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Electron Attachment of SeF₆*

By

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APPENDIX I

Electron Attachment of SeF6*

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The electron attachment cross section of SeF₆ has been measured as a function of electron impact energy in the range from 0.1 eV to 1.5 eV. At electron energies between 0.1 eV and 1.0 eV, the experimentally observed dependence of the capture cross section of SeF₆ on electron energy indicates a relationship to the fundamental vibrational frequencies of the molecule. Experimental evidence can be explained assuming that, in the indicated energy range, electron capture by SeF₆ occurs preferably if simultaneous excitation of the neutral molecule into one of the vibrational states of one fundamental mode is energetically possible. The magnitude of the capture cross section depends on the excited vibrational state. A relatively large cross section was

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Air Force Research Division.

obtained for every alternate state accompanied by a general decrease towards higher levels. The absolute size of the electron attachment cross section of SeF_6 in the energy range of 0.2 eV - 1.0 eV fluctuated between 2 x 10^{-16} cm² and 1 x 10^{-16} cm². Around 1.5 eV dissociative attachment was observed.

INTRODUCTION

During recent years formation of negative ions has received considerable attention because of its intimate relationship to atmospheric physics and to some plasmas of low and moderate temperatures. The purpose of this paper is to discuss experimental results recently obtained in our laboratory on the formation of negative ions of SeF₆ by collisions with electrons having energies in the range from 0.1 eV - 1.5 eV.

In dealing with problems connected to electron depletion processes, one of the quantities of interest is the electron attachment frequency $\nu_{\rm g}$ per electron. In a phenomenological description this frequency may be written as

$$v_n = 8n + Kn^2 \tag{1}$$

where 8 and K are two-body and three-body coefficients of electron attachment respectively, and n the density of electron attaching particles.

This paper deals with attachment through two-body collisions, i.e., with the two-body coefficient 8. The

latter is a function of electron energy E and electron energy distribution f(E) dE encountered in the particular plasma considered. In a statistical description, the coefficient 8 can be deduced from the more general parameter, the electron attachment cross section $\sigma_{\bf a}(E)$ with respect to a monoenergetic, unidirectional swarm of electrons of energy E,

$$\beta = \langle \sigma_{\mathbf{a}} v_{\mathbf{e}} \rangle_{\mathbf{a}V} = \int_{0}^{\infty} \sigma_{\mathbf{a}}(\mathbf{E}) (2\mathbf{E}/\mathbf{m}_{\mathbf{e}})^{1/2} f(\mathbf{E}) d\mathbf{E} , \qquad (2)$$

 m_e = electron mass , v_e = electron velocity.

Equations (1) and (2) serve to define both 8 and $\sigma_{\bf g}({\bf E})$ if the densities are sufficiently low so that the attachment frequency $v_{\bf g}$ is dominated by two body processes. The cross section $\sigma_{\bf g}$ will be measured in cm².

For polyatomic molecules it has been observed (Refs. 1 and 2) that quite frequently negative ion formation in the gaseous phase occurs preferably by direct attachment rather than by dissociative attachment, as is generally the case for electronegative diatomic molecules (Refs. 1, 3, 4, and 6). The term dissociative attachment is used for electron capture followed by dissociation of the molecule into a neutral and negatively charged fragment. Direct attachment is the process of formation of a negative ion preserving the integrity of the parent molecule (Ref. 1).

It has been assumed (Ref. 1) that this behavior might be due to a much longer lifetime τ of an intermediate state

formed initially on electron capture than is generally the case in diatomic molecules. This would allow the polyatomic negative ion to dispose of its excess energy in a secondary process, either a collision or a photon emission, before the surplus energy is again restored to the excess electron.

In this paper, results on experimentally observed electron attachment cross sections of SeF, are presented. molecule was chosen for investigation because it belongs to a very interesting group of chemicals with respect to electron attachment, the hexafluorides of the sulfur group, SF6, Sef, and Tef. The interesting characteristics of this group might be listed in order of their importance as: (1) large known direct electron capture cross section for one member of the group, SF_6 , (Ref. 2); (2) the extremely high symmetry properties of their molecular structure. The equilibrium positions of the seven nuclei are arranged such that the six fluorine atoms occupy the corners of a regular octahedron (Refs. 7 and 8) with the heavy nucleus at its center. This symmetry resembles that of the O_h point group. The first characteristic, large electron capture cross section for SF6, suggests a study of corresponding properties of the other members of the group as compared to SFg, and their possible relationship to specific molecular properties. The second feature, high symmetry, makes this group particularly desirable for investigation because it facilitates a theoretical treatment of the problem. It might therefore be expected

that the hexafluorides of the sulfur group are particularly suited for a combination of theory and experiment to develop a physical understanding of electron capture by polyatomic molecules.

METHOD

Experimental Requirements

Any experimental investigations of electron attachment cross sections are intimately connected with the experimental production of swarms of electrons at low and very low energies which becomes increasingly difficult as one proceeds to lower energies. Low energy electrons are needed because of electron capture by neutral molecules in the gaseous phase occurs only at very low electron impact energies. Moreover, the measurement requires the swarm to beunidirectional and monoenergetic. The two latter requirements are very difficult to satisfy in the electron energy range of interest and consequently one or both conditions must usually be violated. In addition, magnetic fields are very often used to guide the electrons. Consequences of such violations of the basic requirements to be imposed on a suitable experiment according to the definitions, Eqs. (1) and (2), are not easy to judge and they should by no means simply be ignored. It is quite clear that the presence of a magnetic field affects the properties of the electron swarm and might therefore influence its interaction with electronegative molecules. This could become particularly serious if the investigated

molecules possess a permanent magnetic dipole moment as does, for example, O₂. Apart from magnetic fields, disturbing effects might result from other collision processes or if there are undesired interactions of the experimental procedure with the attaching gas. Such interaction might, for example, occur if the electrons are generated by photoemission and the necessary radiation field is allowed to interact with the attaching gas.

Besides the above mentioned considerations which determine the principal feasibility of a chosen method, there are others, not less critical, but relating more to experimental questions. The most important is that of resolving power with respect to electron energy. Another is beam intensity. The resolving power necessary depends largely on what kind of questions are to be answered by the experiment. If only relatively crude, gross effects are desired a resolution of the order of 0.1 eV is guite adequate. It allows one to locate maxima for electron capture cross sections on an energy scale sufficiently accurate for most purposes, and to answer questions concerning the total electron capture properties of a gas as a function of mean electron energy For more pretentious questions, much higher resolving power is desirable. To resolve possible vibrational structure, resolutions of the order of 0.01 eV - 0 1 eV or better are needed and rotational structure would require even more. Just as is the case for

other cross sections, a detailed knowledge of the energy dependence of the electron capture cross section might be very essential for future comparison between theory and experiment, and devices of highest attainable resolving power should therefore be employed.

Electron beam intensities in connection with other pertinent parameters of the particular experiment determine the sensitivity. High electron beam currents result usually in high sensitivities. It should however be stressed that electron beam densities should always be chosen to be small compared to space charge limitations. At low electron energies, this condition imposes critical limitations. Furthermore, sensitivity and resolving power are to a certain degree incompatible with each other so that in the design of a particular experiment these two parameters must be carefully traded for each other depending on the particular requirements. However, resolving power should always be given the first choice because loss in intensity can quite often be compensated for by a suitable sensitivity increase in ion detection techniques.

Experimental Technique

The technique used in these experiments is a retarding potential method. It has been used quite frequently in a very similar form in previous studies on formation of positive and negative ions as well (Refs. 2, 5, and 9).

The principles and limitations of this technique have been discussed elsewhere (Ref. 5) and we can therefore confine ourselves to a fundamental discussion.

The essential part of the experimental apparatus is the attachment tube which is sketched in Fig. 1. It is mounted inside a cylindrical evacuated tube. A beam of thermal electrons, emitted from a tungsten filament is traveling along the axis through an arrangement of apertures. Total electron beam currents are kept in the range of 10⁻⁷ - 10⁻⁹ amp. In order to provide a proper amount of collimation, an axial magnetic field of about 140 oe, generated by a solenoid, is used. It is mounted externally approximately coaxial with the attachment tube. Precise adjustment of the magnetic field is accomplished by two sets of Helmholtz coils arranged in a way to render the axes of all three magnetic fields mutually perpendicular. The retarding potential is applied to the beam at one of the apertures. After the beam has passed this barrier, it contains, under ideal conditions, only electrons having kinetic energies greater than the potential applied. This beam is then brought into interaction with an electronegative gas in the cylindrical reaction chamber. The chamber is limited by two end plates, each containing a hole to allow the electrons to enter and leave the chamber and by cylindrical grid electrically connected to the end plates. This arrangement secures a region nearly free of electric fields at the

axis. The ion collector surrounds the grid on the outside. All the electrons which entered the chamber and did not interact with electronegative molecules are collected after they passed through the exit aperture, giving rise to the measured electron current. Those electrons which do interact are assumed to form negative ions. The latter are, due to their large mass, not collimated by the magnetic field. Very small electric fields at points off the axis aid in guiding the ions to the ion collector where their current is measured. Negative ion currents are in the range from $10^{-9} - 10^{-11}$ amp. Electrons which suffer elastic collisions in the chamber or inelastic collisions not leading to electron capture are assumed to be not capable of leaving the beam because of the collimating magnetic field. On the other hand, an appreciable number of such collisions would change the energy distribution of the beam electrons. Pressure conditions are therefore chosen as to make sure that only a small percentage, in the experiments less than 10 percent, of beam electrons experience a collision of any kind in the reaction chamber. All experiments are done at pressures between 54 Hg and 404 Hg measured by a McLeon gauge. The length of the chamber is 1 cm. The important apertures are kept as small as feasible. This results in a gain of energy resolving power at the cost of sensitivity. Since materials with exceptionally large electron capture cross sections are being investigated, such a sacrifice is advisable.

$$(\pi/4)$$
 d²N f(E)dE

range E, E + dE contained in the unidirectional beam entering the attachment chamber. N is the total electron density in the beam before it is subjected to a retarding potential or attaching agents and d is the beam diameter. The number of electrons per unit length in that same energy range leaving the chamber after interacting with the electron attaching gas is

$$(\pi/4)$$
 d N e $-\sigma_{\mathbf{g}}(\mathbf{E})$ nL f(E) dE

and the corresponding contribution to the total measured electron current $i_{\mu}(E)dE$

$$di_e = i_e(E)dE = (\pi/4)d^2Ne(2E/m_e)^{1/2}e^{-\sigma_a(E)nL}$$
 f(E)dE amp (3)

e = electronic charge

n = density of attaching gas

L = length of attachment chamber

If all electron losses from the beam are due to electron attachment and all negative ions are collected on the ion collector, then the difference between the current entering and leaving the chamber i_e^O (E)dE and $i_e(E)$ dE must be measured as negative ion current $i_n(E)$ dE. That is

$$di_n - i_n(E)dE - [i_e^0(E) - i_e(E)] dE - (\pi/4)d^2Ne$$

$$(2E/m_e)^{1/2} \quad \left[1 - e^{-\sigma_a(E) nL}\right] f(E) dE \quad amp \qquad (4)$$

The measured quantities are the total electron and ion currents as a function of retarding potential which are obtained by integrating Eqs. (3) and (4) over the appropriate energy range. To derive the attachment cross section from the experimental curves they are numerically differentiated with respect to the energy. The ratio

$$\frac{di_n/dE}{di_e/dE} = \frac{di_n}{di_e} = (e^{\sigma_a(E) nL} - 1) \approx \sigma_a(E) nL$$
 (5)

The basic overall experimental arrangement is shown in Fig. (2) The gas, SeF₆ compressed into the liquid phase, was supplied by Allied Chemical Corp., General Chemical Division. It was introduced into the vacuum system by a variable leak. The SeF₆ pressure in the attachment chamber was measured and controlled by a thermocouple gauge and a McLeod gauge.

The variable retarding potentials, supplied by a sawtooth generator, and the negative ion and electron currents
were measured and recorded after proper amplification on a
multi-channel recorder. All measurements were carried out
in two fashions. In one series of experiments all quantities

were measured on a dc basis. In another series, the electron beam was chopped by a 1,000 cps square wave generator. This gave both electron and negative ion currents a square wave form. With proper narrow band pass filters the 1,000 cps components were selected and measured. Both series of experiments revealed essentially identical results. Care was taken in all experiments to cancel contact potentials by properly applied voltages as far as possible.

The applied technique has some inherent shortcomings. Since the electron beam is not monoenergetic and magnetic fields must be used for collimation, two of the principal requirements for an ideal experiment have been violated. Interference from undesired effects can therefore not be ruled out summarily. Measures have been taken to keep those interferences at a minimum, as, for example, application of very low gas pressure. Since the investigated molecule has no permanent magnetic dipole moment, the presence of a magnetic field should cause no difficulties from this point of view. However, its influence on the motion of the electrons might cause difficulties if other collisions occur with comparable cross sections. The fact that the electron beam is not monoenergetic makes the gas interact with an electron assembly essentially different from the one used for the definition of the electron attachment cross section $\sigma_{\rm a}$ (E). Whether this might influence the obtained cross sectional values must be left open. Since the electron beam

is not monoenergetic a varying retarding potential must be applied. This makes it possible to extract the desired quantity by differentiating the measured currents with respect to the retarding voltage (Eq. 3). From an experimental point of view this is a highly undesirable situation because it is well known that in doing so small errors in the measurements might lead to large errors in the results. Therefore, considerable care must be exercised in the experiments to overcome this disadvantage.

Apart from these more principal difficulties there are others which are related mostly to the achievement of a precise low energy cut-off. The resolving power of the device depends a great deal on how well defined this limit is. The obstacles encountered in solving this problem and also the establishment of a reliable energy scale in the range of interest are mostly due to inhomogeneities of contact potentials at the apertures and to undesired voltage gradients. We shall not discuss this point any further since it has been extensively treated. (Refs. 2,4,5, and 6.)

In spite of the disadvantages of the technique, the relative simplicity and dependability when compared to other available methods to measure electron attachment cross sections makes it one of the best methods known. Results might be expected to be quite adequate with a few restrictions which must be answered by applying other methods in the future.

EXPERIMENTS

It has already been pointed out that a precise low energy cut-off of the electron energy distribution in the beam is essential for the method. Whether this condition is satisfied can easily be tested. As is well known, the total thermionic emission as a function of retarding potential ΔV is given by

$$\log J = \log J_g - (5040/T) \Delta V$$
 (6)

 $\mathbf{J_{g}}$ is the saturation current and T the absolute temperature. Figure (3) shows a semi-logarithmic plot of the measured electron beam current as a function of retarding potential. These measurements were obtained after careful cleaning of the attachment tube. The close agreement between theory and experiment shows that the low energy cut-off must be very well defined. Under operating conditions, the electron energy distribution usually becomes distorted because of changing and nonuniform work function due to impurities. This is not particularly serious as long as the low energy cut off remains well defined. Nonuniform fields at the retarding poten. tial aperture result in a loss of definition in the barrier voltage, and, consequently, in a decrease of resolving power. Whether large nonuniformities exist at the retarding poten. tial aperture was tested in the following way. With no attaching gas in the tube, the thermionic energy distribution can be measured in two ways. Either the potential barrier

is applied to the retarding aperture, or directly to the plane electron collector keeping the retarding potential aperture at the same potential as the rest of the tube. Both methods should result in the same electron energy distribution. The measurements in a tube which had been exposed to the investigated gas confirmed this within sufficient limits. Therefore, it can be assumed that the low energy cut-off produced at the retarding potential barrier remains reasonably sharp even after the attaching gas has been admitted to the tube.

The zero point of the energy scale was determined by applying a small voltage to cancel the contact potential difference between the emitter and the first aperture. This potential can be found as the voltage at which the thermionic current just starts to be effected with an energy uncertainty of at most 0 2 eV. We preferred this method over others reported in the literature (Refs. 2 and 5) leaving the absolute energy scale up to a different more precise experiment which is being developed in our laboratory.

The experimentally obtained cross sections for SeF_6 as a function of electron energy has been plotted in Fig. (4). The cross section data were derived from the experimentally determined electron and negative ion currents using Eq. (5). The density of SeF_6 was found by measuring the pressure with a McLeod gauge and assuming the gas temperature to be equal to the room temperature,

DISCUSSION

The experimental cross section plotted in Fig. (4) can be divided into three parts.

At very low energies a steadily increasing capture cross section with decreasing electron impact energy has been observed. However, it should be emphasized that its true behavior gets progressively more uncertain as zero energy is approached because of methodical limitations. We shall therefore put little emphasis on this part in our discussion.

The most striking pattern in the observed energy depend ence of this electron capture curve is a very pronounced structure at medium energies between 0.2 eV and 1.0 eV. The energy separation of the peaks is very slightly increasing from 0.1 eV at the high energy end to about 0.115 eV at the lower energies, corresponding to 806 cm⁻¹ and 930 cm⁻¹ wave numbers.

Another peak, the third part, is observed at the high energy end of the investigated range around 1.5 eV.

In order to understand the general behavior of the electron capture cross section of SeF₆ an attempt was made to relate the observed structure to the molecular properties of the molecule.

It is generally agreed now that SeF_6 , like the other hexafluorides of the sulfur group, has the structure of a regular octahedron (O_h point group) (Refs. 7 and 8). The heavy selenium atom is located at the center of the

octahedron and the six fluorine atoms are grouped around it occupying the corners. The wave numbers of the six fundamental frequencies characteristic to this symmetry are given in Table I.

Since the observed peaks in Fig. (4) are about equally spaced the participation of vibrational states of fundamentals is suggested in the electron capture process. Comparison with Table I shows that the normal frequency v_6 agrees best with the observed separation. The energies of the vibrational states of this fundamental as derived from Raman spectroscopic data are approximately given by

hc $v_6(v_1+1/2)$; $v_6=787~{\rm cm}^{-1}$; $v_1=0,1,2,\ldots$ $v_1=v_1$ brational quantum number. At the high energy end the measured separation of $806~{\rm cm}^{-1}$ agrees to within better than 3% with the required value of $787~{\rm cm}^{-1}$. The measured spacing increases to about $930~{\rm cm}^{-1}$ with decreasing energies. This discrepancy could be due to increasing disturbing effects at the retarding potential aperture, as the repelling voltage is lowered. This point requires further investigation with refined techniques. Nevertheless, it seems highly probable that this part of the electron capture cross section is related to a process in which excitation into vibrational states of one fundamental mode of the neutral molecule during the electron impact is important. We might therefore label this process as vibrational capture. The energy relationship can, in this case, be written as

$$E_{kin} - X^{-} - hc v_{n}(v_{i} - v_{k}) = E ; i > k.$$
 (7)

 E_{kin} is the kinetic energy of the impact electron, χ the (negative) binding energy of the excess electron in the attached state and E the surplus energy.

From the experimental observations and assuming Eq. (7) to be valid it can be concluded that attachment occurs preferably if the surplus energy E becomes zero, i.e.,

$$E_{kin} + \chi^{-} = hc v_n (v_i - v_k)$$
 (8)

In this case all the liberated energy can be used to excite a level of one fundamental frequency. It is probably justified to set $v_k = 0$, corresponding to excitation from the ground state. The higher order peaks would then correspond to excitation into higher vibrational states. It is quite in agreement with expectation that the size of the individual peaks should generally decrease with increasing energies, since the transfer of many vibrational quanta in a single collision can be expected to become less likely as more quanta are involved. This is reflected in the general decrease of the maxima of the measured electron capture cross sections towards greater electron impact energies. The peculiar fact that every second peak appears to be quite small is not yet understood.

In the discussions of the vibrational structure of the capture cross section of SeF_6 we have for simplicity so far

assumed that one fundamental mode is distinguished from all others. This assumption does not necessarily follow from the experiments. As can be seen from Table I the fundamental frequencies of SeF₆ cluster into three groups (Table II).

The resolving power of the device used in the experiments is not adequate to distinguish between members of an individual group. Therefore, each individual peak observed might represent a whole group of closely spaced peaks. It is clear that if excitation of several frequencies is considered Eqs. (7) and (8) must be modified appropriately.

Excitation of more than one fundamental frequency could be employed with appropriate assumptions to explain the observed alternation of capture cross section amplitudes for alternate peaks. There is, however, another fact which might be regarded as support for the assumption that a variety of fundamental frequencies can be excited following electron capture. Contrary to the measurements on SeF_6 , reported in this paper, a smooth dependence of the attachment cross section on electron impact energy has been reported for SF_6 (Ref. 2). This behavior becomes quite plausible on this basis if one considers the fundamental frequencies of SF_6 as compared to SeF_6 .

It can be seen immediately from Table III (Ref. 8) and Fig. (5) that the fundamental frequencies of SF_6 are almost uniformly distributed over the range from 300 cm⁻¹ - 1000 cm⁻¹, whereas in the case of SeF_6 , they show a grouping tendency (Fig. 5).

Consequently, the dependence of the capture cross section on electron energy for SF₆ would be expected to be resembled by a large number of closely separated peaks almost uniformly distributed over the energy range of interest. Employing a device of only moderate resolving power would feign a smooth energy dependence, as has been observed (Ref. 2). For SeF₆ the arrangement of the normal frequencies in groups would indeed result in clustering of large numbers of individual peaks in a regular manner as it appears in our experiments.

At very low energy, a considerable increase in attachment cross section is found. This is in agreement with measurements on SF₆ (Ref. 2) reported in the literature. Dispite some uncertainty in the actual numerical values due to methodical limitations, as pointed out before, the steep increase is probably real. This can be deduced directly from the measured electron and ion currents. The slope of the electron current as a function of decreasing electron energy close to zero energy approaches zero slope much faster than the corresponding slope of the negative ion current. The explanation could be that this large peak corresponds to excitation into the first vibrational state where only a single vibrational quantum is transferred. It is quite clear that measurements of higher accuracy at very low electron energies are needed.

At the high energy end of the range investigated around 1.5 eV, a small peak has been found. It is believed that it corresponds to dissociative attachment

$$SeF_6 + e \rightarrow SeF_5 + F$$

or other dissociative products.

Finally it should be mentioned that due to the construction of the tube, transit times of negative ions generated in the attachment chamber are of the order of 10^{-5} sec. Therefore, conclusions drawn from these experiments are not necessarily valid for negative ions of much longer or much shorter lifetimes.

It is believed that the measurements reflect the relative energy dependence of the electron capture cross section quite well. The absolute values might have uncertainties of as large as 30%. The energy scale is, apart from the uncertainty of the absolute zero point by about 0.1 eV, likely to be accurate to within 10-20%. In particular slight non-linearities are expected to have influenced the energy scale.

CONCLUSIONS

From the experimental evidence presented on the energy dependence of the electron capture cross section of SeF₆ it can be concluded that excitation of vibrational levels on electron capture can be of importance. At the low pressure applied it is unlikely that the observed vibrational structure is feigned by other collision processes but such an

interference cannot be wholly excluded. Since the transit time of negative ions generated in the tube a4e of the order of 10^{-5} sec experimental results refer to negative ions having lifetimes of this order or greater.

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Table I

| Fundamental Frequencies | Wavenumber cm-1 |
|----------------------------|-----------------|
| ν ₁ | 708 |
| ν ₂ | 662 |
| ٧3 | 405 |
| ٧ ₄ | 245 |
| ν ₅ | 461 |
| ν ₆ | 787 |

Normal Frequencies of SeF₆ (Ref. 8)

Table II

| Group | |
|-------|--|
| I | ν ₁ , ν ₂ , ν ₆ |
| II | ν ₃ , ν ₅ |
| III | ٧4 |

Grouping of Normal Frequencies of SeF₆

Table III

| Fundamental Frequencies | Wavenumber cm-1 |
|----------------------------|--------------------|
| ν ₁ | 775 |
| ٧ 2 | 645 |
| ν ₃ | 525 |
| ٧4 | 363 |
| ν ₅ | 617 |
| ٧6 | 965 |

Normal Frequencies of SF₆ (Ref. 8)

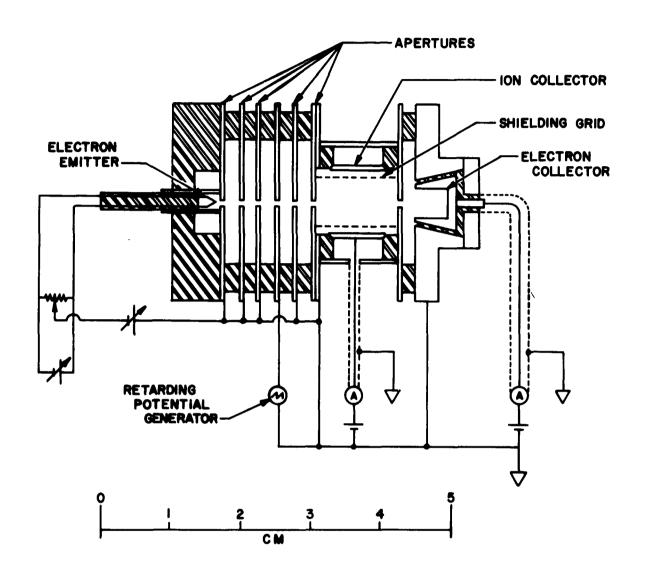
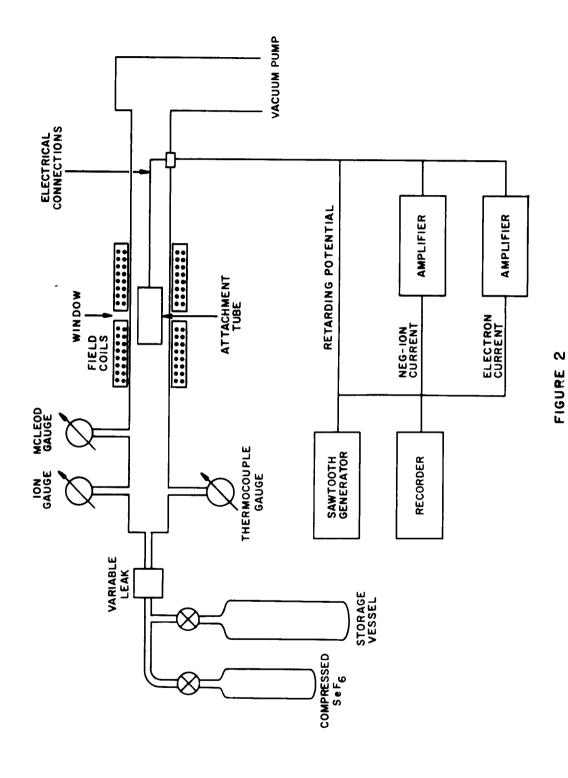
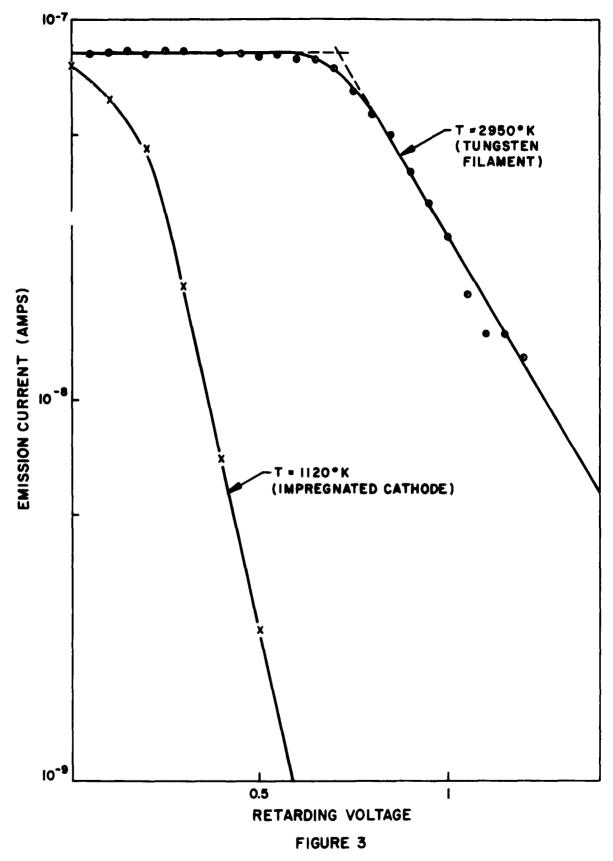


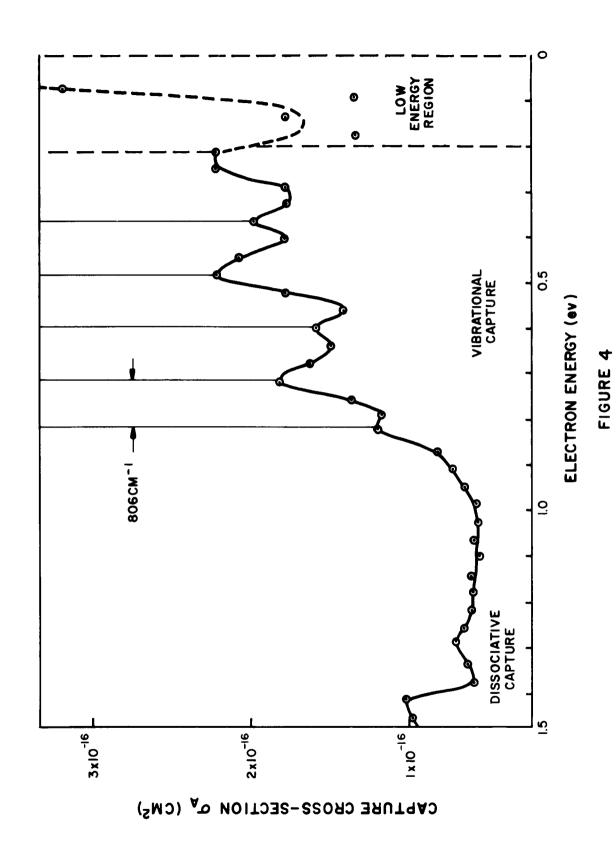
FIG.I ATTACHMENT TUBE



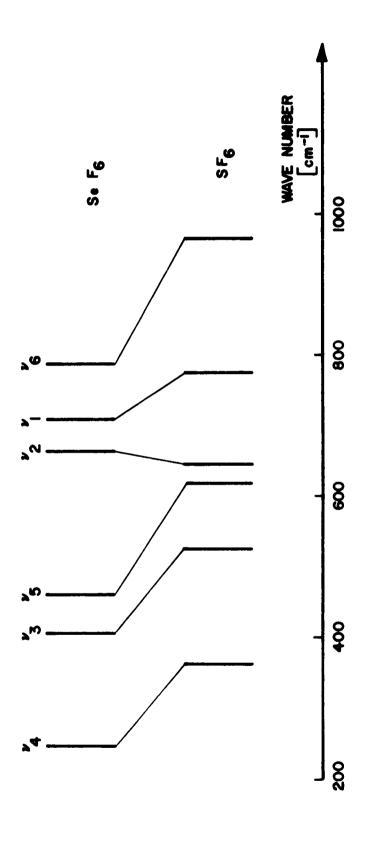
SCHEMATIC OF EXPERIMENTAL APPARATUS



ELETRON BEAM CURRENT AS A FUNCTION OF RETARDING VOLTAGE IN EVACCUATED ATTACHMENT TUBE



4 AS ELECTRON CAPTURE CROSS SECTION OF SeF₆ FUNCTION OF ELECTRON ENERGY.



THE FUNDAMENTAL FREQUENCIES OF SeF6 AND SF6 FIGURE 5