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MASTER

ISOTOPE SEPARATION BY SELECTIVE
DISSOCIATIVE ELECTRON ATTACHMENT

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FINAL TECHNICAL REPORT

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1.0 SUMMARY

This report is in part an account of work performed on Contract EN-77-C-02-4344 issued by the Department of Energy, Office of Advanced Isotope Separation for the period 5/1/77 through approximately 11/30/77. Subsequent funding was expected in the form of a continuation contract, but this funding has not materialized. Uncertainties in the funding situation continued through the early part of 1978, and for this reason the present report was delayed until the status of the project could be properly assessed. It appears at present that additional DOE funding will not be forthcoming until FY 1979 at the earliest. Meanwhile the project is being maintained at a low level of effort on in-house funds.

A description of work performed prior to the present contract on isotopically selective, photo-enhanced production of SF_5^- from SF_6 is included as part of this report, together with work performed on the contract on the analysis and interpretation of the accumulated data. It is shown that the sequence of reactions

can be used in a highly selective fashion. The conditions of the experiment correspond to essentially collisionless operation, and because of the low activation energy of reaction (1.2) the measurements probe the region of collisionless multi-photon excitation where one or a few photons are absorbed. The unexpectedly linear dependence of the measured enhancement of SF_5^- production on the laser power is discussed in the light of measurements by others of the phenomenological energy absorption cross-section made at similar levels of energy fluence. The general conclusion is that the two types of measurement are consistent,

but that in neither case are the underlying non-linear physical mechanisms properly understood.

The wavelength dependence of the SF_5^- enhancement effect displays a red-shift of 8 cm^{-1} relative to the small-signal absorption curve appropriate to the gas temperature of 390°K at which the present measurements were made. This feature is ascribed primarily to hot band absorption effects, with possibly some contribution from the shift associated with non-linear absorption observed by others at these and higher fluence levels. Irrespective of the relative contributions to the red-shift, we can conclude that efficient promotion of the dissociative channel giving SF_5^- from SF_6^* requires that the SF_6 molecule have at least two quanta of vibrational excitation present in the vibrational manifold. This is in contrast to multi-photon dissociation studies in which the observed effects require the absorption of tens of photons. Thus the present type of study has the advantage of directly probing that region of the excitation which is of major importance in all multiple-photon processes.

The primary task under the present contract was the construction of a second-generation experimental apparatus designed specifically for the study of the simultaneous interaction of electrons, photons, and molecules. The collinear electron and laser beam arrangement employed previously has been retained, but a new electron gun design has been adopted which avoids the troublesome interaction of the laser beam with the electron gun filament experienced during the earlier work on SF_6 . The system as a whole has been designed for maximum compatibility with aggressive gases such as UF_6 . The details of the design and construction of this system are given in Section 4 of this report.

The initial intent was to employ the apparatus for the study of BCl_3 , and it was planned to have the equipment constructed for this purpose by the end of 1977. At the time the contract funds were exhausted it was estimated that the project was approximately two months behind this original schedule, for reasons largely beyond our control, involving the delivery of components by outside suppliers. It was clear

at that point that our original estimates of the level of effort, and particularly of the time span, required to build a sophisticated system of the present type were over-optimistic. At the present time it is estimated that assembly and testing of the system, including the additional components which would be required for the study of UF_6 , could be completed within three months of resuming an optimum level of effort on the project. At present the project has only "back-burner" status. The status of the project is discussed in greater detail in Section 5 of this report.

Proposals for future work on this general topic are presented in Section 6 of this report. They include work which is essentially a natural extension of the previous work on SF_6 , directed primarily toward the further understanding of the few-photon absorption mechanism which forms the basis of the selectivity of the present technique and others such as multi-photon dissociation. Work on UF_6 is also proposed, and this was planned until recently to be the core of a second phase of the present contract. Funding for this has not been forthcoming, however, and the next phase of this project remains undecided at the present time.

2.0 INTRODUCTION

2.1 Background

The work described in this report is an outgrowth of experiments which have been performed over the last decade or so both at the Westinghouse Research & Development Center and elsewhere. These experiments were directed specifically at measuring and understanding the process of dissociative electron attachment (DEA) in a large range of molecules, as discussed in sub-section (3.1) of this report. The advent of high-powered lasers in the recent past led to serious consideration of a variety of possible techniques for exploiting the selective excitation which in principle is possible in all molecules to give isotopically selected products. Based on our understanding of thermally enhanced DEA processes, many of which had been previously studied in this laboratory, we proposed¹ that photo-enhanced DEA could be used to selectively produce fragmentation of molecules containing specific isotopes. The details of this scheme are discussed in subsection 3.1 of this report.

In order to demonstrate that this isotope separation scheme is based on sound physical principles, and to provide the necessary additional understanding of the details of the proposed scheme, an experimental program was begun with the objective of demonstrating isotopically selective photo-enhanced production of SF_5^- from SF_6 . This was successfully achieved² early in 1977, prior to commencement of the present contract. The experimental work performed on SF_5^- production from SF_6 with in-house funds is described in Section (3) of this report for the sake of completeness.

2.2 Contract Objectives

At the time the present contract funds became available (May 77) it was appropriate to (i) devote time to the proper analysis and inter-

pretation of the experimental data recently accumulated on SF_5 - production from SF_6 , and (ii) to commence design and construction of a dedicated experimental system to be used subsequently for further studies related to photo-enhanced DEA and its exploitation for isotope enrichment. In so doing full advantage could be taken of the experience gained during the study of SF_6 .

Specifically, the tasks to be performed are described in the contract as follows:

Task I - Design and construction of a second-generation apparatus for the study of laser-induced dissociative electron attachment. This apparatus will be constructed such that the simultaneous interaction of electrons, photons and molecules can be studied. The ability to vary the static temperature of the working gas shall be included as will the ability to operate with corrosive gases, such as UF_6 .

Task II - A complete analysis of the dissociative electron attachment data that has been obtained will be made. The analysis of this data will provide much of the insight that will be required in design of future experiments. In addition, these results will prove to be invaluable in the determination of the utility of this technique for commercial isotope separation.

The work on Task I is described in detail in Section 4, and the work on Task II is summarized as part of Section 3 of this report.

3.0 PREVIOUS WORK ON SELECTIVE SF_5^- PRODUCTION FROM SF_6

3.1 Background

The first reported study of the effect of temperature on a dissociative attachment reaction was that of Hickam and Berg³ who demonstrated that SF_5^- production from SF_6 increased with temperature. Their observation did not create much interest however, possibly because of the difficulty of reconciling it with a subsequent observation⁴ that the total attachment cross-section for SF_6 is insensitive to temperature. Interest in this subject was subsequently stimulated by the work of Fite and coworkers⁵ who found that the production of O^- from O_2 was unexpectedly sensitive to temperature. They found that at higher temperatures the threshold shifted to lower energies by many times kT , and the peak magnitude of the cross-section increased. These effects were convincingly explained by O'Malley⁶ as being due to the dramatic increase in the dissociative attachment cross-section if one attaches to higher vibrational states of O_2 . Similar behavior of O^- production from N_2O was subsequently observed and reported by Chantry⁷. These led to a series of experiments conducted in these Laboratories and elsewhere which examined in detail the temperature dependence of electron attachment in SF_6 ⁸; SF_4 ⁹; $\text{C Cl}_2\text{F}_2$ and CHClF_2 ¹⁰ and SO F_2 ¹¹; CO_2 ¹²; CHCl_3 , CF_3Br and CH_3Br ¹³.

In all the above cases a dependence on gas temperature was found. The inferred strong dependence of the dissociative electron attachment (DEA) cross-section on the vibrational level of the target molecule led us to consider¹ the possibilities of using the process for isotope separation by optically exciting the vibrational mode(s) of one isotopic species:

followed by preferential attachment of low energy electrons to the vibrationally excited species:

The ultimate isolation of the species 1X can then be achieved by conventional physical or chemical processing based on the different properties of XY, X and Y. The work reported in subsections 3.1 and 3.2 were conducted prior to this contract to investigate the feasibility of this approach through a detailed study of the effects of CO₂ laser irradiation on the process

The electron energy dependence of this reaction has been previously measured⁸ over the temperature range 300 to 1100°K. As shown in Figure 1 the dissociative peak at near zero energy grows dramatically as the gas temperature is increased, while the attachment at 0.38eV is relatively insensitive to the gas temperature. If one plots the magnitude of the near zero energy peak versus inverse gas temperature on a semi-logarithmic graph, the result is a straight line, as shown in Figure 2. The slope of this straight line gives an activation energy of 0.2eV for this channel of dissociative electron attachment (DEA).

We interpret these results qualitatively by effective diatomic potential curves as shown in Figure 3. The low energy peak is the result of attachment of near zero energy electrons for those vibrational-rotational states of SF₆ 0.2eV or more above the ground state. The 0.38eV peak is the result of vertical Franck-Condon transition of SF₆ to the repulsive negative ion curve after capturing a ~0.38eV electron.

Based on the temperature dependence data it was anticipated that the zero energy peak in the cross-section could be photo-enhanced. We note in particular from Figure 3 that because of the relative positions

Fig. 1 Semi-logarithmic plot of the SF_5^- signal produced by low energy electron impact on SF_6 . Each curve is labelled with the SF_6 gas temperature. The narrow peak occurs at essentially zero electron energy and the measured width reflects the available energy resolution of ~ 80 meV FWHM.

Fig. 2 Semi-logarithmic plot of the relative SF_5^- signal at the zero-energy peak shown in Fig. 1, versus inverse gas temperature. From the slope of the fitted straight line an activation energy of $E_a = 0.20 \text{ eV}$ is deduced for the reaction $e + \text{SF}_6 \rightarrow \text{SF}_5^- + \text{F}$.

Fig. 3 Schematic potential energy curves of $SF_5 + F$ and $SF_5^- + F$ based on the data of Figs. 1 and 2. The ground electronic state of SF_6^- indicated by the attractive curve gives rise to the zero energy peak of both SF_6 and SF_5 production. The repulsive curve is invoked to account for the broad, temperature insensitive peak in SF_5 production centered at ~ 0.38 eV electron energy. The indicated quantities are the first bond strength of SF_6 , $D(SF_5-F)$; the electron affinities, $EA(SF_5)$ and $EA(SF_6)$, and the activation energy E_a given by Fig. 2.

of the neutral SF_6 and negative ion SF_6^- potential surfaces, the optical energy can be absorbed into the discrete lower vibrational levels of SF_6 , thereby permitting high selectivity, but that subsequent to the attachment of an electron the SF_6^{-*} system has sufficient excess energy to place it in the continuum or quasi-continuum of vibrational states near the dissociation limit. Thus, the optical energy initially fed into a specific mode (ν_3), which is not initially strongly coupled to the dissociation co-ordinate, nevertheless can rapidly become available for dissociation following the attachment of an electron, because all modes of the resulting SF_6^{-*} are expected to be strongly coupled in the quasi-continuum region.

Of the available candidate molecules for demonstrating reactions (3.1) and (3.2) we chose to study SF_6 (i.e. reaction (3.3)) since the following essential conditions for performance of the present study were known to be fulfilled in its case:

- (i) The dissociative attachment cross section increases rapidly in magnitude with increasing vibrational excitation.
- (ii) There exists a monochromatic source of radiation (CO_2 laser) coincident with the active vibrational mode (ν_3) of SF_6 and sufficiently tunable to allow selective excitation of either isotopic species, $^{32}\text{SF}_6$ or $^{34}\text{SF}_6$.
- (iii) The absorption lines of the isotopes are sufficiently separated to allow selective excitation.

3.2 Apparatus

The apparatus used for the present study is a modification of the "High Temperature Apparatus" which has been described previously⁷. Prior to modification this apparatus had been used in temperature dependence studies of low energy electron attachment in a number of gases, indicating SF_6 ⁸. We concentrate here on a description of those features which are particularly relevant to the use of the system in a manner

Fig. 4 A horizontal section view of the electron gun, collision chamber electrode assembly. The various electrodes of the RPD gun are labelled 3A, 3B, 4A and 4B, and the guard electrodes of the electron collector are labelled G1,2. The sizes of the various apertures are listed to the right of the figure. TC is a thermocouple attached to the back of the collision chamber. RS is a radiation shield.

permitting simultaneous interaction of the gas under study with both a photon beam and an electron beam.

A. Collision Chamber

The collision chamber and its associated electron optics are shown in Figure 4. The electron gun filament (Fil) is operated under temperature limited conditions by maintaining a suitable accelerating voltage between it and the first gun aperture in plate 3A. The electrodes 3B, 4A, and 4B are a set of retarding electrodes used for operating the gun in the "retarding potential difference" mode^{14, 15}, giving an effective energy resolution of 80-100 meV. The electron energy scale was calibrated by the known onsets of He^+/He , Xe^+/Xe and the peak position of $\text{O}^-/\text{N}_2\text{O}$. The data is plotted on a scale corresponding to the most probable electron energy of the effective distribution, the estimated accuracy of the latter being 0.1 eV. The diameter of the electron beam was defined by the aperture of electrode 4A to be 0.50 mm. After traversing the collision chamber, the electron beam was collected on the final electrode which also served as a laser mirror (gold coated) to direct the laser beam into the collision chamber. The intensity of the electron beam in the present experiment was maintained in the range $7 - 15 \times 10^{-9}$ ampere except for the measurements performed to check the dependence of the measurements on the electron beam intensity.

The sulfur hexafluoride gas was introduced into the collision chamber from the top at pressures ranging from 10^{-6} to 10^{-4} Torr, monitored upstream by a calibrated high pressure ionization gauge¹⁶. A sample of the negative ions produced in the collision chamber escapes through an ion exit slot (2.8×0.5 mm) under the influence of a weak extraction field supplied by appropriately biasing the radiation shield positively w.r.t. the collision chamber. These ions are then accelerated through an electrostatic lens system which focuses them on the entrance aperture of a quadrupole mass filter, as shown in Figure 5. The mass selected ions impinge on a Spiraltron Electron Multiplier¹⁷ the output pulses from which represent ion counts.

Fig. 5 Schematic diagram of the experimental set-up. The CO₂ laser beam is chopped by a slotted flywheel which also generates the required gating signals. The laser beam is focused by a ZnSe lens mounted external to the vacuum system, and is guided within the vacuum system by the two mirrors so as to pass through the collision chamber collinear with the electron beam.

B. CO₂ Laser and Optics

The low pressure, flowing gas, dc discharge grating-tuned CO₂ laser was chosen for selective-vibrational excitation of SF₆ gas in the collision chamber. The laser discharge tube has an inside diameter of 1.3cm and was housed in an optical cavity having an exit window to rear grating separation of 240cm. A mode selection plate having an 8mm aperture was placed in front of the grating. A single TEM₀₀₁ gaussian mode was achieved for the entire CO₂ (00⁰1-1⁰00) band. The laser wavelength was monitored continuously by reflecting a very small portion of the laser output into a CO₂ Spectrum Analyzer.

The power output of the laser was measured with a calibrated thermopile power meter. To ensure good reproducibility these measurements were always made with the power meter inserted at exactly the same position in the laser beam path, immediately in front of the focusing (ZnSe) lens. The optical power output of the laser was limited by the heating of the discharge tube cathode to 10 watts for most lines, and to 6 watts for the P (46) line.

The ZnSe focusing lens had a focal length FL of 12.7cm and was chosen to be compatible with the electrode apertures arrangement associated with the collision chamber. The lens was positioned such that the focal spot of the laser beam was at the center of the collision chamber. The calculated spot size is 0.20mm in diameter. The beam profile was also measured at several locations in front of and beyond the focal spot by a shielded thermocouple having a spatial resolution of 0.25mm. The measured half widths agree well (except at the focal spot due to detector resolution) with the calculated values. Therefore, the calculated spot size is used to determine the laser power intensity in the collision chamber. The measured transmission efficiency of the laser beam power into the collision chamber, including reflection losses from the ZnSe lens surfaces, BaF₂ vacuum wall window, absorption and scattering losses of the gold coated mirrors and aperture scattering losses from the electrodes, heat shield and collision chamber, was 71%. This factor is

also used to calculate the laser beam intensity inside the collision chamber.

As shown in Figure 5 the laser beam, after passing through the ZnSe focusing lens and BaF₂ vacuum wall window, was directed into the collision chamber by two parallel gold coated mirrors. By this means the laser beam was made coaxial with the electron beam. At the focal spot, the laser beam diameter was 0.20 mm and the electron beam diameter was 0.5 mm.

In order to be able to check periodically and visually the CO₂ laser beam alignment to the electron beam, a helium-neon laser was set up and its beam was made collinear with the CO₂ beam everywhere outside the CO₂ laser cavity by a simple mirror arrangement and a KCl salt plate. The He-Ne beam was first positioned parallel to the electron beam axis and then translated to the center of collision chamber aperture by a beam translator and steering device. At all times the luminous dot of the electron gun filament, as viewed from the electron collector mirror, was used as a guiding target for the He-Ne laser beam alignment. After the He-Ne beam was in good alignment with the electron beam, the CO₂ laser beam was allowed to enter the system.

In the present geometry the laser beam, if properly aligned, inevitably impinges on the electron gun filament. It was found that the resulting additional heating of the filament caused an easily detectable increase in the electron emission. This provided a convenient method for "fine-tuning" the position of the laser beam, by adjusting micrometrically the location of the ZnSe lens in the transverse plane to give the maximum emission from the electron gun filament. This method proved to be an easy and sensitive approach to the problem of achieving optimum laser beam alignment.

For the present work the apertures in the collision chamber (CC) and the heat shield (RS) were enlarged to 1.5 mm diameter in order to minimize the direct irradiation of the collision chamber walls by the laser beam. The profile of the focused laser beam was such that, when

properly aligned, it should not have been intercepted by the collision chamber apertures. Nevertheless the collision chamber temperature, indicated by the Pt-Pt 10%Rh thermocouple attached to its back, was found to rise in the presence of the laser beam, reading a steady state temperature of $\sim 390^\circ\text{K}$ a few minutes after first admitting the beam (8 watts) to the system. Backscattering of laser radiation from electrode 4A appears to be the most likely cause of the observed collision chamber heating.

The objective of the present measurements was to study the effect on the SF_5^- ion signal produced by the interaction of the laser radiation with the gas molecules. In order to minimize the effect on the measurements of the undesired heating of the collision chamber by the laser beam it was mechanically chopped using a slotted fly wheel, with a period which was short (~ 20 msec) compared to the thermal time constant ($\sim$ few minutes) of the collision chamber. Unfortunately, the time constant of the electron gun filament emission was much shorter than the chopping period. It was found that the modulation of the filament emission by the chopped laser beam occurred essentially in phase with the laser radiation. It was therefore possible to take this effect into account in processing the data by simply monitoring the electron current during both the laser "on" and "off" parts of the cycle, and suitably normalizing the corresponding detected ion signals. The signal detection and data accumulation technique employed for this purpose is described in the following section.

C. Data Accumulation

The method used for data accumulation is an extension of a previously described technique¹⁵ for automatically processing the detected signals to give the "difference" signals appropriate to the "difference electron energy distribution" produced by the "Retarding Potential Difference" (RPD) Technique¹⁴. In the present case it was necessary to record both the ion signal and the electron current signal, with the laser on, and off, giving effectively four signal channels in all.

Fig. 6 Block diagram showing the interfacing of the experiment with the multi-channel scaler used in the multi-plexed four inputs mode. See text and Fig. 7 for details of operation.

The present technique can best be understood by reference to Figures 6 and 7, which show respectively a block diagram of the logic pulse and gate generators, and the relative phasing of the various signals. The master clock is the mechanical chopper used to alternately transmit and block the laser beam. Mounted on the same shaft as the main chopper wheel is a second chopper wheel which provides two pulse trains using a suitable arrangement of a small light source, slits, and two photo diodes. Pulses of train A (see Figure 7) occur at each instant the laser is "turned on" by the main chopper wheel. The pulses of train B occur both when the laser is turned "on" and "off", and are used to advance the multichannel scaler (MCS) through the various channels. In the present case the MCS could be operated with four inputs such that data fed to input #1 was accumulated in channels 0-99, that fed to #2 in channels 100-199, etc. Each of the four inputs could be electronically gated. In the present case the gate pulses were provided by a generator giving two identical pulses separately delayed from an appropriate synchronizing pulse, namely train A, the chopper signal coincident with "turning on" of the laser-pulse. The timing of the gate pulse pair relative to the synchronizing pulse is set so that the first gate ("odd") occurred while the laser was fully "on" and the second ("even") gate while the laser was fully "off". By making the gate widths smaller than the on or off periods the technique is made insensitive to the relative lengths of the on and off parts of the chopper cycle, and a mechanically accurate chopper system is no longer essential.

Application of the "odd" gate to inputs 1 and 3 ensures that these inputs are only "live" while the laser is on. Similarly, the "even" gates, applied to inputs 2 and 4 ensure that they are "live" while the laser is off. As indicated in Figure 6, the electron beam current signal is applied in common to inputs 1 and 2, while the ion signal pulses are applied to inputs 3 and 4. Consequently, input 1 produces a record, in channels 0-99 of the MCS memory, of the electron current with the laser "on". Input 2 feeds channels 100-199 and records the electron current with the laser "off". Similarly, inputs 3 and 4

record the equivalent ion signals with the laser "on" and "off".

The electron accelerating voltage is supplied by a digital-to-analog (D/A) converter which "sees" only the two least significant digits of the channel address. Hence, the output of the D/A remains constant while the MCS steps through, for example, channels 0, 100, 200 and 300, and changes by one increment when the MCS moves on through channels 1, 101, 201, 301, etc. through to 99, 199, 299, 399, at which point the sweep is finished. In practice multiple sweeps are used, an even number of sweeps being necessary for the accumulation of RPD data.

In the present application it is necessary to allow a brief settling time between sweeps, due to the capacitive coupling of the rapid "flyback" of the electron accelerating voltage into the electrometer circuit. This is achieved by using one pulse of the train A chopper signals (see Figure 7) transmitted by a delayed gate of sufficient width to always pass at least one of the pulses of train A. The delay is adjustable, and is typically set at a few seconds. It is triggered by an "address overflow pulse" (AOF) available from the MCS which occurs at the end of each sweep. This system ensures that each sweep is initiated on the "laser on" part of the chopper cycle.

3.3 Results

A. Photon Enhanced DEA in SF₆

A typical set of data illustrating the effect of infrared (IR) photon enhancement of DEA in SF₆ is shown in Figure 8. Curve "a" is the retarded - potential-difference (RPD) electron current, ΔI_e , measured at the electron collector (gold coated mirror in Figure 5) as a function of electron energy in electron volt (eV). The CO₂ laser was tuned to the P(28) 936.86cm⁻¹ line in this case, and the laser power output was set at 8.0 watts. Curve "b" is ΔI_e with the laser beam blocked off from the collision chamber, the magnitude of which is smaller than that shown in curve "a". The difference of the two is the result of direct laser heating of the filament. The factor by which the measured electron current was increased with the "laser on" could be found by digitally

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Fig. 7 Timing sequence of the various signals involved in the data-collection using the multi-channel scaler with four separate "simultaneous" inputs. See text for details.

Fig. 8 An example of data showing photo-enhancement of SF_5^- production from SF_6 . Curves a, b, d, and e are the four sets of data accumulated in the multi-channel scaler, corresponding to: (a) the R.P.D. "difference" current ΔI_e with the laser on; (b) ΔI_e with the laser off; (d) the "difference" ion signal with the laser on and (e) the difference ion signal with the laser off, all signals being measured as a function of the electron energy. Curves (a) and (b) differ in magnitude, due to laser heating of the filament, but not in shape, as shown by their normalized difference, curve (c) which is essentially zero over the whole energy range. The equivalent normalized difference curve of the ion signal is given by curve f, which shows the enhancement of the SF_5^- signal produced by interaction of the laser with the gas.

integrating the respective accumulated signals and calculating the ratio of the "laser on" to "laser off" curves. In the particular example shown the result is 1.342. With the MCS used, and a peripheral data processing unit, it was possible to directly process the data in the MCS to provide the difference between the "laser on" signal and the normalized "laser off" signal - in this case multiplied by the factor 1.342. The result of this operation is shown by curve "c". That this curve is essentially zero everywhere indicates that the same enhancement factor of 1.342 applies at all electron energies, as it should.

The corresponding SF_5^- ion signal curves are shown by curves "d", "e" and "f" in Figure 8. We note firstly that curve "e" - the "laser off" signal - reproduces the features expected at $\sim 390^\circ\text{K}$ based on the thermal data shown in Figure 1. In curve "d" - the "laser on" signal - the laser enhancement of the low energy peak is quite obvious. In addition, there is also an overall increase in the ion signal, relative to curve "e", due to the increased electron current present with the laser on. The increase in the ion signal due to the laser interaction with the gas is isolated in curve "f", the difference between curves "d" and "e" after appropriate normalization to the same electron current - after multiplication of curve "e" by the factor 1.342 determined from consideration of the electron current signals. We note from curve "f" that the laser-gas interaction has a significant effect on the near-zero energy peak, but essentially no effect on the broader peak centered at $\sim 0.38\text{eV}$. This is consistent with the previous observation of the effect of thermally populating the higher vibrational states, as shown in Figure 1. We therefore concentrate our attention in the present work on the dependence of the near zero energy peak SF_5^- signal on the electron current, the gas pressure, the laser power and the laser wavelength.

Using a fixed SF_6 gas pressure, laser power and wavelength, the zero energy peak SF_5^- signal was measured as a function of the RPD electron current ΔI_e , with the results shown in Figure 9. The SF_5^- signal plotted corresponds to the peak signal in curve "d" of Figure 8, i.e. with

Fig. 9 Total SF_5^- ion signal (the zero energy peak of curve (d) in Fig. 8) plotted as a function of the RPD difference electron current. In this plot the gas pressure, laser wavelength (P(28), 936.86 cm^{-1}) and laser power (8.0 watts) were kept constant.

a laser power of 8 watts, tuned to the P(28) line. The observed linear dependence is to be expected for the reactions involved, but a convincing demonstration is important in the present case because of the need to normalize the "laser on" and "laser off" ion signals to their respective corresponding electron currents, as discussed above.

Figure 10 shows the variation of the SF_5^- signal with SF_6 pressure with the other relevant parameters fixed, the laser power and frequency being the same as for Figure 9. The observed linear dependence confirms that simple first order kinetics are involved in the attachment process, consistent with the reactions

Here the subscript "zero" means signal with "laser off" and the subscript "laser" means that portion of the ion signal resulting from the absorption of IR photons by gaseous SF_6 .

It is useful to define a photo-enhancement factor, $E(\epsilon)$, given by

$$E(\epsilon) = \left[\frac{(SF_5^-)_{Laser}}{(SF_5^-)_o} \right]_{\Delta I_e} \quad (3.7)$$

where the numerator represents the signal (see reaction (3)) due to the laser beam - gas interaction, while the denominator represents the signal which would have been observed without the laser beam (see reaction (3.4)) but with all other relevant parameters the same. In particular, the effects arising from the change in the RPD electron current ΔI_e with the laser beam on and off are removed by appropriate normalization. With reference to the data displayed in Figure 8, the numerator of Equation (3.7) is given by the signal level in curve "f", while the denominator is

Fig. 10 Total SF_5^- signal, as in Fig. 9, plotted as a function of gas pressure with electron current, laser power (8.0 watts) and laser wavelength ($\text{P}(28)$, 936.86 cm^{-1}) kept constant.

given by curve "e" normalized by the appropriate ratio of the electron currents, i.e.

$$E(\epsilon) = \frac{[f]}{[e]} \cdot \frac{[b]}{[a]} \quad (3.8)$$

In general $E(\epsilon)$ is expected to depend on the electron energy ϵ , the gas temperature and the laser wavelength and power. The latter effect is shown in Figure 11 for the zero-energy peak signal, i.e. $E(0)$ for a fixed laser frequency of 936.86 cm^{-1} (i.e. the P(28) line). The observed linear dependence suggests that the enhancement effect being observed results from the absorption of a single IR photon, rather than from a multiple photon absorption effect. However, such a conclusion is difficult to reconcile with the laser intensity and the known absorption coefficient. This question will be discussed in the next subsection.

B. Frequency Dependence - Isotopic Selectivity

The dependence of the photo-enhancement factor $E(0)$ on the laser frequency was measured from P(6) to P(46) of the $\text{CO}_2(00^0_1 - 1^0_0)$ band. For most lines a laser power of 8.0 watts was used. For the P(46) line where this power level was not attainable the resulting measured $E(0)$ was linearly normalized to 8.0 watts, based on the data of Figure 11. The value of $E(0)$ was measured independently for both isotopes of sulfur, i.e. for $^{32}\text{SF}_5^-$ and $^{34}\text{SF}_5^-$. The results are shown in Figure 12.

Because of the low abundance of the ^{34}S isotope (4.2%) relative to the ^{32}S isotope (95%) the values of $^{34}E(0)$ are less well defined in Figure 12 than those of $^{32}E(0)$ and no significance is attached to the apparently lower peak value of $^{34}E(0)$ compared to that of $^{32}E(0)$. Unfortunately, the red wing of $^{34}E(0)$ could not be mapped with the particular laser used.

It is clear from Figure 12 that operation of the laser on the P(28) line (936.86 cm^{-1}) optimizes $^{32}E(0)$ while operation on the P(44) line (920.81 cm^{-1}) optimizes $^{34}E(0)$. The isotopic selectivity achieved at these frequencies is shown more dramatically by the full data plots

Curve 689581-A

Fig. 11 The measured laser enhancement factor $E(\epsilon=0)$, as defined by equations (3.7) and (3.8) of the text, plotted as a function of laser power measured immediately before the focussing lens. The equivalent power density in the collision chamber is $2.3 \text{ kW/cm}^2/\text{watt}$, and the laser energy fluence is approximately $1.8 \text{ mJ/cm}^2/\text{watt}$, or $9.4 \times 10^{16} \text{ photons/cm}^2/\text{watt}$.

Fig. 12 The laser enhancement factor $E(\epsilon=0)$, as defined by Eqs. (3.7) and (3.8) of the text, plotted for each isotope as a function of laser wavelength. All points were measured with a laser power of 8.0 watts, except for the P(46) data, which was taken with 6.0 watts and normalized linearly to correspond to 8.0 watts. The broken curve is the small signal absorption coefficient of SF_6 at 400°K from ref. 19.

Fig. 13 Showing the isotopic selectivity achieved by photo-enhanced DEA in SF_6 . The four boxes show the results obtained using the P(28) CO_2 laser line at 936.86 cm^{-1} , which optimizes enhancement of $^{32}\text{SF}_5^-$ production, and using the P(44) line at 920.81 cm^{-1} , which optimizes $^{34}\text{SF}_5^-$ production. Curves (d), (e) and (f) are obtained as described for Fig. 8.

displayed in Figure 13. In this figure the upper curves indicate the $^{32}\text{SF}_5^-$ signal while the lower curves are for $^{34}\text{SF}_5^-$. For both isotopes the left hand curve is obtained using the P(28) laser line, while the right hand curve is obtained with the P(44) line. All curves correspond to 8.0 watts laser power, and are obtained by the same data accumulation procedure described with reference to Figure 8.

The isotope shift evidenced in the present effect, from 936.86 cm^{-1} to 920.81 cm^{-1} , is consistent with the known¹⁸ isotope shift of 17 cm^{-1} in the ν_3 absorption band of SF_6 . The peak positions, however, are shifted to the red relative to the absorption peak at this temperature, shown by the broken curve in Figure 12, which is taken from the paper of Nowak and Lyman.¹⁹ The reason for this red shift will be discussed in the next subsection.

3.4 Discussion

The observed linear dependences of both the laser on and laser off ion signals on electron beam strength and gas pressure indicate that the reactions involved are

where n is the number of IR photons absorbed by the SF_6 molecules responsible for the enhanced SF_5^- production. The implied assumption, that reactions (3.5) and (3.6) occur in the sequence indicated, must be recognized, since the reaction sequence

is a priori entirely plausible. The experimental evidence, however, strongly favors the sequence indicated by Equations (3.5) and (3.6). In particular, the high degree of isotopic selectivity evidenced in Figures 12 and 13 is consistent with the photon absorption process

being into the discrete lower, thermally populated states of neutral SF_6 . If electron attachment were preceding photon absorption, the latter would involve $(\text{SF}_6^-)^*$ molecules having a high degree of internal excitation, within ~ 0.2 eV of the continuum corresponding to the $\text{SF}_5^- + \text{F}$ fragmentation channel. In this situation we would anticipate that the absorption tuning curve would be displaced to considerably longer wavelengths, and broadened to an extent which would preclude isotopic selectivity. Neither of these effects are observed and we conclude that the reaction sequence is as indicated by Eqs. (3.5) and (3.6).

The measured linear dependence of the photo-enhancement factor $E(0)$ on laser power, shown in Fig. 11, has been interpreted previously² as an indication that only single photon absorption is occurring. This interpretation becomes suspect, however, when consideration is made of the laser energy fluence ϕ to which the SF_6 molecules are exposed. Linear absorption behavior is normally to be expected only under "small signal conditions" where

$$\phi \sigma_a \ll 1 \quad (3.11)$$

where ϕ is the laser fluence in photons/cm² and σ_a is the absorption cross-section.

In the present experiment the fluence to which each molecule is exposed is determined by the laser power density in the focal region and the time (τ) each molecule spends, on average, within the laser beam. At the low pressures prevailing in the present experiment molecules in the collision chamber make many wall collisions and few intermolecular collisions. Assuming that the degree of vibrational excitation of a molecule leaving the wall is determined primarily by the wall temperature, with very little "memory" of its previous level of excitation, we may regard the experimental situation as being collisionless, and compute the laser beam-molecule interaction time on the assumption of free molecular flight of the molecules through the approximately cylindrical region at the waist of the focussed laser beam. One may show that for molecules having an

isotropic distribution of velocities entering an infinitely long cylindrical interaction region the interaction pathlength is, on average, equal to the diameter of the cylindrical region. At the typical collision chamber temperatures of $\sim 390^\circ\text{K}$ the average thermal velocity of an SF_6 molecule is 2.5×10^4 cm/sec. The measured beam profile outside the focal region was consistent with the calculated spot diameter of 0.2 mm, giving an approximate average exposure time of 0.8 μsec for those molecules entering the irradiation region. Taking into account the measured transmission efficiency (71%) of the lens, mirrors and apertures, this spot size gives a calculated average beam intensity of 2.3×10^3 watts/cm² per watt of laser output incident on the focussing lens. Hence, the average energy fluence at the focal region is approximately 1.8 mJ/cm² per watt of measured laser beam power. At the maximum power (10 watts) used in the present experiments the average energy fluence was 18 mJ/cm², corresponding to 9.4×10^{17} photons/cm².

In order to evaluate Eq. (3.9) we require the value of σ_a , the absorption cross-section. An average value for σ_a may be obtained from the measured absorption coefficient, ϵ , using the relation

$$\bar{\sigma}_a(v) = \frac{\epsilon(v)}{N_A} \quad (3.12)$$

where $\epsilon(v)$ is in cm²mole⁻¹ and N_A is Avogadro's Number. Using a value of $\epsilon(v) = 2 \times 10^6$ cm²mole⁻¹ appropriate to the P(28) laser line¹⁹ used to obtain the data of Fig. 11, we obtain a corresponding value of $\bar{\sigma}_a = 3.3 \times 10^{-18}$ cm². Hence, at the highest power used in Fig. 11 (10 watts), the product $\phi\sigma_a$ reaches a value of at least 3. Since the value of σ_a for that fraction of the molecules responsible for the absorption is actually much higher than $\bar{\sigma}_a$ given by Eq. (3.12), the effects of saturation would normally be anticipated at fluence values much lower than used in the present experiment. Hence, a linear dependence on laser power is not to be expected under the conditions of the present experiment, and the results of Fig. 11 are somewhat surprising. Because of the large values of $\phi\sigma_a$ involved the apparent linearity cannot be interpreted as

the result of small signal absorption processes involving only single photon absorption. The apparent linearity must result from more subtle effects, a complete understanding of which will require more extensive data than is presently available. At this point we can do little more than to place the present work in the proper perspective with other studies of the absorption behavior of SF_6 at intermediate and high energy fluences. Before doing so, however, it should be noted that the data of Fig. 11 does not necessarily indicate that the effective absorption coefficient is essentially constant over the range of energy fluence studied. For example, the absorption of optical energy by the SF_6 may be occurring with a weaker than linear dependence on the energy fluence, but the SF_5^- production may be dependent on the absorbed energy/molecule in a stronger than linear fashion. Thus the combination of two such non-linear effects could lead to the apparent linearity of the Enhancement Factor observed in Fig. 11.

Information regarding the degree of vibrational excitation to be expected under the present conditions remains incomplete, being primarily in the form of average values for the number of absorbed photons per molecule.²⁰ The general subject of collisionless multi-photon excitation (CMPE) has been intensively studied in recent years, primarily with a view to understanding the many experiments which have been performed on multi-photon dissociation of molecules such as SF_6 . The final stage of the latter process, when the molecule has absorbed tens of photons, has been successfully modeled as an essentially classical statistical process describable in terms of conventional unimolecular dissociation theory.²¹ The initial stages of CMPE, which are of particular importance in the present work and are responsible for the isotopic selectivity of any subsequent dissociation process including multi-photon, are still poorly understood. Attempts to theoretically model this process have focussed on the problem of how a single isolated molecule can absorb, say, three or more photons of equal energy when the active mode is sufficiently anharmonic to ensure that only one transition can be in resonance. A number of mechanisms likely to be of

importance have been identified²², including (i) power broadening of the discrete absorption lines²³, (ii) the compensation of anharmonicity by rotations²⁴, and (iii) the partial compensation of the anharmonic shift by anharmonic splitting of the degenerate overtone or combination levels of the active vibrational mode.²⁵

The relative importance of these various contributing processes has not yet been clarified, but it is well established that power broadening alone cannot possibly explain the observed effects at low laser intensities. The recent work of Cantrell and Fox²⁶ emphasizes the importance of taking proper account of vibrational-rotational interactions and the associated selection rules.²⁷ These workers conclude that the compensation of anharmonicity by rotations is the predominant effect at low laser intensities.

In addition to the experimental studies of multiple photon dissociation there have been a number of studies^{20,28,29,30} of the dependence of the energy absorption cross-section of SF₆ on frequency, energy fluence, peak power, pulse duration, and pressure. In particular, the recent work by Lyman, Feldman, and Fisher³⁰ has extended the range of previous studies down to fluence levels of $<1 \text{ mJ/cm}^2$, and has correlated the data from previous studies.^{20,28,29} The remarkable feature of essentially all the measurements is the very weak dependence of the energy absorption cross-section on fluence over a four decade range starting at $<1 \text{ mJ/cm}^2$. Furthermore, the substantial differences in the peak powers used had only a mild effect on the cross-section³⁰, suggesting that power broadening effects are not of major importance. Similarly, the weak dependence on pulse length indicates that inter-molecular collisions are not an essential ingredient, though collisions are effective²⁰ in increasing the mean absorption cross-section.

In summary, the enhancement effects observed in the present experiments have an apparently linear dependence on the laser fluence which is consistent with independent measurements of the average energy absorption cross section in this range of fluence, although neither type of measurement is properly understood at present.

The activation energy of ~ 0.2 eV for reaction (3.3) deduced from the thermal data of Figs. 1 and 2 would suggest that, at most, two ν_3 photons would be required to promote the production of SF_5^- from SF_6 with zero energy electrons. Furthermore, at the operating temperature of $\sim 390^\circ\text{K}$ the absorption of a single photon into the hot bands of SF_6 would raise the average final state energy substantially above 0.2 eV. For example, using Table 3 of ref. 19, we note that the P(28) CO_2 laser photon is on average absorbed into thermally excited levels of SF_6 such that the average final state energy is ~ 0.4 eV. Hence, the enhancement effect should have been occurring at substantially lower fluence levels than were found necessary to detect it.

The reason for this discrepancy is not known at the present time, but two possibilities present themselves. Firstly, in the absence of the laser radiation the SF_5^- signal at zero electron energy was approximately 4% of the total ion signal, $(\text{SF}_6^- + \text{SF}_5^-)$. Hence, if the fraction of SF_6 molecules capable of contributing to photo-enhancement of the SF_5^- through single photon absorption was smaller than, say, 1% for any laser line, then the enhancement effect, though present, might go undetected, since at best a 25% increase in the SF_5^- signal could be produced at low fluence levels. To be capable of contributing to the photo-enhanced SF_5^- signal at low fluence levels, an SF_6 molecule must satisfy two conditions. Firstly, its thermal energy content ϵ_t must lie in the range $(\epsilon_a - h\nu) < \epsilon_t < \epsilon_a$ where ϵ_a is the activation energy of reaction (3.3). At 390°K roughly one third of the molecules satisfy this criterion if we use the value of $\epsilon_a = 0.2$ eV derived from the thermal data of Figs. 1 and 2. Secondly, of this fraction only those which are in resonance with the laser frequency can contribute. This latter restriction is likely to be quite severe, and conceivably could reduce the overall fraction to less than 1%. These same constraints on the molecules capable of contributing to the observed effects could also account for the shape of the enhancement tuning curve shown in Fig. 12.

In principle, the numbers required to properly estimate the fraction of molecules satisfying the above criteria could be extracted from a molecular band contour model of the type employed by Nowak and Lyman.¹⁹ Unfortunately, the detailed information required here is not available from the published results of their analysis.

The second possibility is that the activation energy, ϵ_a , for reaction (3,3) is substantially larger than the value of 0.2 eV derived from the data of Figs. 1 and 2. The evidence of Fig. 2 is considered rather convincing, but it should be mentioned that results of others^{31,32} have been interpreted to give a substantially larger value of ϵ_a , of approximately 0.4 eV. Clearly, if the true value of ϵ_a is this high, the absorption of a single IR photon is far less likely to cause detectable enhancement of the SF_5^- signal, even in a thermally assisted fashion. Multiple photon absorption would then be a pre-requisite, and could conceivably be consistent with the energy fluence levels found necessary in the present work.

The cause of the red-shift, of $\sim 8 \text{ cm}^{-1}$ between the peak of the tuning curve of the enhancement effect and the small-signal absorption curve for SF_6 at an appropriate temperature, seen in Fig. 12, cannot be definitely identified at this time. It is consistent with the explanation that the shift is a hot-band effect, and the tuning curve has essentially the shape of the fractional population of the neutral SF_6 molecules which, at each wavelength, are both resonant with the laser frequency and have an appropriate degree of thermal vibrational excitation. This general effect is believed to be at least partly responsible for the observed shift. However, similar shifts in the energy absorption tuning curve have been observed by others²⁰ in this range of energy fluence, and will presumably also be contributing to the presently observed effect. We note that a shift of similar magnitude was observed by Avrillier and Schermann³³ in their observations of an effect which they ascribe to the process studied more directly in the present work. These authors used much higher SF_6 pressures, and an essentially unfocussed cw CO_2 laser, presumably having much lower power density than in the present

experiments. If the authors' claim that the power levels were sufficiently low to preclude any saturation effects, then the red-shift observed in their work is most likely due entirely to hot-band effects. This would suggest that the same effect accounts for the major part of the red shift observed in the present experiments.

3.5 Conclusions

The work described in this section on the photo-enhanced production of SF_5^- and SF_6 has confirmed the basic physical mechanism proposed on the basis of the earlier study of the thermally enhanced reaction. The importance of using near-zero energy electrons for this particular process is clearly demonstrated by the type of data shown in Figs. 8 and 13. The tuning curve for the enhancement effect shown in Fig. 12, together with the energy fluence found necessary for detection of the effect, allows us to conclude that at least two quanta of vibrational energy need to be present in the SF_6^* molecule for the SF_5^- channel to be strongly favored as the product ion from attachment of very low energy electrons to SF_6 .

The actual number of quanta absorbed by the contributing SF_6 molecules is not definable at this time, but at the laser fluence levels used could be substantially more than one. A proper understanding of this aspect of the overall process will require additional information regarding the detailed mechanisms involved in this region of fluence where non-linear effects are to be expected. It should be noted in this regard that the present process is well suited to the study of the various factors controlling the absorption of a few photons by SF_6 , since the production of SF_5^- is known to proceed at that level of excitation. This is in contrast to multi-photon dissociation studies in which the observed effect requires the absorption of tens of photons. Thus the present type of study has the advantage of directly probing that region of the excitation which is of major importance, and which at present presents the greatest challenge to our understanding of all such processes.

4.0 NEW APPARATUS

4.1 Design Criteria

The main objective of the present contract was to design and construct an apparatus specifically for the purpose of studying the effects of optical excitation on electron-molecule interaction processes. In particular, it was planned to subsequently use the apparatus to continue the study of photo-enhanced dissociative attachment in order to determine the practical feasibility of using the process for isotopic enrichment of elements of commercial interest. Based on the experience gained during the work on SF_6 described in Section 3, we adopted the following guidelines in designing the new apparatus:

- (i) The collinear electron-laser beams feature should be retained, but the interaction of the laser beam with the electron gun filament should if possible be avoided.
- (ii) The system should be capable of operating in the beam-gas mode using a collision chamber as in the previous work, or in a crossed beam mode.
- (iii) The system should be capable of studying aggressive gases, such as UF_6 .

The requirement in (ii) that the system be capable of operating in a crossed beam mode arises primarily from requirement (iii), since in this mode the interaction of the aggressive gas with the critical surfaces can be minimized, and the gas can usually be trapped on a cold surface immediately after it has passed through the interaction region. In order to satisfy requirement (i) we have adopted a trochoidal electron gun design, the principle of which is depicted in Fig. 14. This type of

Fig. 14. Showing the general principle of the trochoidal electron gun chosen to avoid interaction of the laser beam with the electron gun filament, and the interaction geometry of the collinear electron-laser beams with the neutral molecular beam.

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Fig. 15 General layout of the experimental system shown from the side, approximately to scale.

electron gun has been used by a number of workers³⁴ in recent years because of its good energy resolution and its ability to operate at electron energies close to zero. Both of these features are desirable in the studies planned for the present system. Of equal or more importance to the present studies is the feature that the electron beam in the interaction region is displaced from the filament due to its interaction with the crossed E and B fields in the dispersive region of the gun. In the present application the interaction region is followed by a second crossed field region whose function is to again displace the electron beam. By this means the laser beam can be made collinear with the electron beam in the interaction region without interacting with either the electron collector or, more importantly, with the electron gun filament.

The general layout of the main parts of the apparatus are shown in Fig. 15. The interaction region and the mass filter region are separately pumped, and are connected only by the ion entrance aperture of the mass filter chamber. Hence the pressure in the mass filter can be maintained below approximately 10^{-7} Torr even when the background pressure in the interaction region chamber rises substantially due to the gas load.

The details of the individual components are given below under appropriate subheadings.

4.2 Electron Gun and Related Electrodes

The details of the electrode system are shown to scale in Fig. 16, and the individual parts are identified in Table I. The trochoidal electron gun is based on earlier designs³⁴, but differs from them by being somewhat larger. This change was made in order to increase the displacement from the filament of the beam axis in the interaction region. In the present design a displacement of 0.125" (3.1 mm) is used. Figure 16 actually shows a section through the electrode system in the horizontal plane containing both the electron beam and the laser beam. The whole electrode structure is made from molybdenum and supported from the molybdenum block (1), which in turn is supported from a demountable vacuum flange (F1). The main block (1) has three orthogonal holes drilled through

Table I Parts List for Electron Gun
- Refer to Fig. 16 -

<u>Part No.</u>	<u>Description of Part</u>
1	Molybdenum Block - defines collision region
2	"Hat" Compressing Deflector Electrodes
3	"Hat" Compressing Electron Gun Electrodes
4	Filament
5	Filament Support (1 of 2)
6	Deflector Electric Field Electrode (1 of 2)
7	Compression Plate for Attractor Electrode and Extraction Electrodes
8	Cross-Field Extraction Electrode (1 of 2)
9	Attractor Electrode
10	Insulating Ring
11	Repeller Electrode
12	Compression Plate for Repeller Electrode
13-23	Electrode Discs to Define Electron and Laser Beams
24	Sapphire Insulator Balls
25	Filament Cover
26	Monochromator Electric Field Electrode (1 of 2)

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Fig. 16 Detailed scale drawing of the electrode structure of the electron gun and beam deflector electrodes. A horizontal section is shown. The numbered items are listed in Table I.

Fig. 17 Side view of the molecular beam source assembly. The insulated high current feedthrough shown in the figure obscures an identical second one mounted beside it.

Fig. 18 Side view of the vacuum system shown to scale. The numbered items are listed in Table II. This view correspond to that shown in Fig. 15.

retaining the freedom to separately demount the beam source from the vacuum system if desired.

The actual beam is produced by a multichannel array formed by a cluster of small platinum tubes contained within a larger platinum tube. This whole region can be heated by passing a current through the tube containing the cluster, the return path being provided by an outer coaxial tube, also of platinum. This arrangement of the current path causes least perturbation of the magnetic field in the surrounding region. Platinum is chosen for its ability to withstand UF_6 attack at elevated temperatures.³⁵

The source is electrically isolated from its supporting flange, allowing it to be biased in any desired fashion relative to the region where the neutral beam interacts with the electron and laser beams. This feature necessitates the use of two high current feedthroughs, and an insulating section in the gas feed line to the inner platinum tube.

The neutral beam source will be mechanically connected to the base of the molybdenum block via the flange on the lower end of the outer coaxial tube shown in Fig. 17. This connection will include a Macor section to provide electrical separation of the two components.

If it becomes desirable to use the system in the beam-gas mode instead of the crossed beams mode, the unit shown in Fig. 17 will be replaced by a similar unit which provides two parallel gas feed lines to the base of the molybdenum block containing the beam gas interaction region. The two lines will enter the collision chamber through a cover plate which, together with a similar blank plate on the upper face of the molybdenum block, will serve to seal the collision chamber region. One of these gas lines will feed gas to the collision chamber, while the parallel line will be used to monitor the collision chamber pressure.

4.4 The Vacuum System

The vacuum system and the related pumps are shown to scale in Figs. 18 and 19. The various components are identified in the Parts List shown in Table II. The design of the system is quite conventional except

Table II Parts List for Vacuum System

- Refer to Figs. 18, 19, and 20 -

<u>Part No.</u>	<u>Description of Part</u>
1	Diffusion Pumps, 4", all Stainless Steel
2	Chevron Water Baffles, 4"
3	Gate Valve, 4", Metal Bonnet Seal
4	Custom Pump Mounting Nipples
5	Custom LN ₂ Traps, 4", Stainless Steel
6	Right-Angle Bellows Sealed Valves, Viton Seals
7	Custom Trap Nipples
8	Gate Valves, 6", Metal Bonnet Seal
9	Main Chamber containing Interaction Region
10	Gate Valve, 6", Metal Bonnet Seal, Special High Temperature O-Ring Gate Seal
11	Right-Angle Valve, Bakeable
12	Custom LN ₂ Beam Trap Assembly
13	Mass Filter Chamber
14	Flexible Coupling
15	Custom 90° Elbow
16	Support Table
17	Forepump Line
18	Vacuum Gauge Port
19	Forepump Line for Purging Beam Trap (12)
20	LN ₂ Fill and Vent for Beam Trap
21	Floor
22	Magnet Coils
23	Exhaust Blower
24	Bakeable Miniconflat Valves for Purging or Backfilling System
25	Demountable Gas Trap
26-28	Vacuum Gauges
29	Vacuum Valve
30,31	Pressure Valves
32-34	Vacuum Valves

<u>Part No.</u>	<u>Description of Part</u>
37	Purge Gas Flow
38	Gas Handling Forepump
39	Gas Handling System
40	Controlled Leak Valve
41	Boundary of Bakeable Section
42	Mechanical Forepumps
43	Purge Gas Supply Tank
44	Purge Gas Pressure Regulator
45	Butterfly Valve
46	Flexible Stainless Steel Hose
47	Exhaust Duct
F1	Conflat Flange (8") Supporting Electron Gun Assembly, etc.
F2	Conflat Flange (8") Supporting Quadrupole Mass Filter Assembly
F3	Conflat Flange (6") Supporting Channeltron Multiplier Ion Detector Assembly
F4,5	Conflat Flanges (4-1/2") for Laser Beam Windows

Fig. 19 Plan view of the vacuum system drawn to scale. The view shown in Fig. 18 is looking from the lower side of this figure. Numbered items are listed in Table II.

for the extensive use of gate valves and the provisions which have been made for purging various parts of the system in order to remove gases trapped on the various liquid nitrogen cooled surfaces. In particular, item 12 is a neutral beam trap which can be cooled with liquid nitrogen. Use of a large bellows seal allows the trap to be lowered into the crossed beams chamber, in which position it acts as a neutral beam "dump", provided the gas involved has a sufficiently low vapor pressure at liquid nitrogen temperature, as for example in the case of F_2 and UF_6 . After each "run", when the neutral beam has been turned off, the cold beam trap can be retracted into its own housing chamber and the gate valve (10) closed. The gas which evaporates from the trap as it is allowed to warm up is removed through the side valve (11) and can if necessary be subsequently trapped on a removable trap. The latter procedure is indicated in Fig. 20, which shows schematically the plumbing circuits of the whole vacuum system. As indicated in Fig. 20 the beam trap housing (12) can be purged by admitting a suitable gas such as dry nitrogen through the small vacuum valve (24) and pumping it away through valve (11) into the fore-line (19). Depending on the arrangement of the line valves (33) the gas may either be discharged through the mechanical pump (38) into the exhaust duct (47), or retained in the demountable trap (25) for later disposal.

A similar procedure will be used as necessary to purge and clean the large liquid nitrogen traps (5). It is expected that this will be necessary only infrequently for the trap below the interaction region chamber, and possibly not at all for the trap below the mass filter. For this reason there is no gate valve below this trap.

The plumbing network has been designed to accommodate aggressive gases, such as UF_6 . All vacuum lines, valves, and chambers are of stainless steel. Vacuum seals are of nickel, copper or viton. Viton gaskets will be employed below the custom liquid nitrogen traps (5). Above these traps copper gaskets will be employed on the mass filter pumping stack, while nickel gaskets will be used on the main collision chamber pumping stack.

Fig. 20 Schematic diagram of the vacuum system and associated plumbing. The numbered items are listed in Table II, and correspond to the items numbered in Figs. 18 and 19.

The plan view of the vacuum system (Fig. 19) shows the size and positions of the two coils (22) which will provide the collimating magnetic field for the electron beam. The coils are air cooled, and should be capable of providing a field of 150 gauss at the electron gun region. The coils surround the two optical windows, mounted on flanges F4 and F5, through which the laser beam enters and leaves the vacuum system. The support for the coils has been designed to permit rotation of the field about two independent axes. This degree of control will facilitate proper alignment of the field relative to the trochoidal electron gun.

The quadrupole mass filter is mounted on flange F2 (Figs. 15, 18 and 19) and extends forward so as to be as close as possible to the interaction region. The quadrupole filter is preceded by a quadrupole lens section whose main function is to steer the ion beam into the filter. The plate containing the entrance aperture to the mass filter section is mounted from the vacuum envelope and forms a reasonably tight seal to the envelope. An electrical break is interposed between this plate and the envelope, allowing the potential of the plate to be adjusted for optimum ion transmission.

Ions transmitted by the mass filter impinge on a continuous dynode type multiplier whose output pulses are counted by conventional circuitry.

5.0 STATUS OF PROJECT

This report is primarily an account of work funded by DOE (formerly by ERDA) from May 1, 1977 through November 30, 1977. The primary objective of this phase of the project was the design and construction of the experimental system described in Section 4. At the time of designing the system the intent was to employ it to study BCl_3 during the next contract phase. It was planned that the construction phase of the work would be completed by the end of 1977, to coincide approximately with the end of the initial contract period. A proposal for the continuation of the work along these lines was submitted in July 1977. As a result of discussions with the contractor, this proposal was subsequently revised to place emphasis on the study of UF_6 rather than BCl_3 . The revised proposal, submitted in December 1977, was approved at the technical level in January 1978, and work was planned on the assumption that additional contract funds would become available within the next few months.

The construction phase of the work has suffered from delays from a number of sources. At the end of 1977 it was estimated to be approximately two months behind our original schedule, with a number of major components ordered from outside suppliers still undelivered. In view of the anticipated delay in further contract funds it was decided at that time to delay completion of the liquid-nitrogen-cooled beam trap and to apply the funds originally set aside for that item, together with additional in-house funds, to the other aspects of the construction program. In this way the program was sustained at an optimized reduced level for the first few months of 1978.

At the time of writing (May 1978) all of the major items required for the construction of the apparatus are on hand, except for the liquid-nitrogen-cooled beam trap. Construction of this item will be resumed as

soon as additional funds become available. At this point it has become necessary to relegate this project to "back-burner" status. It is estimated that assembly and testing of the apparatus, including the additional components required for the study of UF_6 , could be completed within three months following resumption of funding.

A secondary objective of this contract was to complete the analysis and interpretation of the previously accumulated data on the selective photo-enhanced production of SF_5^- from SF_6 . This task has been completed, as described in Section 3 of this report. Our understanding of the mechanisms involved is not complete, however. A question requiring further exploration concerns the observed linear dependence of the enhancement on laser power. At the power levels employed we would have anticipated some evidence of saturation effects, on the basis of known absorption cross sections. Some possible future experiments to further explore this question are discussed in the next section.

6.0 FUTURE WORK

The work suggested in this section is directly related to the important question of whether the process of photo-selective DEA is likely to be feasible in UF_6 , and if so, under what conditions of laser power, etc. Two distinct experimental studies are suggested, both of which could be performed in the new apparatus described in Section 4 of this report.

The suggested work on UF_6 , discussed below in subsection 6.1, is that proposed formally³⁶ in December 1977, and has already received technical approval of the contractor. The work on SF_6 , suggested below in subsection 6.2, has not been discussed previously.

6.1 Study of DEA in UF_6

The important question of whether photoselective dissociative electron attachment can be used to enrich uranium cannot be answered at this point due to incomplete knowledge regarding the attachment processes in candidate uranium bearing molecules. Previous work^{37,38} has been confined to UF_6 and has shown that the reaction

occurs at room temperature with a threshold at approximately 0.9 eV and a peak at 2.1 eV.

Work³⁸ on reactions of the type

where A is an alkali atom, has shown that UF_6^- is strongly bound in its ground state with an electron affinity of 5 eV. Similarly, the threshold

for the reaction

has provided an estimate of 4 eV for the electron affinity of UF_5 . Recent estimates³⁸ of the bond strength $D(\text{UF}_5 - \text{F}) = 3.0$ eV lead to the conclusion that Reaction 6.1 is exothermic, and that the reaction observed in previous work proceeds through an electronically excited intermediate state of UF_6 which is repulsive in the Franck-Condon region. This situation is represented by the potential energy curves shown in Fig. 21. In this figure the repulsive curve passing through the shaded Franck-Condon region, labelled $(\text{UF}_6^-)^*$, is that responsible for the production of UF_5^- at electron energies in the region of 2 eV. The curve labelled UF_6^- (X) represents the ground electronic state of UF_6^- .

The well depth of this curve is known from the measured electron affinity, but the general shape of the curve is speculative. In addition, a number of other bound UF_6^- states are known³⁹ to exist, and will lie somewhere between the two UF_6^- curves shown. These bound states are expected to cross the neutral UF_6 state curve somewhere at smaller internuclear distances. Such a crossing is indicated in Fig. 21 for the UF_6^- ground state curve, occurring at point P. Similar points will exist for the other bound UF_6^- curves. Because of the displacement of the point P from the Franck-Condon region of the low-lying UF_6 vibrational states, dissociative attachment via the UF_6^- (X) state is not seen at low temperature. In the situation indicated, however, it is clear that by exciting the UF_6 molecule to vibrational states adjacent to point P, it becomes possible to attach very low energy electrons directly into the UF_6^- state, which will subsequently dissociate.

The above discussion indicates that for the present interests it is essential to establish whether such a process occurs in UF_6 by searching for the appearance at suitable elevated temperatures of a zero energy UF_5^- or F^- peak. If such a process exists it would be ideally suited to the exploitation of photo-selective DEA for uranium enrichment.

There is no published data available on the temperature sensitivity of DEA in UF_6 . A study has been performed at the Lawrence Livermore Laboratory, but no report is as yet available. Private communication indicates that these workers⁴⁰ found no change in the shape of the main attachment peak, corresponding to Reaction 6.1. The difficulties encountered in working with UF_6 were, however, such that the energy scale calibration was only approximate, and the possibility that the attachment peak moved bodily to lower energies without a shape change could not be ruled out. This does not appear likely, however. Of more importance is whether these workers were able to operate their electron gun at very low electron energies (<0.2 eV), at the elevated gas temperatures. Such operation is difficult under any circumstances, but is essential to a proper search for the process discussed above. The crossed-beam system employing the magnetically collimated electron beam, described in Section 4, is believed to offer the best chance of achieving this.

6.2 Further Studies in SF_6

In the course of the work on SF_5^- production from SF_6 , described in Section 3.0, it was not possible to properly interpret the measured dependence on laser power of the enhancement of the SF_5^- signal. Furthermore, a definitive explanation of the observed red-shift of the tuning curve could not be given, partly because the dependence of the tuning curve on laser power was not explored. At the laser fluence levels used non-linear absorption effects are definitely to be expected, but were not detected in the limited region of parameter space which was explored. It is possible, for example, that the dependence on laser power, though apparently linear at the P(28) laser line, would have exhibited non-linearity at the P(16) or P(20) lines, since at these wavelengths the mean absorption coefficient would be larger, and according to other work²⁸, has a much stronger dependence on fluence than does the P(28) wavelength.

At the time of performing the measurements on SF_6 there was insufficient time to explore these various questions. Also, with the new apparatus it is anticipated that the enhancement effect should be detectable at lower fluence levels, since the interfering effect of the laser

Fig. 21 Semi-quantitative potential energy curves for UF_6^- and UF_5^- based on the work of refs. 37 and 38. Previously observed production of UF_5^- (ref. 37) is postulated to arise from the repulsive $(UF_6^-)^*$ state. Attachment to the attractive ground state of UF_6^- would require excitation of the UF_6^- target to a level at or above the curve crossing point, P.

beam heating of the electron gun filament will be absent. It is therefore suggested that the energy fluence and wavelength dependence of the SF_5^- enhancement effect be fully explored using the new system, with a view to providing a better understanding of the non-linear absorption effects which should be present. In so doing, the ability to operate in the crossed beams mode will provide an important check on the assumption that the conditions of the previous work could be regarded as "collisionless". These studies could be particularly fruitful since SF_5^- production from SF_6 directly probes the critical region of excitation involving absorption of a few photons. The resulting data would help develop the understanding of the mechanisms contributing to the absorption of the first few photons in any multiple photon absorption process.

During the study of SF_5^- production some preliminary measurements⁴¹ were made of the effects of temperature and/or laser irradiation on the process

The preliminary data indicates that this process is enhanced by vibrational excitation of the target SF_6 , and that this can be achieved by a combination of thermal and optical excitation. At higher laser power levels it is anticipated that the process could be enhanced significantly by optical excitation alone. The process is of interest because it provides the opportunity to study the dependence on laser power and frequency of a process having an activation energy substantially greater than thermal energy, as is likely to be the case in UF_6 . The number of IR photons which need to be absorbed in this case (~ 10) is intermediate between that required for enhancement of SF_5^- production from SF_6 (~ 2), and that required for multiphoton dissociation (~ 40). The range of optical power levels required for such a study could be achieved in part with the same basic laser as was used in the study of SF_5^- production from SF_6 , with the aid of shorter focal length lenses. A complete study, however, would probably require the use of a more powerful laser, preferable a long pulse TEA laser.

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