the filament and contact potentials in the system. This voltage shift was also verified by measurements of the ion current variation with energy near threshold in water vapor. This data also required a 3 V shift to correlate with the known appearance potential in water, 12.6 V.[4]

RESULTS AND DISCUSSION

The experimental results for Cl_2 and F_2 are plotted in Fig. 1 over the energy range of 15–100 eV. Also shown for comparison is the previously determined cross section variation in Ar as measured by Rapp and Englander-Golden.[5] The dashed lines are the average of several measurements. The experimental variation was less than ±7%. These data have been corrected for the 3 V energy shift to lower energies, as described above. These data were obtained over the entire voltage range with a single gas mixture, and the experiment was subsequently repeated with a fresh mixture.

The data are subject to several errors:

(1) The relative mole fraction of the halogen and the argon constituents were measured with the capacitance monometer during filling of the gas chamber. This measurement is accurate to 5%.

(2) Mass discrimination effects can arise due to diffusive separation through the orifice isolating the mass spectrometer, to a variation with mass in the ion detection efficiency or to mass discrimination effects in the quadrupole. The diffusive separation is expected to be

very small as a result of the similar species masses.[6] The ion detection efficiency is probably nearly invariant with mass because of the large acceleration applied to the ions, 2500 V. Measurements in He/Ar and Ne/Ar mixtures gave the expected[5] ion signal ratios thereby precluding any significant discrimination effects in the quadrupole.

(3) The energy spread in the electron gun is not known. This effect should be negligible near the peak cross section where the energy dependence is small.

Based on these error sources, we believe the peak cross sections to be accurate to ±15% relative to the Ar data.

We are not aware of any other measurements of the maximum ionization cross section of any halogen by electron impact. In an attempt to order the maximum cross section results, we have observed a striking correlation of these cross sections with the square root of the species polarizability.[7] This is shown in Fig. 2 for a wide variety of atomic and molecular species. The cross section data were obtained from the survey of Kieffer,[3] and the polarizability data were taken from several sources.[8,9] The only species which do not appear to obey this correlation are the alkali metals which show the largest polarizability of all atoms.[8] One general feature of the alkali cross sections is that they reach a maximum at very low energies. The other cross sections generally reach a peak in the vicinity of 100 eV.

FIG. 2. Correlation of maximum ionization cross sections by electron impact with the square root of the species polarizability. The present experimental cross section measurement for Cl₂ is shown together with the estimated error bar.

For the alkali metals the interaction at such low energies is probably influenced by the detailed atomic and molecular structure. For the higher energy cases the interaction will be much less sensitive to any detailed structure. In this case one would expect the interaction potential to vary with the polarizability. In the absence of any other effects this leads to a cross section dependence which varies with the square root of the polarizability as first described by Langevin.[10]

It should be emphasized that the simple relationship which we have empirically observed is between the maximum of the electron cross section and the square root of the polarizability.

Also shown in Fig. 2 is our measured value of the Cl₂ maximum cross section which is in reasonable agreement with this correlation based on its previously measured polarizability.[9] We are unaware of any measurement of the polarizability of F₂, but based on the observed correlation and our present cross section measurement, we would estimate that the polarizability of F₂ is ∼8 × 10⁻²⁵ cm³.
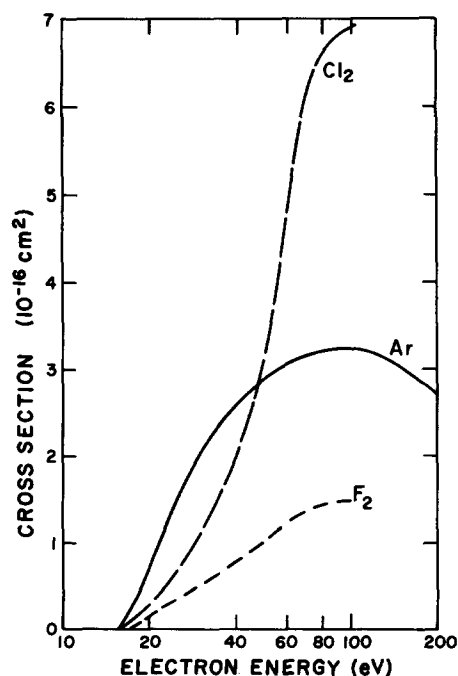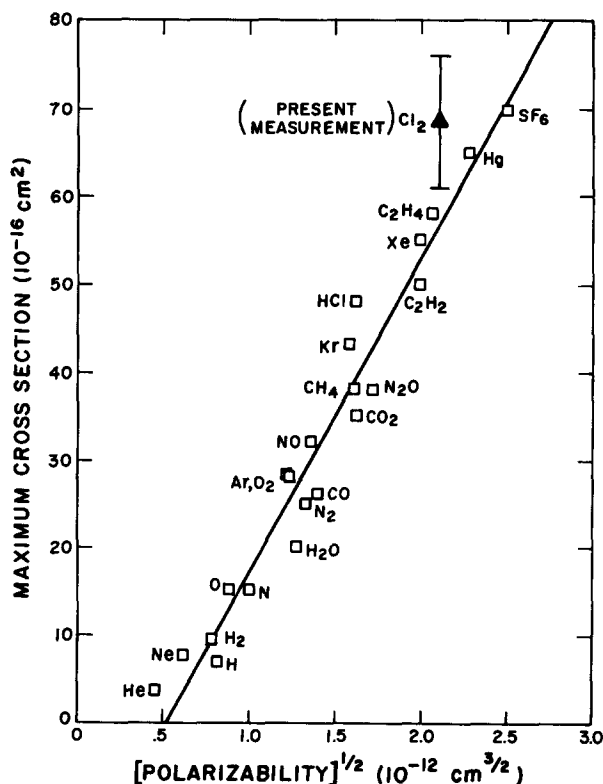

FIG. 1. Variation of the ionization cross sections with electron energy. The dashed lines are the present experimental measurements obtained relative to the argon cross section which is shown by the solid line (Ref. 5).

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Density and Viscosity of Liquid ND₃*

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The density and viscosity of liquid ND_3 have been measured over the temperature range from $+30°$ to $-25°$ and compared with the density and viscosity of liquid NH_3. At any given temperature, the ratio of densities ρ_{ND_3}/ρ_{NH_3} is 1.187 ± 0.001 and the ratio of viscosities η_{ND_3}/η_{NH_3} is 1.20 ± 0.01. The fact that both ratios are independent of temperature suggests that the strengths of intermolecular interactions are essentially the same in the two liquids and that the density and viscosity differences are to be attributed to differences in molecular size and mass. The density ratio indicates that the molecular volume of NH_3 in the liquid is $\sim 1\%$ larger than that of ND_3 while the viscosity ratio indicates that the viscosity varies directly as M/V_m (V_m = molar volume) for these two liquids.

I. INTRODUCTION

For NMR relaxation studies in liquid NH_3 and ND_3, the liquid viscosity is an important parameter since it influences certain motional correlation times which may be important in determining the relaxation rate. The viscosity of liquid NH_3 has been measured by several groups[1-3] over a wide range of temperatures and published values are readily available. For liquid ND_3, on the other hand, the only published values to our knowledge are those due to Hutchison and O'Reilly[4] who, in a study of viscosities of potassium–ammonia solutions, list values for the viscosity of their pure solvent ND_3 at $+20.0$, 0.0, and $-33.6°C$. We therefore decided to make a more complete set of measurements covering the temperature range from $+30$ to $-69°C$ using a modified Ostwald viscometer of the type described by Hennel and Krynicki[5]. Since the method requires that the density of the liquid be known at the temperature of the viscosity measurement, and since the only published density values of which we are aware are those of Hutchison and O'Reilly[6] at $+20.0$, 0.0, and $-33.7°C$, we have made a more complete set of density measurements covering the temperature range from $+20$ to $-26°C$.

II. EXPERIMENTAL

A. Density Measurements

The density of liquid ND_3 under its equilibrium vapor pressure was measured in the pycnometer shown in Fig. 1. The pycnometer was made by sealing a 2 ml Pyrex, heavy-walled pipette ($\approx$2 mm wall thickness) to a piece of heavy-walled ($\approx$3 mm wall thickness) 19 mm o.d. Pyrex tubing and forming a rounded bottom on the tube as shown. The pipette stem is graduated to 0.01 ml and can therefore be read quite easily to ± 0.005 ml. The pycnometer volume was calibrated by weighing the H_2O required to fill it to various levels on the stem. The level was read with the pycnometer immersed in a bath whose temperature was known to $\pm 0.1°C$. At temperatures in the region of 23–24°C, the volume in ml as a function of liquid level in the pycnometer stem is given by

$$V = 7.2677 + 1.007(1.885 - r), \qquad (1)$$

where r is the reading on the pipette scale at the level of the liquid meniscus in the pycnometer stem. Duplicate calibrations of the pycnometer were in agreement to better than 0.02%. As is evident from Eq. (1), the volume of the pycnometer bulb to the 1.885 reading on the stem is 7.2677 ml. The constant factor of 1.007 in the second term reflects the fact that the pipette bore is uniform over its entire length but the scale markings yield volumes which are too low by 0.7% at room temperature.

The pycnometer was filled with NH_3 by condensing NH_3 vapor from a system of known volume filled to the requisite pressure at room temperature to provide roughly the amount of NH_3 needed to fill the pycnometer with liquid to a level near $r = 0$. The pycnometer