

Electron impact ionization cross sections of F_2 and Cl_2

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Total ionization cross sections for the production of positive ions by electron impact ionization of F_2 and Cl_2 have been measured over the energy range 12 to 100 eV. The technique involves the ionization of a modulated molecular beam with cross sections determined by measurement of a calibrant gas. Mass spectrometric measurements insured that impurities did not contribute to the measured ion currents. The 70 eV ionization cross section of F_2 was found to be $1.1 \times 10^{-16} \text{ cm}^2$, and the 70 eV ionization cross section of Cl_2 was $7.1 \times 10^{-16} \text{ cm}^2$.

I. INTRODUCTION

Absolute ionization cross section measurements have generally been confined to the rare gases and to the more chemically stable, simple diatomic and polyatomic molecules.¹⁻¹⁰ The experimental difficulties encountered in measuring the cross sections of relatively unreactive species are considerable, and it is therefore not surprising to find only one report of the measurement of the ionization cross sections of molecular fluorine and chlorine.¹¹

Accurate measurements of the electron impact ionization cross sections of reactive gases such as fluorine and chlorine in a conventional apparatus must necessarily be complicated by several factors. The principal of these factors would be an additional ion current due to the ionization of gas phase products of the chemical reactions of either fluorine or chlorine with the materials from which the apparatus is constructed. Absolute pressure measurements may also be affected by these same reactions, and chemical attack of thermionically emitting filaments must also be considered as another source of experimental uncertainties.

We feel that another cross section measurement on fluorine and chlorine is warranted for the intrinsic scientific value, and also because these molecules are of practical value in ionized media for material processing. In this study we employ a molecular beam apparatus¹² as a gas inlet, and the ion source of a mass spectrometer as a total ion current detector. The use of a specially constructed, well collimated molecular beam source to supply halogen molecules to the ionization region circumvents many of the experimental difficulties mentioned above, but it also introduces the requirement that the flux of molecules into the ionizer must be accurately calibrated. We have therefore explored the use of a free-jet molecular beam operating at low Mach numbers as a means of introducing gases accurately and reproducibly into an ionizer. The free-jet technique might be used in place of conventional methods for a wide variety of reactive or unstable molecular species.

II. EXPERIMENTAL PROCEDURE

Measurement of ionization cross sections by a modulated molecular beam technique^{12,13} makes possible the removal of ion currents from background gases, which

is quite useful when reactive materials are under study. Total modulated ion currents for 100 μA electron emission were measured by synchronous detection of the ac ion current at the final collimating plate in the ion source. The nominal electron energy range used was 12 to 102 eV. The F_2 and Cl_2 cross sections vs electron energy were calculated using argon, oxygen, and krypton calibrants. The experimental procedure was checked for accuracy by measuring the ionization cross sections of O_2 and Kr using Ar as a calibrant in this apparatus and comparing the results thus obtained with published values. In all cases, the ion currents for the calibrants were referenced to the data published by Rapp and Englander-Golden,¹ with a suitable adjustment to the electron energy scale.

Our apparatus has a 76 cm path from the nozzle to the ionizer center line, collimated into three stages of pumping. The mass spectrometer is a 21 cm radius single focusing magnetic instrument, with a nominal resolution of 1000. A diagram of the apparatus is given in Ref. 14, but some changes have been made for the purpose of this study, and require description. The chopper has been moved to the low pressure side of the skimmer, resulting in a modulated path length of 51.3 cm. The beam has a 0.58 cm diam. entry to the ionization region. To increase electron flux, the electron beam opening has been expanded to a 0.20 by 0.53 cm oval and covered with an 80% transparent steel mesh of 0.003 cm wires.

Molecular beam sources specifically designed for halogen gases were constructed. Fluorine beams were obtained from a nickel source¹⁵⁻¹⁸ with a 0.076 cm orifice diameter. Total ion current measurements were conducted with the source resistively heated to 100°C to prevent HF formation caused by the adsorption of water. A NiF_2 passivation layer was obtained by a flow of F_2 through the source at successively higher temperatures up to 800°C prior to the cross section experiments. The Cl_2 source was constructed from high density carbon¹⁸ with an orifice of 0.076 cm diam. and was also resistively heated to 100°C, to prevent any formation of HCl.

Commercially available gases (99.99% pure) were used without further purification except for a -78°C bath to trap water from the O_2 and Ar, and a NaF treat-

ment to remove HF from the F_2 . Mass spectrometric analysis of these gases under conditions identical to the total ion current measurements detected no impurities. Gas pressures determining the flow characteristics from the orifice were varied over the range of 2.0 to 10.0 Torr, as measured by a Monel capacitance manometer.

III. RESULTS AND DISCUSSION

A. Energy scale and dependence

Absolute cross-section normalization for our calibrants as a function of electron energy was based on the published data of Rapp and Englander-Golden.¹ Their work was chosen because it represents a consistent set of data on each of the calibrants chosen for this study over the electron energy range that is used in our instrument. Rapp and Englander-Golden's data are also the reference point for theoretical calculations¹⁹ of the atomic ionization cross sections (which we use for the ionization cross section of atomic fluorine in other studies); their data merge accurately with the higher energy data of Schram,⁹ and they are generally accepted as the standard in the field.

Our ion current data for a calibrant gas were converted to a cross section measurement at only one electron energy. This point was chosen to be the measured energy of 70 eV, where the energy dependence of the cross section is weak and only a small error would then be expected from the uncertainty in the experimental energy scale. The remaining cross section values were then determined from this 70 eV value, and the whole curve was then shifted to match the known energy dependence. Agreement between the two sets of data should be obtained if all the experimental variables are constant over the energy range.

An energy axis shift of -3.7 eV was necessary to match our experimental Ar curve with that of Rapp and Englander-Golden.¹ This energy shift can be reasonably attributed to contact potentials, the energy spread of the electron beam, and the potential drop across the filament. An additional shift of $+0.5$ eV for energies of 24 eV and below was necessary to compensate for the tendency of the ion source to extract ions from a different location in the ionizer chamber at low electron energy. An uncertainty of ± 1 eV in the measurement of the electron energy and a calculated half-width of 0.4 eV in the electron energy place an accuracy limit of ± 1.4 eV on the energy axis.

B. The method

The total ionization cross section of a species from an absolute measurement at any specific electron energy is given by

$$Q_T = I / (I_e \eta N_0 d), \quad (1)$$

where I is the ion current, I_e is the electron current, η is the efficiency of ion collection, N_0 is the number density of molecules in the ionization chamber, and d is the length of the effective electron path. Determination of the cross section of a test gas using the ion current ratio with a calibrant gas means the division of two

relationships expressed by Eq. (1), yielding

$$Q_T(1) = Q_T(2) \frac{I_1}{I_2} \frac{[I_e \eta(2) N_2 d]}{[I_e \eta(1) N_1 d]}. \quad (2)$$

Equation (2) can be reduced since d and I_e are identical in both sets of measurements:

$$Q_T(1) = Q_T(2) \frac{I_1}{I_2} \frac{N_2 \eta(2)}{N_1 \eta(1)}. \quad (3)$$

Equation (3) was used to compute the cross section of a test gas $Q_T(1)$ using $Q_T(2)$ of the calibrant gas and the total ion current ratio I_1/I_2 at each electron energy. The value of $Q_T(2)$ is the cross section for the calibrant gas measured at each electron energy after the one-point adjustment to the reference value described previously.

The successful application of Eq. (3) requires that we know the ratio of number densities N_2/N_1 in the ionizer, and the ratio of the collection efficiencies $\eta(2)/\eta(1)$. I_e and d must also cancel exactly. In our instrument the value of I_e is the total electron current collected by the Faraday cage and d is the path of the electron beam at its intersection with the molecular beam. Variations in either of these parameters from one series of measurements to the next are expected to be minimal, since the electron beam is precisely located and magnetically collimated, and the gas flux into the ionizer is sufficiently low to preclude significant effects due to surface chemistry (e.g., changes in secondary electron yield or creation of insulating films on conducting surfaces).

We must be able to derive the number density ratio of the molecules in the ionizer in order to obtain a cross section from Eq. (3). This ratio is obtainable from equations describing the flux of molecules on the axis of a molecular beam, provided the flow from the molecular beam nozzle (orifice) is characterized by a Mach number of 4 or larger. It is not necessary to know the actual flux, but the functional form of the flux relationships must be accurate for monatomic and diatomic gases. The flux at any point off the beam axis (within the ionizer) is essentially the same as that on the center line, since the geometry of the instrument produces a maximum angular divergence of 0.45° across the detector. In other words, the number density is essentially constant at any point within the ionizer, and the classical problem of optimizing the intersection of the molecular beam with the ionizing electron beam is minimized.

An orifice diameter of 0.076 cm and a mean free path of 3.5×10^{-3} cm for Ar translate to a Knudsen number of 0.046 at the lowest pressure used in these experiments. The terminal Mach number for a supersonic argon beam is given by²⁰

$$M_T = 1.17(K_n)^{-0.4}, \quad (4)$$

where M_T is the terminal Mach number and K_n the Knudsen number. Equation (4) yields $M_T = 4$. A similar calculation for Cl_2 results in an M_T of 4.7. The gas flow from the orifice is in the free-jet regime, even at the lowest pressures used. The center line flux in the ionizer is therefore described by²⁰

$$f = N/v = C_v A_T V_0 N_0 (\pi x^2)^{-1}, \quad (5)$$

where f is the center line flux, N is the number density in the ionizer, v is the final velocity, C_γ is a constant equal to 1.085 for monatomic gases of $\gamma=5/3$ (γ is the ratio of specific heats C_p/C_v), and equal to 0.7687 for diatomic gases of $\gamma=7/5$. A_T is the area of the orifice, V_0 is the stagnation velocity [$V_0=(2kT/m)^{1/2}$], N_0 the number density behind the orifice, and x the beam center line distance from the orifice to the point of interest. Equation (5) may be solved for N_1 and N_2 , substituted into Eq. (3), and simplified, yielding

$$Q_T(1) = Q_T(2) \frac{I_1}{I_2} \frac{C_\gamma(2)}{C_\gamma(1)} \left(\frac{M_1}{M_2}\right)^{1/2} \frac{v_1}{v_2} \frac{\eta(2)}{\eta(1)}. \quad (6)$$

The final velocity of the gas after expansion will be proportional to the mass of the gas molecule, and hence the final velocity ratio will reduce to $(M_2/M_1)^{1/2}$. (The nozzle temperature is the same for both gases and conversion of rotational or vibrational energy to translational energy is neglected for these low Mach number expansions.)

We are then left with

$$Q_T(1) = Q_T(2) \frac{I_1}{I_2} \frac{C_\gamma(2)}{C_\gamma(1)} \frac{\eta(2)}{\eta(1)}. \quad (7)$$

The remaining unknown ratio $\eta(2)/\eta(1)$ may be determined by recognizing that acceleration of ions from the 100 μ A magnetically collimated electron beam should be space-charge limited,²¹ and follow an $E^{3/2}/M^{1/2}$ dependence. The result for the same electric field for both gases is a simple expression for the determination of the ionization cross section of a test gas relative to that of a calibrant:

$$Q_T(1) = Q_T(2) \frac{I_1}{I_2} \frac{C_\gamma(2)}{C_\gamma(1)} \left(\frac{M_1}{M_2}\right)^{1/2}. \quad (8)$$

C. The results

The simplifications used to arrive at Eq. (8) from Eq. (6) were tested by the following:

TABLE I. 70 eV ionization cross sections.

Species	$Q_T (\times 10^{16} \text{ cm}^2)$	Calibrant	$Q_T (\times 10^{16} \text{ cm}^2)$
			Ref. 1
Kr	4.30	Ar	4.21
O ₂	2.33	Ar	2.38
	2.28	Kr	
			Ref. 11
F ₂	1.13	O ₂	1.2
	1.10	Ar	
	1.08	Kr	
Cl ₂	7.26	O ₂	5.3
	7.10	Ar	
	6.95	Kr	

(a) Measurement of the final velocities of the species after acceleration; the experimental error involved gave a range of values which bracketed the $(M_1/M_2)^{1/2}$ ratio, for each of the gas pairs chosen;

(b) Measuring the ion current ratio for Kr and Ar, and using the known 70 eV cross sections to compute the ratio $\eta(2)/\eta(1)$; we obtained 1.38, and $(M_2/M_1)^{1/2} = 1.45$.

Further checks of accuracy and self-consistency were made by determining the O₂ ionization cross section from argon and krypton calibrants. A large C_γ correction (1.41) occurs for both calibrants, but significantly different corrections are obtained from the $(M_1/M_2)^{1/2}$ term (0.62 and 0.89 for Kr and Ar). The 70 eV ionization cross sections measured for O₂ and Kr using Eq. (8) are given in Table I, along with the values reported by Rapp and Englander-Golden. Figure 1 shows plots of the following: $Q_T(\text{Ar})$ as a function of electron energy after the one-point calibration procedure, $Q_T(\text{Kr})$ as a function of electron energy, and $Q_T(\text{O}_2)$ as a function of electron energy. $Q_T(\text{Kr})$ and $Q_T(\text{O}_2)$ were determined

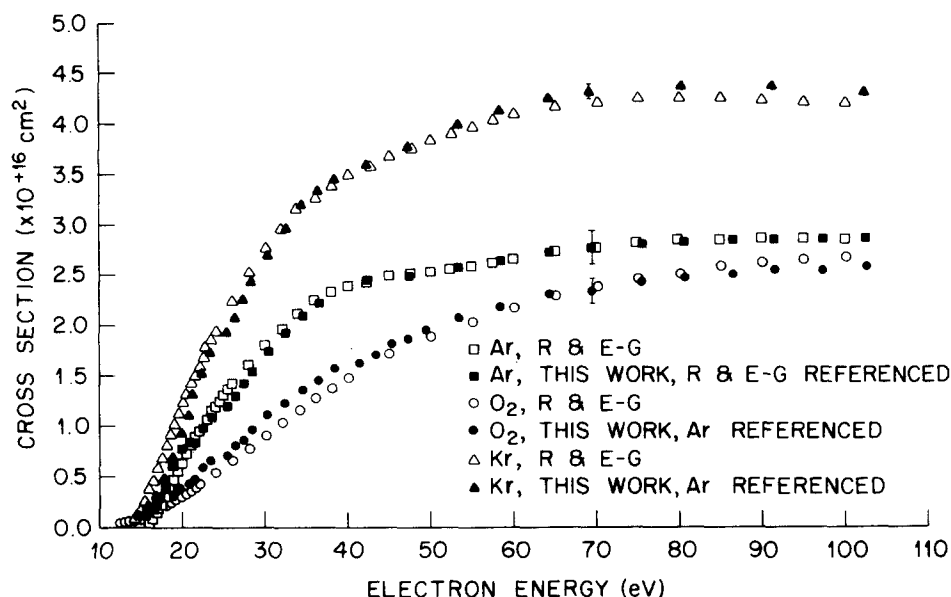


FIG. 1. (a) The ionization cross-section curve for argon normalized to the value of Rapp and Englander-Golden at 70 eV, and adjusted to match their energy scale. (b) The ionization cross-section curves for krypton and oxygen obtained relative to our argon data. The data of Rapp and Englander-Golden are also plotted.

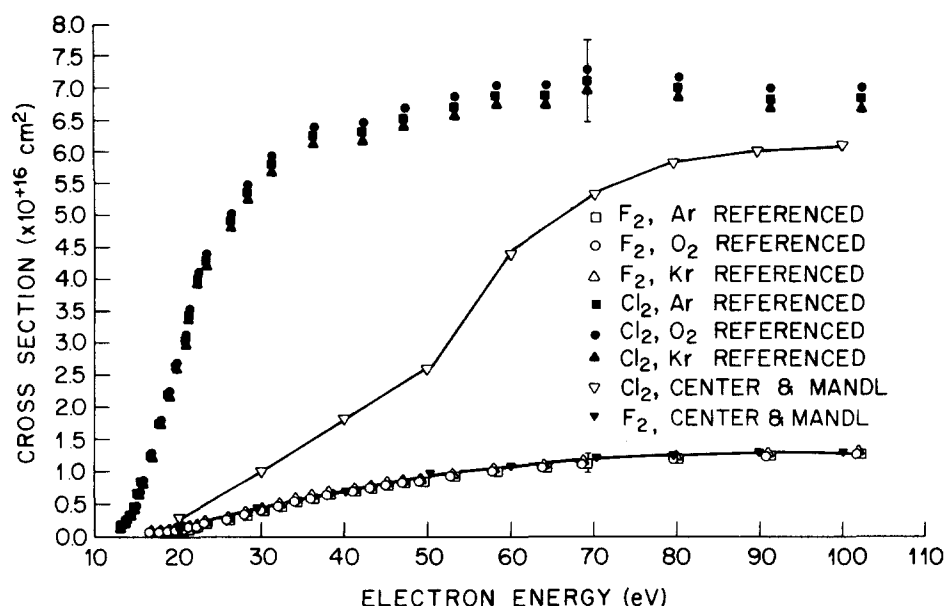


FIG. 2. The ionization cross sections of fluorine and chlorine determined as a function of electron energy using oxygen, argon, and krypton calibrants. The data of Center and Mandl (Ref. 11), corrected to cm², are also included.

from our argon data, and the values reported by Rapp and Englander-Golden are also plotted for the purposes of comparison.

We consider the agreement between our 70 eV oxygen and krypton ionization cross sections with the reported values to be excellent, and we are confident that the simplifications used to arrive at Eq. (8) are warranted. The agreement of the energy dependence of our oxygen data below 40 eV and our krypton data below 30 eV shown in Fig. 1 is somewhat less than ideal, but we judge it to be satisfactory, since our range of experimental error includes the literature values.

Table I also includes the 70 eV cross sections measured for fluorine and chlorine using oxygen, argon, and krypton calibrants. The self-consistency of the values from each of the calibrants further increases our confidence in the use of Eq. (8), and this method in general. The 70 eV cross section for fluorine is in good agreement with the value taken from Ref. 11. (The values given in Ref. 11 are actually in units of Πa_0^2 , and were converted to cm² for the comparisons in this paper.) The 70 eV cross section for chlorine does not agree as well with the data reported in Ref. 11, and the origin of the disparity is in the energy dependence. The energy dependence of the chlorine and fluorine cross sections is shown in Fig. 2, along with the data taken from Ref. 11. Figure 2 shows that the disparity in the chlorine ionization cross section between our measurements and those of Ref. 11 increases as electron energy decreases, but agreement is good for energies of 80 eV and above (e.g., at 90 eV we measure 6.8×10^{-16} cm², and the value obtained from Ref. 11 is 6.0×10^{-16} cm²). We cannot offer any explanation for the observed disparities at electron energies below 80 eV, but we note that the qualitative shape of our ionization cross section curve is in better agreement with those reported for other diatomic molecules.¹⁻³ Ionization cross section values of chlorine and fluorine are given in Table II. These data are averages of results for each of the

three calibrant gases, since the experimental error at any energy for a given calibrant gas included the range of values obtained with the other two.

The data reported in this study were taken using a

TABLE II. Ionization cross sections of F₂ and Cl₂.

Electron energy (eV)	$Q_T(\text{F}_2) (\times 10^{16} \text{ cm}^2)$	$Q_T(\text{Cl}_2) (\times 10^{16} \text{ cm}^2)$
102	1.25	6.82
91	1.21	6.82
80	1.17	7.00
69	1.10	7.10
64	1.05	6.87
58	1.00	6.87
53	0.91	6.71
49	0.84	
47	0.82	6.54
45	0.79	
43	0.74	
42		6.31
41	0.69	
38	0.64	
36	0.59	6.25
34	0.56	
32	0.49	
31		5.80
30	0.43	
28	0.35	5.35
26	0.28	4.90
23	0.20	4.28
22	0.15	4.00
21	0.14	3.44
20	0.10	2.65
19	0.08	2.20
18	0.04	1.75
17	0.02	1.24
16		0.85
15		0.68
14		0.34
13.5		0.17

molecular beam inlet pressure of 8.0 Torr, to insure that the gas flow from the orifice was in the supersonic regime, and hence Eqs. (6) or (8) can be used to calculate Q_T . Cross-section data at 70 eV were also taken at 2, 4, 6, and 10 Torr inlet pressures, with no differences outside of the range of values shown in Table I at 6 or 10 Torr. At pressures below 4 Torr, discrepancies in the self-consistency checks of about 20% were observed, and we attribute these discrepancies to the molecular beam flux not being adequately described by Eq. (5). Finally, we note that impurity ions such as HF or HCl could not be detected when the ion beams were subjected to mass analysis.

IV. CONCLUSIONS

We have applied a molecular beam technique using calibrant gases to the determination of the ionization cross sections of fluorine and chlorine. The 70 eV values of the cross sections are 1.1 and 7.1×10^{-16} cm², respectively, in good agreement with the only previous measurements for these gases. The technique has been shown to accurately measure the ionization cross sections of krypton and oxygen using argon as a calibrant, and is completely self-consistent for measurement of the cross sections of fluorine or chlorine using argon, oxygen, and krypton as calibrants.

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