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A REVIEW OF LASER ISOTOPE SEPARATION OF URANIUM HEXAFLUORIDE

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ABSTRACT

There is continuing world-wide interest in the possibility of enriching uranium by a laser process which uses uranium hexafluoride. Since no actual commercial plant exists at present, this review examines the key areas of related research. It concludes that such a process is feasible, that it must employ an adiabatic cooling system, with UF_6 the minor constituent in a predominantly monatomic or diatomic carrier gas, that the necessary infrared and/or ultraviolet-visible lasers are in a state of development bordering on the minimum required, and that the economics of such a process appear highly promising.

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COOLING; EXCITATION; EXPANSION; GAS LASERS; INFRARED RADIATION; INFRARED SPECTRA; LASER ISOTOPE SEPARATION; MATRIX ISOLATION; ULTRAVIOLET RADIATION; ULTRAVIOLET SPECTRA; URANIUM HEXAFLUORIDE; URANIUM ISOTOPES; VISIBLE RADIATION; VISIBLE SPECTRA

CONTENTS

1. INTRODUCTION

Information on the separation of the uranium isotopes by laser isotope separation (LIS) processes using uranium hexafluoride (UF_6) emanates primarily from the various institutes of the USSR Academy of Sciences (Ambartzumian et al. at the Spectroscopy Institute, Basov et al. at the Lebedev Physics Institute), the Los Alamos Scientific Laboratory (LASL) in the United States of America (Robinson et al.), from numerous patents mainly of German origin and most recently from the Exxon Laboratories who are better known for their studies on LIS using atomic uranium.

However, so significant are the commercial and political aspects of this area of work that the Americans and, to a far greater extent, the Russians, have talked of their work on the LIS of UF_6 only in general terms, and patents have disclosed little of quantitative value, being concerned mainly with the enunciation of principles. Apart from the general assertion that the LIS of UF_6 must work, the only quantitative support for this belief, is a three line statement from the Los Alamos Laboratories in 1976 to the effect that they had separated the isotopes on a laboratory scale using an unspecified two-laser process and a comment* from Los Alamos staff that they were passing a two-laser process over to the Oak Ridge Laboratories for pilot plant development.

Hence, this assessment of the LIS of UF_6 is not based on an evaluation of direct data from a demonstrated commercial process, there being no such process at present. Instead, it uses three criteria (the most important of the many relevant criteria) to evaluate the significance of work in a wide spectrum of research areas for a possible UF_6 based process.

The three criteria used here for an efficient, economic UF_6-based LIS process are that there must be

(i) a system with appropriate spectral conditions: for all practical purposes this means that the separation must be carried out in the gas phase where isotopic differences in the absorption spectrum are most likely to be resolved and preserved;

(ii) lasers of appropriate wavelength, efficiency, power, spectral purity, repetition rate, reliability and (low) capital cost; and

* Made to Dr A Ekstrom, AAEC, during overseas visit, June-July 1980.

(iii) an efficient photochemical process which preserves the laser-induced selectivity under practical conditions.

In Section 2 of this report is a review of both the most recent work on the infrared spectra obtained under conditions of adiabatic cooling, and ultraviolet-visible (UV/VIS) spectra obtained under conditions of matrix isolation, as well as the more classical aspects of this subject. Section 4 deals with the adiabatic expansion (flow cooling) technique. While flow cooling has been known for many years, its use for improving spectroscopic resolution is quite recent, and the problem of achieving high gas densities without condensation in supersaturated streams has only recently been investigated*.

Section 4 treats infrared lasers, particularly those in the 16 μm spectral region, and assesses the many totally different approaches, studied or under study, to a practicable, high powered, high repetition rate, 16 μm laser. Since excimer lasers are by far the most promising candidates for a suitable UV/VIS laser ($\leq$ 410 nm) these are discussed in Section 5. Finally, Section 6 deals with the laser irradiation of UF_6 and Section 7 contains the conclusions of this assessment.

2. SPECTROSCOPY

Advantages in the use of UF_6 as the process gas for LIS include: (a) UF_6 has a significant vapour pressure at and below room temperature, (b) isotopic spectral differences are due entirely to the uranium atom since fluorine is monoisotopic, and (c) the technology of producing and handling the gas on an industrial scale exists. It should also be noted that a very high degree of enrichment of the sulphur isotopes has been obtained by Basov et al. [1975] for the analogous SF_6 molecule. For these and other reasons, the spectroscopy of UF_6 continues to hold great interest.

* In 1976, Kelly and Struve discussed the technique from a spectroscopic viewpoint following the Los Alamos disclosure [Nucleonics Week, 6 February 1976]: In Section 3 of this report, it is the gas dynamics of the technique which is of primary concern.

2.1 Infrared Spectrum of Gaseous UF_6

The infrared spectrum of UF_6 has been determined by a number of authors [e.g. Bar-Ziv et al. 1972]. The main absorption bands are listed in Table 1. The ν_3 (16 μm) absorption band, being the strongest, is the centre of interest for LIS studies of UF_6.

Unlike the $^{32}SF_6$ and $^{34}SF_6$ ν_3 absorption bands which are fully resolved at room temperature, the ν_3 bands of $^{235}UF_6$ and $^{238}UF_6$ are not. Figure 1 shows that, although the isotopic shift of ~ 0.55 cm^{-1} is clearly visible at room temperature, it is much smaller than the FWHM (full width at half maximum) of the band.

The fractional population of the 10 lowest-lying vibrational states of UF_6 is shown as a function of temperature in Figure 2 for $30 < T < 170$ K, from which it is clear that < 10 per cent of the molecules are in the ground state at 170 K. Less than 1 per cent are present in the ground state at room temperature. By comparison, SF_6 has $\sim$ 30 per cent of the molecules in the ground state at room temperature. Thus, the room temperature spectrum of UF_6 consists of thousands of superimposed hot bands, and lowering the gas temperature is an obvious way of simplifying the spectrum. Hot band conditions in UF_6 at 120 K are comparable with those in SF_6 at room temperature.

The spectrum of UF_6 cooled to 50 K by expansion through a nozzle is shown in Figure 3a, together with the room temperature spectrum. Because of signal to noise limitations, only the Q branch of the spectrum can be seen. The spectra of SF_6 with and without cooling in this way are shown for comparison in Figures 3b and c. These spectra were all taken with a conventional spectrometer. Higher resolution spectra of UF_6 cooled by nozzle expansion were obtained with tunable diode lasers and show Coriolis splitting of individual lines. The temperature of Q band resolution is such that a substantial fraction ($\sim$ 30 per cent) of the molecules can be made to interact with a single laser frequency, provided the effective laser band width is comparable to the width of the Q band.

Nozzle expansion of UF_6 is clearly a means by which the gaseous isotopic spectra of UF_6 can be fully resolved at pressures having a practical significance (Section 3). If, by contrast, UF_6 is cooled conventionally (equilibrium conditions) to temperatures where similar spectral resolution is

attained, it becomes a solid with negligible vapour pressure. Thus, only non-equilibrium dynamic cooling is practical for LIS methods which rely on a temperature-assisted resolution of the absorption spectra.

2.2 Ultraviolet-visible Spectrum of UF_6

The UV/VIS absorption spectrum of gaseous UF_6 has been studied in a number of laboratories for more than 35 years, e.g. Lipkin and Weisman [1942], Hurst and Wilson [1972] and De Poorter and Rofor-de-Poorter [1978], but none of the data obtained had sufficient structural detail to justify more than a superficial analysis of the spectrum.

The first detailed analysis of the structure of UF_6 was published in 1976 by Lewis et al. at the LASL and based on their observations of complex vibronic structure on the broad absorption features of UF_6 which was matrix-isolated in argon at 14 K. They were not concerned with isotopic structure and their results did nothing to dispel the usual notion that if UF_6 is to be used for LIS, then a two-photon process (infrared to discriminate, UV/VIS to dissociate) is essential.

Subsequently, similar work by Grzybowski and Andrews [1978] at lower solute/solvent ratios found strong, sharp, highly structural fluorescent spectra in samples where the solute/solvent ratio (UF_6:A) was 1/1800. They also observed that this structure coalesced into broad bands when the solute/solvent ratio was greater than 1 in 800. Their results demonstrated a strong solute-solute interaction and also explain why Lewis et al. [1976] failed to observe highly structural spectra, their solute/solvent ratio being 1 in 20. The results obtained by Grzybowski and Andrews have been confirmed by Miller et al. [1979] who further noted that the line width was $< 3\ cm^{-1}$ in argon and krypton matrices at 12 K. These results strongly suggest that the first excited electronic state of UF_6 is bound (stable). Corroborative evidence for such a state is provided by Andreoni et al. [1977] and Benetti et al. [1976] who observed fluorescence in gaseous UF_6 at room temperature. These latter studies, which explored the dependence of the fluorescence decay and quantum yield on pressure, temperature and excitation wavelength also provided valuable information on the photochemistry of UF_6.

The existence of a bound (stable) excited state is highly significant. In the past, isotopic resolution of the electronic spectrum of UF_6 has not been possible, and this can now be attributed to spectral congestion resulting

from hot band transitions rather than spectral broadening associated with an unbound excited state. We believe that reducing this spectral congestion through adiabatic cooling to low temperatures (see Section 3), enables the spectrum of gaseous UF_6 to be isotopically resolved. It is intriguing that high resolution UV/VIS spectra of UF_6 under these conditions have never been reported in the literature. Consequently, there is a distinct possibility that uranium enrichment can be achieved by a process in which a single UV/VIS photon will both isotopically discriminate and photo-dissociate a UF_6 molecule.

3. NON-EQUILIBRIUM COOLING BY ADIABATIC EXPANSION

3.1 Introduction

Greene and Milne [1970] pioneered the use of adiabatic cooling techniques in their low temperature work on simplification of the microwave spectra of condensable gases. This was followed by Smalley et al. [1974] who made a laser spectroscopy study of the high resolution fluorescence spectrum of NO_2 in supersonic molecular beams generated by free jet expansion. In 1976, in a brief note in the February issue of Nucleonics Week, Los Alamos workers claimed that they had isotopically resolved the infrared spectrum of UF_6 at 50 K in a Mach 5 gas stream. This claim was analysed by the present authors (unpublished work) who concluded that these temperatures could not have been achieved in a Mach 5, free jet expansion of pure UF_6. Subsequently, Jensen et al. [1976], also from Los Alamos, revealed that such low temperatures at these modest Mach numbers were achieved by the co-expansion of UF_6 in a carrier gas under ducted flow conditions.

Apart from cooling, the expansion process must simultaneously generate gas densities sufficiently high to be of commercial interest (the vapour pressure at temperatures low enough for isotopic resolution (< 60 K) is negligibly small ($< 10^{-20}$ Pa)). In free jet expansion, gas densities $< 10^{12}$ cm^{-3} are unlikely to be exceeded, and the resulting long irradiation paths and high pumping costs make such an approach uneconomic. However, the situation appears to be quite different for ducted flow for which gas densities $< 10^{16}$ cm^{-3} at 50 K have been claimed by Los Alamos workers [Robinson et al. 1976]. Such claims appear to be reasonable in view of the published work on SF_6.

3.2 Ducted Nozzle Expansion of UF_6

The basic ducted nozzle is a converging/diverging channel and the general equations (for example, see Shapiro [1952]) governing the flow of a perfect gas in such a channel under abiabatic, isentropic conditions are

$$\frac{T_o}{T} = 1 + \frac{\gamma-1}{2} \cdot M^2 \qquad (1)$$

$$\frac{P_o}{p} = (1 + \frac{\gamma-1}{2} \cdot M^2)^{\gamma/\gamma-1} \qquad (2)$$

and

$$\frac{n_o}{n} = (1 + \frac{\gamma-1}{2} \cdot M^2)^{1/\gamma-1}$$

where γ = the ratio of specific heats, M = Mach number, T_o, p_o and n_o are the temperature, pressure and gas densities above and T, p and n the same parameters below the throat of the nozzle.

Two sets of values of these parameters are given in Table 2 covering the range M = 2 to 7. The upper set (γ = 1.67) corresponds to the flow of monatomic gases and the lower set (γ = 1.40) to the flow of diatomic gases (also in the table are A_t and A, the area of channel at and below the throat of the nozzle, and the stagnation pressures P_o and P_o (see Section 3.4)).

These values show clearly that temperatures of the order of 50 K reported by Jensen et al. [1976], are readily obtained in mono and diatomic gases at modest Mach numbers (M = $\sim$ 5), which are well within the capability of present-day wind tunnel design, while the pressure ratios p_o/p are markedly less than those considered necessary ($\sim 10^5$) in free jet expansion. Further, since the gas density, not the pressure is significant in a separation process, it is important to note that the gas density ratio (n_o/n) for a given value of M is lower than the pressure ratio.

Since the ratio of the specific heats of UF_6 is close to unity (γ = 1.06 at room temperature), equations (1) and (2) predict that very high, impracticable, pressure ratios would be required to achieve a beam temperature of 50 K. Hagena and Henkes [1960] established an experimental value of T = 120 K for a Mach 5 expansion of pure UF_6 which is in reasonable agreement with that predicted by the above equations when allowance is made for the

increase in γ with decreasing values of T. This difficulty can be avoided by the co-expansion of UF_6 in either a monatomic or diatomic carrier gas at small molar fractions of UF_6. A 1 per cent molar fraction of UF_6 reduces the γ value of a monatomic and a diatomic gas to 1.61_3 and 1.38_2 respectively, i.e. by less than 4 per cent, so that the temperature (T) achieved is essentially that produced by the carrier gas alone. A 10 per cent mixture reduces γ to 1.357 which is still sufficient for effective cooling.

3.3 Supercooling and Condensation

The minimum gas density attainable in a supercooled beam of UF_6 contained in a carrier gas is set by various condensation processes. While condensation of pure gases in supersonic nozzles has been studied over many years (for example, see Wegener and Wu [1977]), very little information is available on nucleation within dilute gas mixtures.

In 1978, Wu et al. published the results of experiments in which dilute mixtures of SF_6 in argon were cooled by expansion at low Mach numbers and the onset of condensation determined by Rayleigh scattering of light from a He-Cd laser downstream of the nozzle. They showed (Figure 4a) that the condensation pressure p_k had a temperature dependence similar to that of the equilibrium vapour pressure (p_∞) and that condensation densities of up to 10^{17} cm^{-3} and 4×10^{14} cm^{-3} could be obtained at temperatures of 100 and 50 K respectively. Figure 4b shows the effect of nozzle design on the condensation pressure. Similar work on the expansion of SF_6 (and presumably UF_6) is known to have been carried out at Los Alamos (see references in Kim and Person [1978a]) but the results have not been published. Wu's work was limited to M = 2.8 (max.), while the Los Alamos workers presumably used values of M = $\sim$ 5.

The factors governing the onset of condensation are not clearly understood but it is known that the degree of supercooling attained is dependent on the rate of cooling, with the higher cooling ratios favouring condensation processes, and independent of the molecular weight of the gas, at least to the first order. Thus, it is probable that condensation pressures comparable to and possibly higher than those of Wu are attainable by the nozzle expansion of dilute mixtures of UF_6 in argon at Mach 5. Expansion in He should give higher p_k values than for expansion in argon because of the higher supersonic beam velocity. Thus, the results of Wu et al. provide valuable corroborative evidence for the claim made in the Los Alamos patent of Robinson et al. [1976] that a 10 per cent mixture of UF_6 in helium could be

cooled to 30 K at a gas density (of UF_6) of $\sim 5 \times 10^{16}$ cm^{-3}.

Note also that (i) higher gas densities are possible if sufficient spectral resolution is available for a process at higher temperature, and (ii) higher cooling rates can be achieved by the use of strongly divergent nozzles and/or a low molecular weight carrier gas.

3.4 Practical Considerations of Adiabatic Cooling

In the apparent absence of any detailed estimates of the cost of a UF_6 laser LIS process, there has been agreement that the pumps (and pumping costs) were likely to be a major cost component; higher values are expected for p_0/p, since the pumps would have to encompass both the laminar and molecular flow regimes. The realisation that gas densities of $n \cong \sim 10^{16}$ cm^{-3} at p_0/p values of 100 to 500 at Mach 5 are attainable has clarified the situation and makes it clear that pumps need to be considered for only the laminar flow regime.

In a practicable adiabatic expansion system, gas dynamic temperatures of the (carrier) gas downstream of the expansion nozzle would be used to minimise pumping costs. Under these conditions, it would be the stagnation pressures (P_0 upstream) and P_0' (downstream) of the system which determine the compression ratio of the gas recirculation pumps. Table 2 lists values of P_0/P_0' for a system in which the expansion nozzle is followed by a divergent diffuser, and the system operated under conditions of normal shock recovery. For $M \cong \sim 5$ and $T \cong \sim 50$ K, the compression ratio is of the order of 10 (more sophisticated systems give even lower values).

Roots blowers fulfil these requirements; they operate in the laminar flow regime and have compression values of this order of magnitude. In many ways they are ideal for this application; they operate in an oil-free environment, have minimum wear because the pumping surfaces are not in contact with the pump walls, and are commercially available in a form suitable for handling UF_6. A full analysis of pumping costs is beyond the scope of this report but a cursory estimate suggests it would be less than $1000 p.a. for a facility employing a 1 watt laser.

Finally, it is important to consider the effect of gas density on the optical path required for efficient use of the laser irradiation. The optical path is inversely proportional to both gas density and adsorption cross

section and, for free jet expansion, it was estimated to be impracticably long. For ducted expansion in which $n \simeq 10^{16}$ cm^{-3} and 63 per cent of the radiation is absorbed by $^{235}UF_6$ molecules, the optical path length was estimated to be $\sim 10^3$ m. This is still long but not impracticable; it can be decreased by operation at higher values of n but the upper limit of n is a complex function of many parameters, including mechanical, spectroscopic, photochemical, etc.

4. INFRARED LASERS FOR LIS IN UF_6

4.1 Introduction

Granted that the spectral conditions for LIS in UF_6 can be provided by adiabatic cooling, the next important requirement is a laser that will operate reliably for long periods at the required wavelength, band width, repetition rate and power level. For commercial application, the presently favoured two-photon approach (see Section 6) requires infrared lasers of at least 100 watt average power (at 16 μm), UV/VIS lasers of $\sim$ 40 W average power and repetition rates of $\sim$ 10 kHz. For multiphoton dissociation, energy fluences of 1 - 10 J cm^{-2} are required and at high repetition rates.

Semiconductor diode lasers (see, for example, those described by Hinkley et al. [1978]) have been used extensively for the generation of infrared radiation, but are restricted to spectroscopic studies and laboratory experiments concerned with 'demonstration of principles'. Many other optical pathways have been explored in the search for an infrared laser suitable for LIS of UF_6: these may conveniently be grouped under four headings:

(i) difference frequency generators,

(ii) optical parametric oscillators,

(iii) coherent resonant Raman devices, and

(iv) optically pumped devices.

Because of the large number of laser transitions which overlap known UF_6 absorption bands, Doppler fine tuning may be sufficient for efficient optical coupling with (iii) and (iv) type devices.

4.2 Difference Frequency Lasers

These lasers use non-linear optical effects in solids to generate continuously tunable infrared radiation. The limitation of this class of laser can be illustrated by reference to the Los Alamos work [Piltch et al. 1975] on the mixing of CO and CO_2 radiation in single crystal chalcopyrite ($CdGeAs_2$) and which produced 40 μJ of 16 μm radiation. The device suffered from the fundamental difficulty that the CO laser is inherently a long pulse device (the 5.8 μm line having a characteristic pulse width of 3 μs) whereas the CO_2 laser pulse is typically of ∿ 0.5 μs duration. Thus temporal overlap, and hence efficiency, is low. Development of a short pulse-length CO laser is required if reasonably high efficiency is to be obtained. If the CO_2 pumping laser is operated under normal pressure, the output is line tunable; high pressure operation of the CO_2 laser allows continuous tuning.

Another basic problem with this class of laser is the difficulty of obtaining large mixing crystals of good optical quality. In general, inherent crystal inhomogeneities cause broadening of the tuning curves and orders of magnitude differences in mixing efficiency from point to point across the crystal faces. Recent studies by Feigelson et al. [1980] indicate that the problem can be ameliorated by self-annealing, but it remains unlikely that this class of laser will be scalable to pulse energies beyond a few hundred microjoules, while bulk heating will probably limit operation to low average powers.

4.3 Parametric Oscillators

The first optical parametric oscillator in the infrared was that of Giordmaine and Miller [1965] who used a crystal of $LiNbO_3$ pumped at 532 nm to generate radiation from 0.96 to 1.15 μm. Byer et al. [1974] of Stanford University subsequently used an Nd:YAG laser to pump $LiNbO_3$ and so produce up to 1 mJ of radiation continuously over the range 1.4 to 4.4 μm.

The first parametric oscillator at 16 μm was that of Wenzel and Arnold [1976]. They used the 2.87 μm line from an HF oscillator-amplifier to pump a CdSe crystal and produce idler outputs of 100 μJ, with band widths of 1.8 to 9 cm^{-1} over the tuning range and pulse lengths of ∿ 100 ns.

Later, Andreou [1977] and Hyer et al. [1979] separately described a similar device consisting of a Nd:YAG driven, $LiNbO_3$ parametric oscillator

with non-linear mixing of the signal and idler wavelengths in CdSe. The radiation had a peak power of $\sim$ 5 kW, pulse energy of $\sim$ 5 μJ when grating tuned, linewidth of $\sim$ 2.6 cm^{-1}, and pulse duration of $\sim$ 10 ns. The laser operated at repetition rates up to 20 Hz.

Since a prime motivation for Andreou's work was the generation of narrow ($\sim$ 0.5 cm^{-1}) linewidths without the use of high loss etalons, it is apparent that this goal is difficult to obtain. In addition, the tuning curves were very sensitive to small changes (10^{-4}) in the refraction index so that the tuning curve varied within and between crystals. Parametric oscillators therefore, like difference generators, cannot be readily scaled up.

4.4 Raman Processes in Liquids and Gases

In 1976, Kung and Itzkhan generated 8.5 and 16 μm radiation by stimulated electronic Raman scattering from potassium vapour in a heat pipe excited by two dye lasers operating at 404.6 and 582.2 nm, and produced an estimated 10 mW of 16 μm radiation at 1 kW pumping power.

Frey et al. [1977] utilised the large Raman gain in liquid nitrogen, pumped by a ruby excited dye laser to generate, by stimulated Raman scattering (SRS), a continuously tunable output up to 1.7 mJ/pulse, having a bandwidth of $\sim$ 1 cm^{-1} and a photon scattering efficiency of 20 per cent.

The potential for high energy conversion efficiency and scale-up is the main reason for interest in SRS from gases. Byer [1976] proposed such a system using rotational Raman scattering from H_2 gas at 77 K pumped by a CO_2 laser, and predicted a 10 per cent energy conversion efficiency. Similar predictions were made by Konev et al. [1977].

Efficient conversion from pumping radiation to SRS radiation requires very careful optical design because of the low Raman gain of H_2 at 16 μm and because pump thresholds are higher than those predicted theoretically (see Laser Focus, April 1978). However, these problems have been overcome by Rabinowitz et al. of the Exxon Laboratories who, in 1980, revealed that they had generated 1.6 J, 20 MW pulses at 623 cm^{-1} by Raman shifting CO_2 radiation in hydrogen at an efficiency of 55 per cent (maximum theoretical efficiency = 64 per cent). Thus, with a CO_2 laser efficiency (electrical input to optical output) of $\sim$ 20 per cent, the overall efficiency is $\sim$ 10 per cent as predicted. This is a major step forward. The principal remaining problem is

the need to increase the repetition rate from 1 to about 10^4 Hz.

4.5 Optically Pumped and Energy Transfer Systems

Optical pumping of gaseous molecules in the infrared is analogous to pumping of dyes in the visible, and is one of the simplest and most direct means of inducing new laser transitions in mid-infrared. Highly reliable and efficient lasers (CO, CO_2, HF, etc.) are available for pumping; the main problem is that of establishing coincidence between the pump and absorption lines of gases with suitable laser emission. Optically pumped lasers are almost always line rather than continuously tunable. Where a suitable laser gas cannot be directly excited, optically pumped lasers have been developed which depend on collisional energy transfer.

4.5.1 Sixteen μm lasers pumped by HF lasers

One such laser system has been assembled by Buchwald et al. [1976] who used an HF laser for direct pumping of various isotopes of CO_2. Numerous lasing lines in the 4.3, 10.6 and 17 μm regions were obtained, and the system was said to be capable of scale-up. However, while the HF laser is a high power source emitting up to 10 MW/pulse, its output between 2.6 and 2.0 μm contains up to 25 lines, and it does not operate efficiently on a single line. Consequently, HF pumped systems are limited to non-critical matching systems.

4.5.2 Sixteen μm lasers pumped by HBr and CO

Osgood [1976] used an HBr laser to pump a resonant absorber (HBr) followed by collisional V-V transfer to CO_2 to generate 'useful' 16 μm radiation. However, HBr pumped lasers appear to have limited potential for scale-up because of the relatively modest ($\sim$ 100 mJ) outputs currently available.

Pulsed CO pumping lasers can deliver a few joules output but, as noted in Section 4.2, their long pulse lengths lead to poor temporal overlap and hence low overall efficiency.

4.5.3 Sixteen μm lasers pumped by CO_2 lasers

The CO_2 laser can be operated at high powers on many single wavelengths in the 9 and 10 μm bands, and so can be used to pump many molecular

transitions. It is the most important pumping laser developed to date for the generation of 16 μm radiation.

Efficient energy down-conversion (to 16 μm) requires at least four conditions to be met. They are:

(i) saturation of the lasing transition by a high-powered pump matched to the absorption line,

(ii) establishment of the resonance condition,

(iii) creation of a suitable absorption path, i.e. optical cavity, and

(iv) constraints on the optical density of the medium arising from collisional deactivation.

Laser systems which have been developed and which attempt to meet these conditions may be divided for convenience into two categories, the single-photon and the two-photon pumped.

Single-photon pumped, 16 μm lasers

Although not a 16 μm laser, the CO_2-pumped 12 μm, NH_3 laser must be included because of its potential use in UF_6 irradiation. By pumping one of the lines of the fundamental, ν_2 vibrational band of NH_3 with a CO_2-TEA laser (R16 line of 9.4 μm band), Chang and Magee [1976] induced population inversion with respect to the ground state and generated, at $\sim$ 12 μm, 5 kW pulsed output at 1.5 MW pump power. This is the greatest power yet achieved in an optically pumped molecular laser. An energy conversion efficiency of 11 per cent has been reported for this laser [Tiee and Wittig 1978a] which has since been used to generate 16 μm radiation in an InSb spin flip Raman laser. Thus, a single CO_2 laser, which could be scaled up to achieve gigawatt levels via current state-of-the art technology, can generate radiation close to the 16 μm (ν_3) and 12 μm ($\nu_3 + \nu_5$) absorption bands of UF_6.

However, the most important CO_2 molecular infrared laser available was first described by Tiee and Wittig at the 1978 Atlanta Conference [1978a,b]. They excited the $\nu_2 + \nu_4$ level in CF_4, producing an (erratic) multiline output of $\geq$ 100 mJ for a 10 J input and achieved a line tunability between 612 and 653 cm^{-1} and a conversion efficiency of 5 per cent in their basically simple

configuration. This was, at that time, the most powerful 16 μm laser available, and as such it generated intense developmental effort.

Experimental efforts to overcome the instability problem are well under way. Stein et al. [1978] have used an intracavity low pressure gain cell in a high pressure CO_2 laser cavity to induce frequency narrowing of the pump. This, together with telescopic matching of the pump outlet to the lowest order mode of the 16 μm resonator, has increased the energy output per pulse from 0.5 to 15 mJ on the 615 cm^{-1} transition, with a quantum yield of 15 per cent. The output energy increase depends in part on the frequency displacement of the narrowed pump line for the particular absorption feature. In multiline operation of CF_4, P and R branch lasing is much stronger than Q branch lasing [Jones et al. 1978].

In addition to the instability problem, other aspects of this laser that must be considered, if it is to be commercially used for uranium enrichment, include:

(a) The ability to fine-tune with respect to a UF_6 transition (cf. the spectral studies of Kynazev et al. [1979] on weakly forbidden vibration-rotation transitions in CF_4 in relation to continuous tunability in the 16 μm region);

(b) Cavity design, including the method of introducing the pump beam into the resonator (these configurations usually involve multiple paths because of the low absorption coefficient of combination bands and the need to avoid long cavities; for example, see Telle [1979]);

(c) The repetition rate, which governs the average power and hence the laser capital costs of the enrichment process (Baranov et al. [1978] studied the dependence of output energy on pump energy, gas pressure and composition at repetition rates up to 100 Hz);

(d) Development potential for increasing output (Baranov et al. [1978] have observed saturation of the output at 0.1 J with a peak efficiency of $\sim$ 1 per cent. Since the CF_4 laser is a low gas pressure laser, there is reasonable doubt that significantly higher outputs at high repetition rates are possible).

While the CF_4 laser is, clearly, a simple and effective device, its development into a commercial model will, if possible, require a substantial effort. Similiar considerations apply to two other 16 μm molecular lasers, the nitrogen-sulphur-fluorine (NSF) laser of Fischer [1980] and the perchloryl fluoride ($FClO_3$) laser of Rutt [1980].

Two-photon pumped, 16 μm lasers

The first experimental demonstration of two-photon pumping to generate 16 μm radiation was that by Barch [1975] who used the non-linear SF_6 molecule. In this case, off-resonant pumping of the intermediate state was possible because of the several SF_6 lines existing within the 720 MHz bandwidth of CO_2 laser 10 P(14) pump line. Power output was not given, but Barch noted that it decreased rapidly with increasing pressure, indicating that lasing was from an excited combination band. High efficiencies were predicted for an optimised system.

Another two-photon laser based on the excited vibrational-rotational levels of $^{14}NH_3$ was described by Pummer et al. [1978], following earlier work by Jacobs et al. [1976]. Increased attention was paid to the optimisation of the system by changing pump intensities, relative beam polarisation, pulse length, NH_3 pressure and irradiation path length. Four wavelengths were generated at 12.11, 13.72, 13.85 and 15.95 μm. The first two can be suppressed by suitable intracavity absorbers, such as $(CH_2Cl_2)_2$. Off-resonance pumping by as much as 300 MHz was evaluated using the optical Stark effect. Output was 1 mJ at $\geq$ 10 per cent conversion efficiency and a maximum of 30 per cent was predicted. This system appears to have the advantages of potential for scale-up and high pulse repetition rates, and to be capable of average powers of $\sim$ 1 W.

4.6 Other 16 μm Lasers

Free electron lasers have attracted considerable interest recently because of their potential for reaching high power levels and because they can, in theory, be continuously tuned by changing the electron energy. These lasers rely on an electron beam which passes through a spatially varying transverse magnetic field where energy is extracted by scattered photons. To date, most work has been concerned with the physics of such lasers but amplification has been observed at 10.6 μm, oscillation at 3.5 μm and stimulated super-radiant emission at 400 μm (see Laser Focus, August 1980,

p.72). It is not unlikely that studies of a 16 μm laser of this kind are in progress, but none has so far appeared in the literature.

A laser of a totally different kind has been described by Wexler and Wagnant [1979]. They studied an electric discharge gas dynamic laser in which an N_2/He mixture was supersonically expanded and then mixed with CO_2 to generate 16 μm radiation in a 5-pass optical cavity configuration. They obtained a 5 W output at 4800 Hz (the highest repetition rate yet obtained) at an output energy per pulse of 1.1 mJ. This system was reliable and with further development to improve the efficiency (0.1 per cent) and peak power obtained, could meet the requirements for the LIS of UF_6. In a separate theoretical study Suzuki et al. [1980] predicted that high power levels at high repetition rates can be obtained from a conventional gas dynamic CO_2 laser in which a fast 9.4 μm pulse is injected downstream of the throat nozzle in order to populate the upper (16 μm) level. Clearly, there is room for further development of this class of laser.

5. EXCIMER LASERS

5.1 Introduction

Copper/copper halide lasers which have the very desirable characteristics of high output power, high efficiency and high repetition rate, and which are used in the atomic LIS process have, unfortunately, too long a wavelength for UF_6. Generally, UV/VIS lasers for use with UF_6 must operate at wavelengths $\leq$ 430 nm. Of the various lasers which operate in this region, the nitrogen laser (λ = 337 nm) can be immediately excluded because of its low overall efficiency ($\sim$ 0.01 per cent). Likewise, flash lamp pumped devices are not discussed since their development seems to have foundered on the problem of adequate lifetime at high powers and repetition rates of interest.

The only class of UV laser which has the potential for adequate efficiency ($\geq$ 1 per cent) at high powers and high repetition rates is the excimer laser. With few exceptions, these lasers are line tunable only so that, barring a fortunate line coincidence, they will most likely serve as the pump for some other conversion device, e.g. a dye laser or possibly a stimulated Raman scattering device for up or down conversion of the pump radiation.

The three criteria which determine the overall efficiency of a UV/VIS excimer laser are that

(i) the radiation life-time of atoms or molecules must be between 10^{-9} and 10^{-6} s,

(ii) the rate of decay of the lower level must be high, since it sets a limit to the intracavity flux that can be utilised before a 'bottlenecking' occurs, and

(iii) the laser discharge load should be well matched to the network that produces the electric pulse for good electrical coupling; this places a strong preference on laser media which can be discharge-pumped in a stable, non-arcing manner.

These criteria have led workers to look for systems in which the lower level is rapidly depopulated. This can occur in a number of ways, including collisional quenching, pre-dissociation and dissociation. This last is the fastest, and characterises excimer lasers where the lower level disappears in a time of the order of 10^{-12} s. Thus large cavity fluxes can be used for efficient extraction of the energy from the upper laser level and lead to the maximum efficiency obtainable within the limits of kinetic branching ratios and the quantum efficiency of the pathway(s) used to formulate the upper level.

The discussion that follows is devoted primarily to excimer lasers formed from rare-gas halides. Excimer lasers based on halogen molecules (I_2 laser at 342 nm, Br_2 at 292 nm and Cl_2 near 260 nm) form a small complementary set and are of little use for the LIS of UF_6 since their characteristic wavelengths lie in the vacuum UV. An understanding of the chemistry that leads to excited rare-gas halides or halogen molecules requires a knowledge of competing kinetic paths, as well as the mechanism whereby each path varies with mode of excitation, pressure and gas composition. This aspect is not treated (in depth) in this report which is concerned largely with the results attained for given laser systems rather than the detailed mechanisms of them.

5.2 Developments in Rare-gas Halide Lasers

Most of the early systems, including the first excimer laser of Ewing and Brau [1975a], were pumped by relativistic E-beams. These lasers were

necessarily high pressure devices in which excitation was caused by three-body collisions. However, the complexity of such lasers hindered their development and application, so that there has been increasing interest in the development of electric discharge devices. These are of two basic types:

(i) E-beam controlled discharges, and

(ii) avalanche mode discharges.

E-beam controlled discharges, which use low intensity electron beams to ionise the gas volumetrically, stabilise it and thus prevent it from arcing, have long pulse lengths and high energy outputs per pulse. Avalanche devices appear to offer the fastest route to medium powers, short pulse lengths (few tens of ns) and high pulse repetition rate (kHz).

The KrF laser has a sharp emission band bear 250 nm. It is one of the most efficient excimer lasers and has received the greatest attention in theoretical studies based on alkali halide models. It has been developed mainly in the E-beam pumped configuration and, to a lesser extent, in the discharge pumped configuration. A large KrF laser has been ordered by Los Alamos, reportedly for its two-photon UF_6 separation program (Laser Focus, September 1978, p.979).

While the fluorescence efficiency of $Ar/Kr/F_2$ mixtures is high, their laser efficiency is even higher [Bhaumik et al. 1977]. Using a high intensity relativistic electron beam, Ewing and Brau [1975b] obtained an efficiency of 15 per cent (600 mJ out for 4 J deposited in the cavity) from 0.3 per cent F_2, 6 per cent Kr, and 93.7 per cent Ar, at a total pressure of 300 kPa. Nitrogen trifluoride was also used as a source of fluorine (F) but the overall efficiency was lowered, probably because of branching which leads to lower yields of KrF*. Longer laser pulses have been obtained in KrF lasers with high cavity fluxes, thus demonstrating the absence of lower energy level bottlenecks. The ultimate efficiency of relativistic, electron beam pumped, rate-gas halide lasers is limited by the amount of energy, W, required to form rare-gas ions and metastables. Thus the maximum efficiency of an electron beam pumped, KrF laser in an Ar buffer is $\frac{h\nu(KrF)}{W}$ = 24% (av.). The maximum achievable efficiency has been estimated to be < 8 per cent and, in practice, the 'wall plug' efficiency is 1-3 per cent, sufficient for an economic LIS process.

By way of contrast, the maximum efficiency of a discharge pumped laser is limited by the energy E* required to form the lowest energy, rare-gas metastable species. Thus the quantum efficiency of a discharge pumped, KrF laser is $\frac{h\upsilon(KrF)}{E^*(Kr)}$ = 50 per cent. The maximum achievable efficiency has been estimated to be ∿ 25 per cent.

An important feature of E-beam, controlled discharge, KrF lasers is the role played by the halogen-bearing species in discharge stabilisation. The fast reaction of F_2 with Kr* enhances discharge stability further by keeping the metastable density relatively low. No such stabilisation occurs in discharge pumped, Xe_2^* lasers. E-beam controlled discharge lasers have an additional advantage over pure E-beam pumped systems in that the bulk of their energy comes from the discharge rather than through a thin foil.

Early transverse discharge (avalanche mode) KrF lasers were low in both efficiency and power, but current devices are increasingly attractive. A feature of these lasers is the fact that the formation of the excited molecules is not dominated by three-body collisions as in E-beam pumped devices but by efficient two-body harpooning reactions, i.e. reactions which occur by way of an ionic-covalent curve crossing. Greene and Brau [1978] have developed a theoretical model of UV pre-ionised, transversely discharged KrF and ArF lasers which account for the time dependence of the discharge, the kinetics of the atomic/molecular species and free electrons, and the growth of laser emission.

Discharge type excimer lasers are usually pumped by a Blumlein circuit or more often by an L-C inversion circuit similar to those used for pumping nitrogen and CO_2 lasers. Although CO_2 lasers do not give as high a peak output as nitrogen lasers, they are easier to construct and have larger discharge volumes: they also require auxiliary pre-ionisation to obtain a uniform discharge. One important advantage of discharge pumped lasers is that they may enable high average powers at high repetition rates to be obtained at lower circuit costs than do pure E-beam devices.

Table 3 presents data on typical, rare-gas halide lasers over this period of development (1976-1980) from which it can be seen that overall efficiencies are of the order of 1 per cent and thus much less than predicted achievable values. Also, there is an inverse relationship between output energy and repetition rate, and average powers have risen very slowly from less than 1 watt to a few tens of watts. The KrF laser of Fahlen [1980] decreased to ∿ 60

per cent of its initial output after a few hours running. Clearly, development of these lasers is difficult and many problems have still to be overcome before they can operate reliably at the high powers and repetition rates required for commercial separation.

5.3 Developments in Halogen Lasers

E-beam excitation of argon/I_2, Br or Cl_2 mixtures, whose emission spectra are similar to those of the rare-gas halides, has been demonstrated by Chen and Payne [1976] and McCusker et al. [1976]. Although the lower laser level in Ar/I_2 or Br_2 mixtures is bound, rapid depopulation takes place by collisionally induced pre-dissociation. For Ar/Cl_2 mixtures, direct depopulation through dissociation is also possible. Lasing has been induced also in mixtures of Ar/Xe/CF_3I but is better in Ar/HI and Kr/HI [Ewing and Brau 1975b]. Peak outputs are of the order of a few MW at efficiencies of $\sim$ 2 per cent. Br_2 and I_2 excimer lasers are similar but their power outputs are not high, probably because of self-absorption and bottle-necking. Woodworth and Rice [1978] recently described an F_2 laser operating at 157 nm with a peak power of 7 MW, an intrinsic efficiency of 3.5 per cent, and using a high pressure mixture of He and a few hundreds of pascals of F_2. All these devices operate at low repetition rates (< 10 Hz). However, a fast discharge F_2 laser with similar characteristics to the above E-beam devices and said to be capable of operating at high repetition rates has been described by Hohla and Pummer [1979].

Overall, halogen-type excimer lasers have lower outputs, narrower bandwidths, restricted wavelengths and lower repetition rates than rare-gas halide lasers, and they suffer from corrosion problems. They do not appear to be as significant for the LIS of UF_6 as do the rare-gas halide lasers.

5.4 Tuning UV Radiation to UF_6 Transitions

Rare-gas halide lasers, halogen lasers and the comparatively recent mixed halogen lasers [Diegelmann et al. 1979] all use diatomic species for their active medium and are line-tunable only. Apart from fortunate coincidences, they cannot be exactly tuned to UF_6 transitions (absorption lines). They can, however, be used as pumps for continuously tunable dye lasers. Dyes have been developed which, when pumped with a KrF laser, will lase down to 311 nm [Zapke et al. 1980] while an XeCl laser has been used to pump dyes covering the range from 340 to 710 nm [Uchino et al. 1979] with a maximum efficiency of 40 per

cent in the visible. However, the stability of such dyes under high repetition rate, high power operating conditions must be taken into account. Dye stability is a problem in the atomic LIS process (which uses visible radiation) where it has been overcome by the use of expensive recirculation, purification and dye make-up equipment. It is likely to be a much more serious problem at the shorter wavelength being considered for potential UF_6 processes. A further problem with dye lasers is super-radiance at high powers leading to loss of coherence.

Wavelength shifting can be achieved also by stimulated Raman scattering. Djeu and Burnham [1977] observed intense electronic Raman emission from Ba vapour pumped by an XeF laser, the optical conversion efficiency being greater than 90 per cent. Loree et al. [1977] observed a conversion efficiency of $\sim$ 50 per cent in the first Stokes shift of H_2, D_2 and CH_4 when pumped by ArF and KrF. Both of these are examples of line shifting; however, in Loree's study, the first anti-Stokes line was also generated at an exceptionally high efficiency (approximately half the first Stokes line). This result can be linked with the recent work of Bischel et al. [1979] who used efficient photolytic pumping methods to overcome E-beam absorption problems in KrF, and generated 483 nm radiation with a tunable bandwidth of 40 nm. This raises the possibility that exact matching to a UF_6 transition can be achieved by continuous tuning of the pumping laser (without the use of dyes) and up-converting its output at high efficiency ($\sim$ 25 per cent) up to the required value. High power pumps are required for the generation of high power Raman emission, 200 J from XeF and 300 J from KrF [Avouris 1980]

Finally, as noted above, diatomic excimer lasers are not continuously tunable; however, triatomic excimer lasers are. The first such laser was described by Tittel [1980a] who obtained lasing from Xe_2Cl centred at 518 nm: he predicted that it could be tuned across its entire 450-550 nm fluorescent band. This has been followed by the further announcement [Tittel 1980b] that lasing emission has been obtained from Kr_2F at 436 nm, at a bandwidth of 25 nm, and with a probable tuning range of 380-480 nm. Since the techniques developed for rare-gas halide lasers should be transferable to this new class of laser, it is likely that they may provide a single continuously tunable source of UV radiation covering the wavelength of interest for the LIS of UF_6. It remains to be seen whether they can be developed to the necessary levels of power, repetition rate and reliability.

6. LASER IRRADIATION OF UF_6

6.1 Matrix Isolated UF_6

Matrix isolation is a well known technique for studying photochemical reactions in an inert or reactive solid matrix which is cooled to liquid helium temperatures and in which molecules can undergo reactions uncomplicated by thermal effects. Given the spectral simplification that accompanies cooling to such temperatures, it is not surprising that this technique has attracted attention for use in laser induced dissociation/isotopic separation reactions.

Ambartzumian et al. [1976] appear to have been the first to attempt such studies with infrared radiation. They used pulsed CO_2-TEA lasers, at powers of 5-30 MW cm^{-2}, and claimed isotopic enrichment in an SF_6:Ar mixture (1:500 to 1:2000) which was held on a CsI substrate mounted on an He cryostat. Their results have, however, been questioned by Davies et al. [1978] who were unable to confirm them. Bernstein [1977] has reported the beginnings of a program of uranium isotope separation based on the use of $U(BH_4)_4$, but has so far published no irradiation results.

An unexpected development in this area is the observation that matrix isolated materials can be photochemically affected at infrared laser power densities of only a few mW cm^{-2}. At the 1978 Atlanta Conference, Livermore workers disclosed that they had irradiated the ν_3 band of UF_6 in a matrix of SiH_4 at 10 μm, and that new absorption bands had appeared which they attributed to UF_5 or UF_4 [Catalono et al. 1978]. These results have been questioned by a Los Alamos worker, P. Robinson [private communication 1979], who interpreted them in terms of laser heating. However, the work of Poliakoff et al. [1978] on $Fe(CO)_4$ in a CH_4 matrix seems to demonstrate conclusively that isotopic selectivity is possible, and that reactions can be induced by low power lasers (< 5 mW cm^{-2}) provided there is good coincidence between laser output and the reactant absorption band.

The Livermore work does not lend itself very well to enrichment since the ν_3 band was too wide (~ 16 cm^{-1}) for adequate spectral resolution. However, since the absorption band of the molecule depends on the matrix material, suitable UF_6-matrix combinations may possibly be found, giving bandwidths < 5 cm^{-1}, and significant isotope selectivity could be achieved by using side band excitation. Nonetheless, while these studies on solid UF_6 reactions are

scientifically interesting, it is difficult to see how the process could be scaled up to commercial requirements.

6.2 Gas Phase UF_6

6.2.1 Single infrared photon excitation

Gurs et al. [1976] advanced the idea that isotope selective excitation of UF_6, with a single vibrational quantum, could lead to isotope selective photochemistry. Eerkens [1976] claimed to have achieved a separation factor of 1.1 by this means but his claims have not been substantiated. Gurs' idea was based on the use of the CO laser and the 3 ν_3 band of UF_6, and Eerkens' on the CO laser and the $\nu_3 + \nu_4 + \nu_6$ combination band. (Undoubtedly similar claims will be made for the ν_3 band and the 16 μm laser.) In both cases, the isotope separation is to be achieved by selective reaction of laser excited UF_6 with some co-reactant.

Gurs' and Eerkens' claims assumed that differences in the reaction rates could be described by

$$k^o \propto \exp(-E/kT)$$

$$k^* \propto \exp(-\overline{E-h\nu}/kT)$$

where k^*, k^o are the rate for excited and unexcited UF_6, E is the bimolecular activation energy and, ν, the photon energy. The ratio of the reaction rates for the ^{235}U and ^{238}U isotopic species is therefore

$$k^*/k^o = \exp(h\nu/kT) \quad .$$

Unfortunately, while the ratio can be quite significant at or below room temperature, even for 16 μm photons, the theoretical basis of this approach is wrong. During thermal activation to the transition state at E-hν, the initial laser discrimination will always be lost (since deactivation is always more efficient than activation) and subsequent reactions will be isotopically non-selective. Alternatively, the quantum yield will be prohibitively small. The special case which occurs when E is comparable to h , is also difficult to realise in practice. Generally, laser enrichment is practical only when the energy of excitation is comparable to the reaction activation energy and, for vibration excitation with an infrared laser, only multiphoton excitation can

achieve this condition.

6.2.2 Single UV/VIS photon excitation

The intense ($\tilde{B}$-$\tilde{X}$) absorption band centred at ~ 260 nm (see Figure 5) would be ideal for isotope separation purposes if the spectrum in this region could be isotopically resolved under adiabatic expansion conditions. However, although no such experimental investigation of this region has been published, the work of Kroger et al. [1978] makes it clear that no isotopically resolved spectrum can exist in this absorption band. Using a polarised, 210 nm laser beam, they observed that the F atoms in the photo-dissociated, photo-fragment spectrum were asymmetrically distributed in that plane which is at right angles to the laser beam; it appears that the photo-activated UF_6 was dissociating within this rotational period of the UF_6 molecule. This observation eliminates the possibility that rotational, and therefore isotopic, structure will occur in this spectral region. The observation by Andreoni et al. [1978] that no fluorescence occurs from UF_6 irradiated at 270 nm further corroborates this conclusion.

A different situation prevails in the relatively low intensity ($\tilde{A}$-$\tilde{X}$) absorption band covering the spectral region 340 to 420 nm. As discussed in Section 2.2, there is strong evidence to suggest that under appropriate conditions, probably adiabatic cooling, isotopically resolved spectra will be found in this region.

The fluorescence measurements of Andreoni et al. [1977] suggest that the crossover point for intersystem crossing from a dissociative electronic state which correlates directly with ground state UF_5 and an F atom, lies at about 27 900 cm^{-1}. Horsley et al. [1980] have irradiated UF_6 at wavelengths above and below this energy level. Irradiation of pure UF_6 and 1:5, UF_6/N_2 mixtures at 50 to 100C at argon ion wavelengths of 363.8, 35.1 and 350.8 nm gave quantum yields of 0.5 to 1, depending on the temperature. (The quantum yield was here defined as the number of molecules removed from the system per photon.) Using both infrared absorption and laser snow detection methods, they further showed that the rate of depletion of UF_6 in a static cell was of the order of 2×10^{-1} Pa s^{-1} W^{-1}. This rate increased to 2 Pa s^{-1} W^{-1} (corresponding to quantum yield of 2) when hydrogen was introduced to scavenge the F atoms produced in the dissociation. Horsley et al. considered the reaction sequence to be

$$UF_6 + h\nu \rightarrow UF_5 + F$$

$$F + H_2 \rightarrow HF^+ + H$$

$$H + UF_6 \rightarrow UF_5 + H \quad .$$

The possibility that other reaction pathways are feasible, e.g. a bimolecular reaction of H_2 with electronically or vibrationally excited UF_6, indicates the need for careful control of irradiation wavelength and power in order to avoid loss of selectivity by scrambling reactions. The conclusion reached by Horsley et al., that at most only 1/10th of the absorbing molecules will undergo photo-deprivation, is probably the result of a calibration error. Although Br_2 (used in the calibration procedure) has an unbound upper state and can be totally dissociated, UF_6 with bound upper and lower states cannot be totally dissociated because these levels cannot be repopulated in a molecular beam.

A further method by which UF_6 can be separated is by enhanced reaction of the selected, excited isotopic species with other atomic species. Horsley's group also considered this probability from a theoretical standpoint and concluded that Br and I, but not H, atoms could be useful for selective reaction with vibrationally excited species. However, this process appears to be of no practical consequence since, in addition to the provision of activated UF_6, it is also necessary to generate Br (or I) atoms in situ and these, as well as reacting as above, can also collisionally deactivate vibrationally excited molecules through V-T processes.

6.2.3 Simultaneous infrared and UV/VIS photon excitation

This approach, first suggested by Robieux and Auclair [1965] and analysed by Struve [1972], achieves isotope selectivity by single quantum vibrational excitation of one species only, while a single UV/VIS quantum, selectively absorbed by the vibrationally excited species, provides the energy necessary to initiate photochemical reactions. This approach, in conjunction with adiabatic cooling, was used at LASL (Laser Focus, 1976) to achieve some degree of uranium enrichment. The research program concerned with scientific feasibility has now been successfully completed, and the method is being developed at Oak Ridge under the sponsorship of Department of Energy (DOE) [Haberman 1980]. Cost estimates [Robinson et al. 1976] compared very favourably with those of centrifuge enrichment (Table 4).

The main difficulty, but one in which continuous progress is being made [Mace 1981], is the provision of high powered, high repetition rate laser radiation sources which will operate for sufficiently long periods between overhaul/replacement. Birely et al. [1976] estimate laser fluence requirements of $\sim$ 10 kW/cm^2 and $\sim$ 2 kW/cm^2 for the infrared and UV/VIS lasers respectively. Also, the infrared laser wavelength must be within $\pm$ 0.02 cm^{-1} of the ν_3 absorption peak of UF_6, and this additional requirement may eliminate many 16 μm sources otherwise suitable for room temperature irradiation of UF_6.

6.2.4 Multi-photon infrared excitation

Isotope selective infrared laser induced multiphoton dissociation of SF_6 was reported in 1975 [Ambartzumian et al. 1975; Lyman et al. 1975] using pulsed CO_2 lasers in the energy fluence range of 1 to 100 J cm^{-2}. Since then, infrared multiphoton induced dissociation has been observed in many molecules, such as OsO_4, MoF_4 and NH_3. However, isotope selectivity, when measured, was found to be small for the heavy elements. Although the separation of the ^{32}S, ^{34}S isotopes was practically 100 per cent in SF_6 where the isotopic absorption bands are fully resolved, the enrichment fell markedly to a few per cent for the relatively light SeF_6 [Tiee and Whittig 1978c] and MoF_6 [Freund and Lyman 1978] molecules where the isotopic spectral shift is small (1.6 cm^{-1} for the ν_3 vibration in SeF_6) and considerably less than the absorption band profile width.

In UF_6 and similar molecules, the anharmonicity problem associated with $\nu^n \rightarrow \nu^{n+1}$ excitation to the quasi-continuum is overcome by using high powered lasers to induce power broadening. For UF_6, the isotopic spectral shift is $\sim$ 0.2 cm^{-1}/amu, and the energy fluence necessary for dissociation ($\sim$ 1 J cm^{-2}) is comparable to that for SF_6. Since fluences of this magnitude introduce power broadening of the order of the isotopic shift, there is little value in adiabatically cooling UF_6 to provide the resolution necessary for isotopic selectivity.

To overcome this loss of selectivity caused by power broadening, it has been suggested that isotope selectivity could be maintained by infrared irradiation at power fluences where only a few photons (1-3) are absorbed and the spectrum of the infrared excited UF_6 is shifted to a lower frequency where the unexcited isotopic species becomes transparent. The excited species is then irradiated by an infrared laser of different frequency to the

dissociation limit. This process was first described by Ambartzumian et al. [1978] for the separation of the osmium isotopes in OsO_4.

Such a process has been patented for UF_6 by Kaldor and Rabinowitz [1976] who used a 16 μm laser to activate the molecules and a CO_2 laser to dissociate them; no technical details, in particular separation factors, were disclosed. Tiee and Whittig [1978d] described a similar system in which a CF_4 laser was used to excite UF_6 so that the 8.6 μm transition of unexcited UF_6 was broadened and shifted to allow excited UF_6 molecules to absorb 9.6 μm CO_2 laser radiation. Enhancement factors of 1 to 100 in the dissociation were obtained but no mention was made of enrichment. Alimpiev et al. [1979] have reported the dissociation of UF_6 at room temperature by both multiphoton CF_4 laser radiation and the combined action of CF_4 and CO_2 lasers. As expected under these conditions, a mass spectrometric investigation of the residual UF_6 gas failed to show any isotopic selectivity.

7. CONCLUSIONS

The only UF_6-based process confirmed to give some degree of enrichment is based on sequential infrared plus VIS photon excitation. Processes based on single or multiphoton infrared irradiation with 16 μm or CO_2 lasers are unlikely to achieve significant separation, although multiphoton excitation will readily cause photo-dissociation. The demonstration of UV/VIS fluorescence in UF_6 indicates the presence of an excited state sufficiently long-lived for LIS purposes. However, until the adiabatically cooled spectrum of UF_6 in the region of 400 nm is known, no firm conclusions can be drawn as to the feasibility of a separation process based on a single visible photon.

Adequate spectral resolution for either the infrared plus VIS process or the conceptual VIS process requires the co-expansion of UF_6 with a monatomic or diatomic gas; for all practical purposes it cannot be attained by expansion of UF_6 alone. Co-expansion and the correct use of shock waves in the expanding gas have the beneficial side effect that the process can be carried out at relatively high pressures where pumping costs are much lower and the gases can be protected from background impurity contamination. High supersaturation can be achieved in this process with $dT > 45$ K and probably as high as 100 K. The engineering of an adiabatic expansion system is a major exercise, with the literature suggesting a development period of two to three years for the Smalley system.

Although the CF_4 laser is likely to accomplish the infrared activation of UF_6 no one yet has fine tuned it to the appropriate UF_6 lines. Recent developments indicate that the Raman shifted CO_2 laser is a more likely source of tunable, high powered 16 μm radiation.

Excimer lasers based on the rare-gas halides are the most promising UV/VIS lasers. After three years of development they are only now approaching the minimum requirements with respect to power, efficiency and particularly repetition rate. The attainment of an adequate service life for these devices has posed problems which are very difficult but appear, nevertheless, to be capable of solution. This area is clearly one calling for significant and innovative ideas.

We lack practical data on

- the problems of constructing and operating a complex system which utilises adiabatic expansion, high resolution infrared lasers and high powered UV/VIS lasers;
- the photochemical efficiency; and
- the collection efficiency.

Hence, at this stage, we cannot make a critical assessment of the existing cost estimates of a UF_6 based LIS process.

Major overseas laboratories have devoted a great deal of time and effort to the problem of evolving a commercial LIS process based on UF_6. Reliable estimates of the cost of enrichment by such a process will become available only when a pilot plant based on such a process is constructed and operated, and results made available.

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TABLE 1

MAJOR ABSORPTION BANDS OF INFRARED SPECTRUM OF UF_6

Assignment	Frequency (cm^{-1})*	Relative Absorption Cross Section
$\nu_1 + \nu_3$	1291 (7.7)	2.0×10^{-3}
$\nu_2 + \nu_3$	1157 (8.6)	2.3×10^{-3}
$\nu_3 + \nu_4$	827 (12)	9.5×10^{-4}
ν_3	625 (16)	1
ν_4	186 (54)	5×10^{-2}

* Values in parenthesis are the corresponding wavelengths (in μm)

TABLE 2

GAS DYNAMIC SUPERSONIC NOZZLE PARAMETERS

Mach No.		2	3	4	5	6	7
	T(K)	129	75	47	32	23	17
Specific	p_o/p	8	32	100	263	625	1250
Heat Ratio	n_o/n	4	8	16	29	38	71
$\gamma = 1.67$	A/A_t	1.5	3	6	10	16	24
	P_o/P'_o	1.3	2.3	4	7	11	17
	T(K)	167	107	71	50	37	28
Specific	p_o/p	8	37	154	530	1600	4200
Heat Ratio	n_o/n	4	13	36	91	190	385
$\gamma = 1.40$	A/A_t	1.7	4	11	25	53	120
	P_o/P'_o	1.4	3	7	16	53	64

Note $T_o = 285$ K

TABLE 3
PERFORMANCE DATA ON SOME EXCIMER LASERS DEVELOPED
IN PERIOD 1976-1980

Laser	Output (mJ)	Specific Output (mJ/L)	Overall Efficiency (%)	Repetition Rate (Hz)	Average Power (W)	Source
KrF	3	0.3	0.3	20	0.06	Wang [1976]
(248 nm)	130	2	1.3	-	-	Burnham and Djeu [1976]
	50	0.5	1	-	-	McKee et al. [1977]
	10	-	-	400	3.3	Wang [1978a]
	100	-	1	2000	-	Fahlen [1978]
	-	-	0.5	1000	200	Fahlen [1980]
	2000			1		Lumonics Data Sheet [1980]*
XeF	10	1	1	20	0.2	Wang [1976]
(350 nm)	65	1	0.65	-	-	Burnham and Djeu [1976]
	0.4	0.1	0.16	200	0.055	Christenson [1977]
	3	-	-	500	-	Wang [1978b]
	10	-	-	400	3.3	See Ref.26 of Wang [1978a]
	12	-	-	2000	24	Wang and Gib [1979]
ArF	60	1	0.65	-	-	Burnham and Djeu [1976]
(193 nm)	6.8	0.2	0.06	5	0.004	Kudryantsev and Kuzmina [1977]
	-	-	-	130	10	Lambda Physik Data Sheet [1980]*
XeCl	9	-	-	400	1.6	Wang [1978a]
	350	-	-	-	-	Sze [1979]

*Taken from data sheets of commercial manufacturers

TABLE 4
COST STRUCTURE OF 9 x 10^6 SWU/y CAPACITY
ENRICHMENT PLANTS (1976)

Enrichment Process	Capital Costs M	Power Required MW	Power Costs* M	Other Costs M
Diffusion	3100	2430	426	36
Centrifuge	2040	243	43	194
Laser	130	24	4	16

*Power costs 0.02/kWh

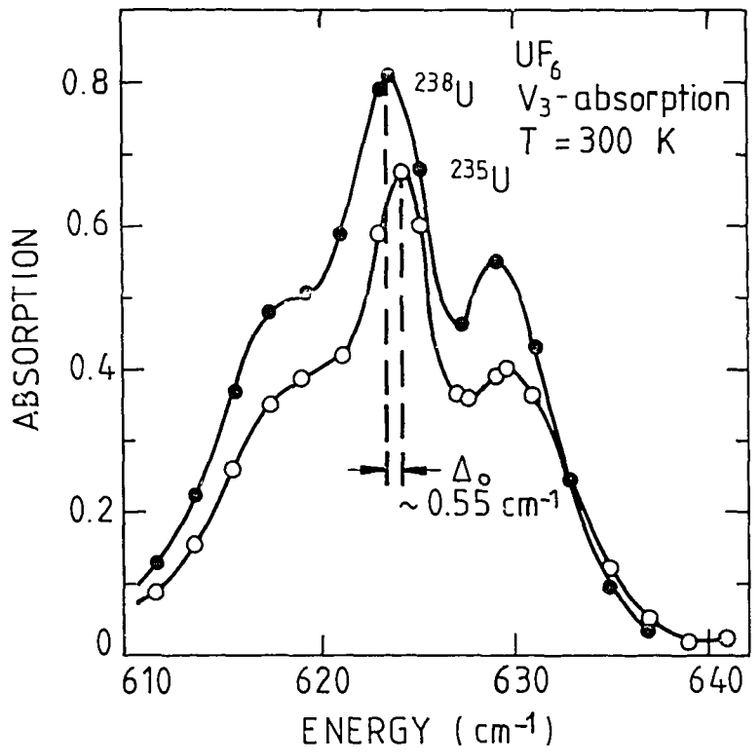


FIGURE 1. INFRARED ABSORPTION SPECTRUM OF UF_6 AT ROOM TEMPERATURE (after Jetter 1975)

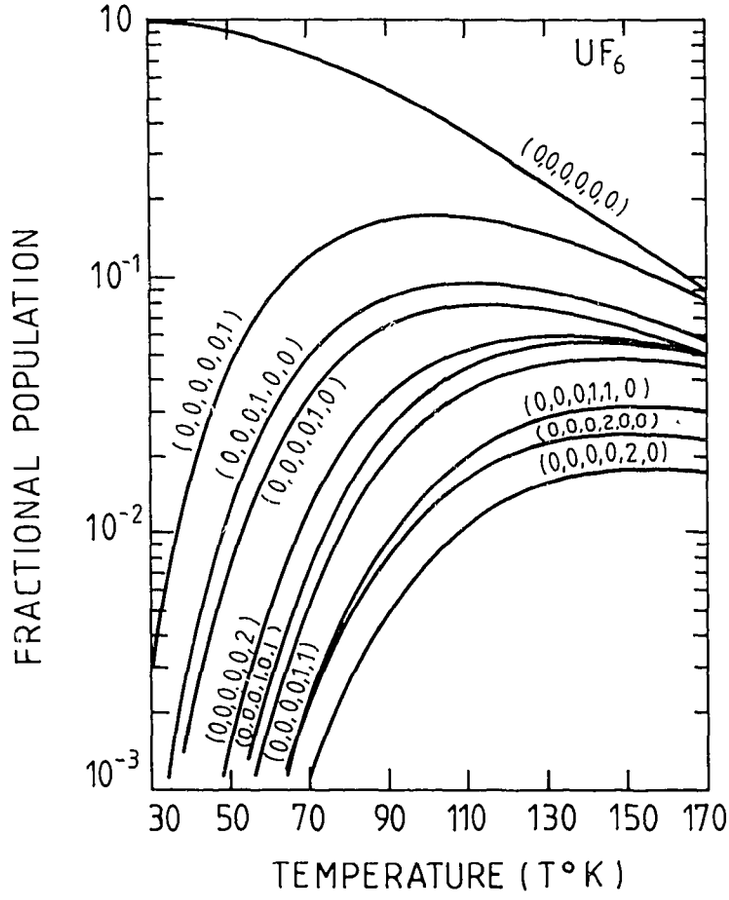
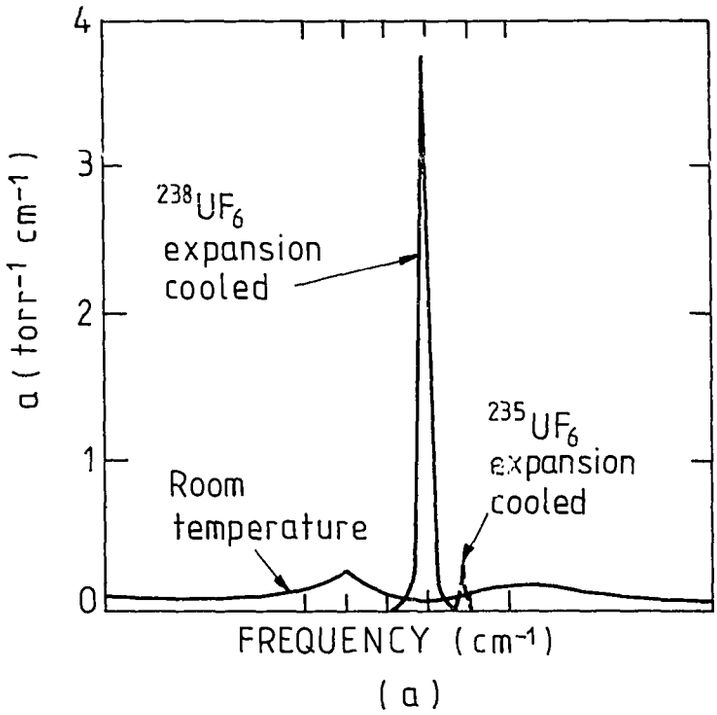
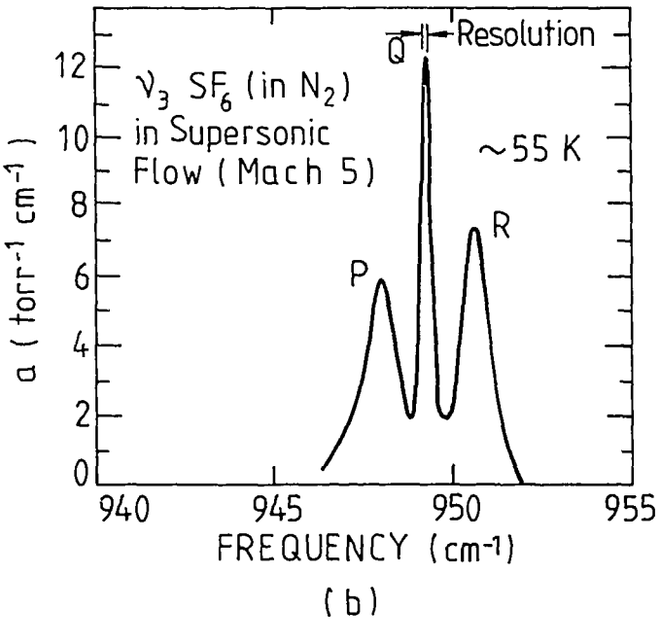


FIGURE 2. POPULATION OF TEN LOWEST VIBRATIONAL STATES vs TEMPERATURE (K) (after Jensen et al. 1976)





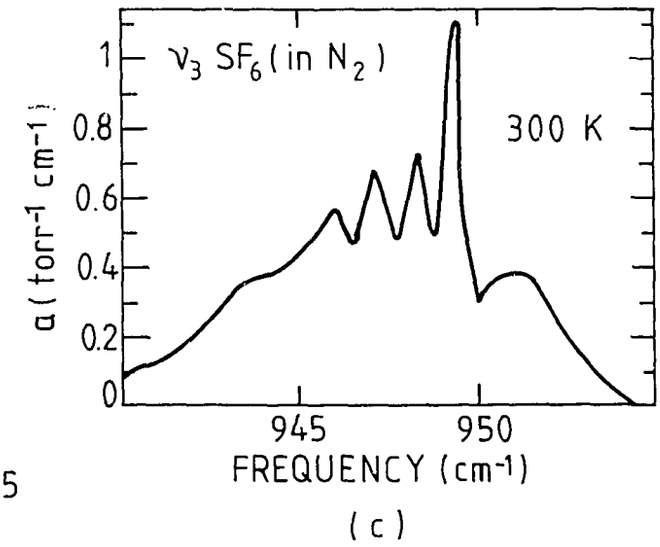


FIGURE 3a. ABSORPTION SPECTRUM OF UF_6 COOLED BY EXPANSION THROUGH A NOZZLE

FIGURE 3b. ABSORPTION SPECTRUM OF SF_6 AT 55 AND 300 K AND 3c. (after Jensen et al. 1976)

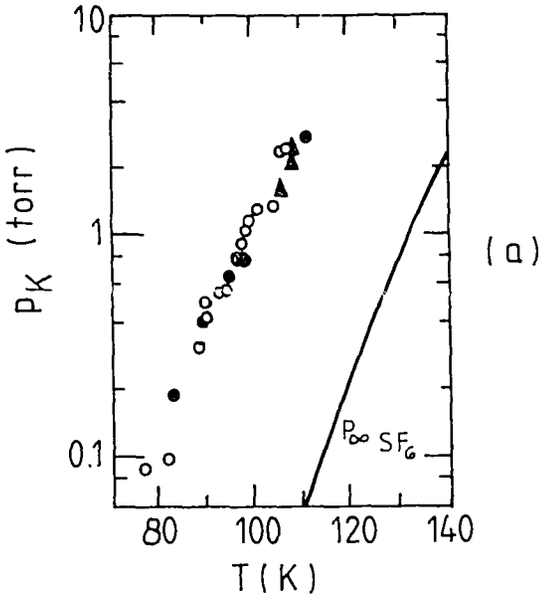


FIGURE 4a. ONSET OF SF_6 CONDENSATION vs TEMPERATURE

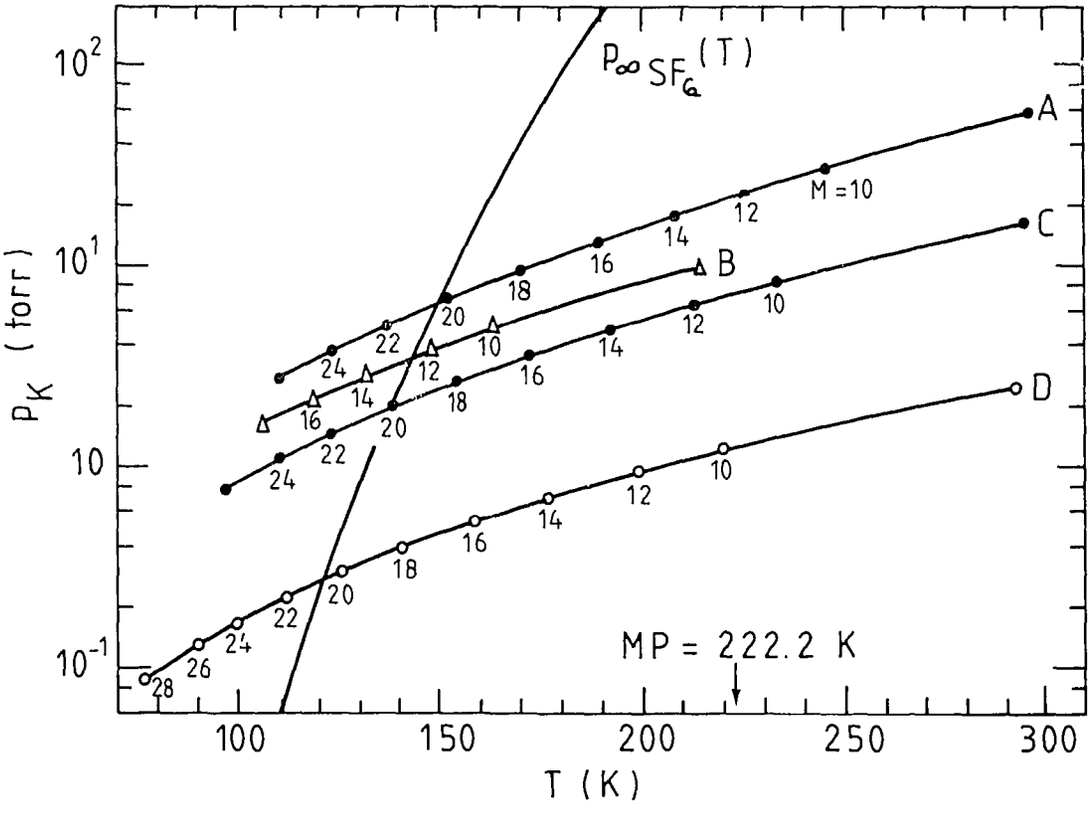


FIGURE 4b. EFFECT OF NOZZLE DESIGN ON CONDENSATION PRESSURES (p_k) (after Wu et al. 1978)

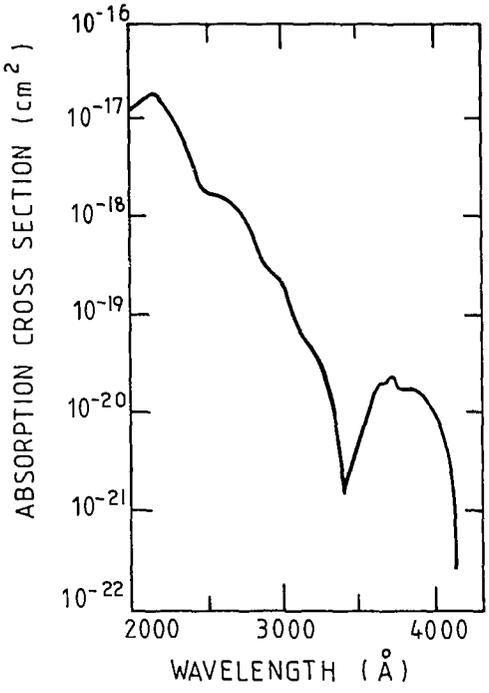


FIGURE 5. UV/VIS ABSORPTION SPECTRUM OF UF_6
(after De Poorter and Rofor-de-Poorter 1978)