

LASER APPLICATIONS IN CHEMISTRY

D. Keith Evans
Chair/Editor

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Laser Applications in Chemistry

D. Keith Evans
Chair/Editor

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LASER APPLICATIONS IN CHEMISTRY

Volume 669

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Session 3—Laser Spectroscopy

James P. Reilly, Indiana University, USA

Session 4—Laser Induced Chemistry II

Michael Ivanco, Atomic Energy of Canada Limited, Canada

LASER APPLICATIONS IN CHEMISTRY

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INTRODUCTION

For this conference, papers were sought that reported investigations of chemical systems that could not be done or would have been much less informative without the use of a laser. The conference papers did show that lasers are a powerful tool for the investigation of chemical dynamics and kinetics. International interest in laser applications was indicated by the fact that research results from eight countries were discussed. These were divided into three groups, which were presented in these four sessions: (1) Isotope Separation and Related Photochemistry, (2) and (4) Laser Induced Chemistry, and (3) Laser Spectroscopy. The first session centered on the presentations on infrared laser induced isotope separation (669-01) and isotope separation of an atomic vapor based on multiphoton ionization (669-06). Other papers covered the range of theoretical investigations of energy transfer (669-10) to optimizing an application of laser chemistry for recovery of tritium (669-03). The collection of papers in this session provide a good overview of the state of development of applications of lasers to the problem of enriching the isotopes of many elements.

Two sessions on laser induced chemistry could only indicate the range of possibilities. Invited talks covered use of lasers to probe reactive systems (669-11, -16, -27, -31) while other discussion ranged from preparation of well-defined high pressure systems (669-12) through low temperature chain reaction initiation (669-13) to deposition on substrates (669-28). Included in this session was a theoretical analysis of multiphoton transitions, which concluded that intensity dependence measurements may not reflect the photon order of processes (669-30).

The session on laser spectroscopy was an impressive collection of techniques for investigating surfaces (669-22) and the evolution of a collection of molecules as they change from individuals to a bulk ensemble by studying clusters in a molecular beam (669-21, -24, -25). Papers on measurements of inverted systems (669-23) and the fundamental shape of transitions in large molecules (669-26) completed this session.

The most interesting overall aspect of this conference was the breadth of applications of lasers. A short meeting such as this can indicate how much may be possible in understanding and controlling chemical processes by using lasers. I look forward to further advances as new lasers and new techniques are developed.

D. Keith Evans

Atomic Energy of Canada Limited, Canada

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LASER APPLICATIONS IN CHEMISTRY

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Session 1

Isotope Separation and Related Photochemistry

Chair

D. Keith Evans

Atomic Energy of Canada Limited, Canada

Invited Paper

Selective Multiphoton Decomposition Studies Relating to the Separation of Hydrogen Isotopes*

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Abstract

Three markets exist for processes capable of separating hydrogen isotopes:

(1) separation of D from H, (2) separation of T from D, and, (3) separation of T from H. The selective Multiphoton Decomposition (MPD) process has been proposed for each of these markets and a search has gone on, in several countries, for the suitable working molecule for each of these separations. In this paper the incentives for the separation of hydrogen isotopes are listed, the MPD process is outlined, and the search for suitable working molecules is reviewed.

Introduction

The use of lasers for isotope separations has been researched in many countries since about 1970. This work has generated much interest in the large scale industrial applications of lasers that would follow the successful construction of a plant at the scale of a laser-based uranium enrichment facility. To many, this project is seen as the important first step that will make possible other large scale chemical applications using lasers. Similarly, there is also the belief that the development of lasers for the U.S. Strategic Defence Initiative will help to provide industrial lasers for use in non-military applications.

The current production capacity for enriched uranium fuel for pressurized light water reactors of about 39 to 45 SWU/year is in excess of the market of 22 to 25 SWU/year. However, the excess capacity is expected to decline to a deficit by the turn of the century¹. The Atomic Vapor Laser Isotope Separation (AVLIS) program at the Lawrence Livermore National Laboratory in California is projecting enrichment costs sufficiently low that AVLIS proponents hope to capture much of the uranium enrichment market.

The other large scale market for isotopic enrichment is enrichment of the isotopes of hydrogen. This market includes:

(a) Separation of deuterium (D) from protium (H) (D/H)
D occurs as a natural stable isotope in hydrogen at a concentration of about 150 ppm, and is enriched to >99.8% D in the form of heavy water for use as a moderator and a coolant in CANDU[®] reactors. As with the uranium enrichment market, heavy water production is currently in a surplus position at a production rate of about 1000 Mg/year.

(b) Recovery of tritium (T) from deuterium (T/D)
T is formed by neutron capture in the moderator and coolant of heavy water reactors. It would build up to a maximum (steady state) value of about 21 ppm; but, because of inventory replacement and for safety reasons, levels have never reached this value. Recovery both reduces radiation hazard to station personnel and provides a valuable commodity for fusion studies and, eventually, for fusion power plants.

(c) Recovery of tritium from protium (T/H)
In the reprocessing of reactor fuels, T in H₂O is encountered at levels of about 0.07 ppm. Recovery of this T is desirable for environmental reasons.

* Issued as AECL contribution number 9207

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Laser Isotope Separation (LIS) has been demonstrated for isotopes such as those of carbon, and sulphur. However, the existing market for the production of isotopes of elements other than uranium or hydrogen has not been sufficiently large to justify the construction of laser based production facilities.

Conventional Hydrogen Isotope Separation Processes

Chemical Exchange Processes

Most of the world's heavy water is produced by the GS bithermal chemical exchange process between hydrogen sulphide and water. The GS process extracts only about 18% of the deuterium in the feed water, meaning that about 1.6×10^6 litres/hour of water must be processed for a 400 Mg/year heavy water plant. A process recovering a greater fraction of the feed water deuterium will probably have a lower energy cost than the GS process. Bithermal chemical exchange between other molecular pairs have higher recoveries but are limited in size. Nonetheless successful plants using HD/liquid NH_3 have operated in France and India and a pilot study has been completed with the HD/aminomethane system. Both processes have relatively low energy demands but require catalysts. Since both need a large source of hydrogen, they are currently parasitic to another industrial process and limited in production capability.

Another potential chemical exchange process using a water feed is the H_2/HDO exchange process. This process recovers more (42% theoretically) of the deuterium from the liquid feed than the GS process and the energy costs for a comparable size plant are also lower. Characteristics of the four chemical exchange processes are summarized in Table 1.

Table 1: Characteristics of Four Bithermal Exchange Processes which can be used for the Commercial Production of Heavy Water.

	$\text{HDO}/\text{H}_2\text{S}$	HDO/H_2	HD/NH_3	$\text{HD}/\text{CH}_3\text{NH}_2$
% of Feed D Recovered (Theory)	22	42	50	55
Energy (GJ_t/kg of D_2O) (a)	30	9	7	11
Catalyst Required	No	Yes	Yes	Yes
Deuterium Source	H_2O	H_2O or H_2	H_2	H_2

(a) expressed in terms of thermal energy equivalent

Other separation processes

Another process coupled with the demand for the production of hydrogen, is the combined electrolysis catalytic exchange process (CECE). Under conditions where hydrogen generation costs are low, the CECE process is the most economically attractive process for heavy water production.

Cryogenic distillation of molecular hydrogen is favoured as the basis of plants for recovery of tritium within Canada, France and the United States. Catalyzed isotopic exchange between hydrogen and water is used in the first stage to transfer tritium to the feed stream of the cryogenic unit. This can be done effectively with platinum catalysts in the vapour phase or, as will soon be demonstrated at CRNL, with catalysts designed to function in the presence of liquid water. For tritium recovery energy costs are less important than for D_2O processes; since the quantity of material to be processed is very much smaller.

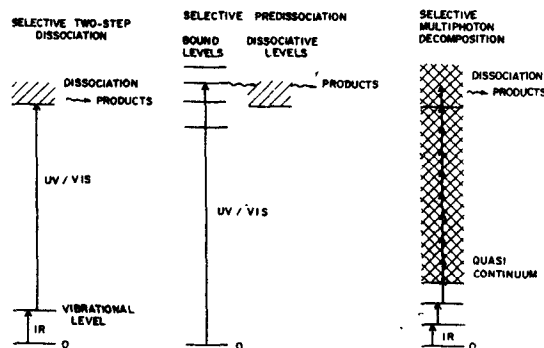


Figure 1: Schematic diagrams of three laser based enrichment schemes which have been considered for separation of hydrogen isotopes. These processes are briefly discussed in the text.

Laser Isotope Separation Processes

Process descriptions

Several LIS processes, illustrated in Figure 1, have been considered for hydrogen isotopes. There is an important advantage for a process that will work directly on either water or natural gas (the only deuterium containing molecules sufficiently abundant to be the primary feed for a heavy water process). One early scheme^{2,3} using water was the selective two-step dissociation process. The first infrared (IR) laser was tuned to an absorption of the HDO molecule, frequency shifted from H₂O absorptions. A second ultraviolet (UV) laser was tuned to decompose only the vibrationally excited HDO molecules. This scheme was unsuccessful for two reasons: (1) the onset of the UV photodissociation of water has an ill-defined threshold. This results in very poor selectivity for the combination of IR and UV lasers unless the IR laser is tuned to a very high overtone of the -OD stretch mode. The low extinction coefficients for these overtones, compared to the fundamental, makes the efficient use of IR photons difficult; (2) the dissociation of water produces H and OH radicals which will rapidly isotopically equilibrate with the undissociated water unless they are efficiently scavenged. This scavenging is difficult.

A second early suggestion⁴⁻⁶ for hydrogen LIS was the laser induced selective predissociation of a D or T containing molecule. Since neither water nor methane undergo predissociation, it was necessary to use a working molecule (e.g., formaldehyde) which could be redeuterated by exchange with water or methane. Although high selectivities were demonstrated using formaldehyde, its exchange with water required a catalyst, and formaldehyde decomposed on catalytic surfaces used for exchange. It also polymerised spontaneously at pressures above about 10-20 Torr. In addition, the well resolved tunable lasers which were required for high selectivities were of quite low electrical to photon conversion efficiencies.

Following the discovery⁹ of the multiphoton decomposition (MPD) process and further, that this process could be isotopically selective¹⁰, the search began for suitable working molecules for hydrogen isotope LIS. It soon became evident that water and methane are unsuitable for efficient MPD since their relatively small number of atoms give rise to a

bottle-neck for MPD¹¹. Consequently, the search widened to find suitable working molecules for LIS of hydrogen isotopes. Some important criteria for a suitable working molecule are:

(1) Optical Selectivity: The ratio of absorption by the molecules containing the desired, to those containing the undesired isotope $S(\phi)$, for fluence ϕ , should be sufficiently large to prevent: (a) loss of photons through absorption by the undesired species; (b) loss of isotopic enrichment through decomposition of working molecules containing the undesired species; (c) makeup costs for replacing working molecules containing the undesired species that are decomposed. This criterion is discussed in a seminal paper by Marling, Herman and Thomas¹².

(2) Chemical Exchange: The rate of exchange between the working molecule and H_2O or CH_4 , equation (1):



determines the size of the contacting towers. In fact, the exchange step is similar to the chemical exchange step in the bithermal process and the energy and capital costs of the LIS process are sensitive to the exchange step. It is important that losses of the working molecule be minimal.

(3) MPD versus Fluence: To minimize laser-induced materials damage and for efficient use of photons, the working molecule should ideally decompose at $\phi < 4 \text{ J/cm}^2$.

(4) MPD Products: The products containing the desired isotope should be stable or easily scavenged to prevent loss of selectivity and the desired isotope should appear in as few products as possible to minimize purification and ease product recovery.

(5) Separation factors: The heads separation factor, β , (the ratio of heads to feed isotopic ratios), or the tails separation factor, γ , (the ratio of feed to tails isotopic ratios) depend on the application and should be sufficiently large. For example, for D/H, β should be >1600 ; for T/D, γ should be >3 . Several methods (Table 2) have been used to measure directly or to infer relevant photochemical separation factors. Very few studies of overall process separation factors have been reported.

(6) Non-linear Optical Properties: At high laser intensities, such non-linear effects as self-focusing can occur. These must be allowed for in the design of photolysis cells.

(7) Other Properties: Other properties such as toxicity, volatility, solubility, stability, cost and others may also be important considerations.

Current research on H isotopes LIS is centered on the search for suitable working molecules fulfilling the criteria above. A list of molecules which have been considered, and the relevant chemical and photochemical properties of each is given in Table 3. For many of these molecules, there are still significant gaps in knowledge. Since the early 1980's, fluoroform has been the molecule most fitting the criteria for a working molecule for D/H and T/H separation. However, fluoroform is deficient in criteria 2 and 3, leading to heavy water costs probably comparable to the G.S. process¹². Chloroform exchanges with water more rapidly than fluoroform; however it requires MPD fluences only slightly lower than fluoroform. The alcohols undergo virtually instantaneous exchange with water; but they require very large fluences for MPD. Recent studies in China⁶ show dichlorofluoromethane to be an interesting potential working molecule for D/H separation. Work in Japan and elsewhere on large molecules, which should undergo MPD at low fluences, show that i-heptafluoropentane may be suitable for T/H separation. The search for suitable working molecules continues, and the potential for practical LIS schemes for hydrogen isotope separation is good.

In addition to the search for new potential working molecules, more detailed understanding of the MPD process is revealing new ways to improve both the efficiency and the selectivity of MPD for molecules already studied. Some of these new techniques include the creative use of collisions, using multiple laser sources tuned to pump different regions of the excitation ladder, and the use of electric and magnetic fields¹³. While the

ideal conditions for hydrogen isotope LIS are still not known, progress in this area, as in the search for ideal working molecules, is still being made.

Table 2: Convention for the classification of measured enrichment factors according to the experimental techniques employed.

- I Photolysis of actual isotopic mixtures.
- II Photolysis of the individual isotopic species.
- A. Determination of enrichment factors from actually separated or easily separable stable products.
- B. Determination of enrichment factors from a transient intermediate which may later exchange or further react.
- C. Determination of enrichment factors from unreacted initial molecules following photolysis without physical separation of products.
- D. Inference of enrichment factors from an analysis of products not containing the desired isotope.

Table 3: T/D and T/H Separation by the Selective MPD Process. Note the following Abbreviations are used: C12 and C13 respectively denote a $^{12}\text{CO}_2$ and a $^{13}\text{CO}_2$ Laser; NL denotes an ammonia laser. The numbers for the properties discussed are as follows: 1. Optical Selectivity. 2. Chemical Exchange. 3. MPD versus Fluence, $f(\phi)$. 4. MPD products. 5. Separation Factors. 6. Non-Linear Optical Properties and 7. Other Properties. Separation factors are described by the experimental categories IA to IID as defined in Table 2.

Comments

References

A. Molecules Containing an -OH Group

1. Formic Acid (HCOOH)

- 1. D/H: $S(\phi)$ high for DF laser, T/D, T/H not studied (14,15)
- 2. Very rapid with water, slow with methane
- 3. MPD requires high ϕ or collisions, small molecule behaviour (15)
- 4. Two channels: $\text{H}_2\text{O} + \text{CO}$ and $\text{H}_2 + \text{CO}_2$ (14,15)
- 5. $\beta_{\text{H}}=25$ (IA) for $\text{HCOOH}/\text{HCOOD}=50\%$ and $P=0.6$ kPa. β_{H} varies as P^{-1} (15)
- 7. Corrosive, decomposes, miscible with water, dimer formation in vapour phase (16)

2. Methanol (CH_3OH)

- 1. D/H: $S(\phi)$ high for DF laser, T/D, T/H not studied (14,15)
- 2. Very rapid with water, slow with methane
- 3. Collisionless MPD: HF, $f(\phi)=\exp(-3500/\phi)$; C12, $f(\phi)=\exp(-150/\phi)$. Collisions assist MPD. (17-21)
- 4. Primary Products: CH_3 , OH, H_2 ; Observed Products: CO, CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , H_2O , CH_2 (17-25)
- 5. $\beta_{\text{H}}=25$ (IA) for $\text{CH}_3\text{OH}/\text{CH}_3\text{OD}=50\%$ at $P=0.27$ kPa, varies as P^{-1} (17)
- 7. Easily handled, slightly toxic, miscible with water

3. Ethanol ($\text{C}_2\text{H}_5\text{OH}$)

- 1,2,7 Similar to methanol (26)
- 3. $f(\phi)=\exp(-8/\phi)$ $P=1.0$ kPa, CO_2 laser, pulse width 10 ns (27)
- 4. Observed products: H_2 , CH_3CHO , C_2H_4 , H_2O , CH_4 , C_2H_6

B. Halomethanes

1. Fluoroform (CHF_3)

- 1. D/H: $S(25)=900$, with C12 10R(26), higher with 10R(27); T/H: $S(\phi)$, high with C12 9R(14). T/D: $S(\phi)$ high with C12 (12,37)
- 2. H_2O requires catalyst, D enrichment in fluoroform (38)
- 3. $f(\phi)=(\phi/27)^3$, $\phi<27$, natural abundance (12)
- 4. Primary Products: HF, CF_2
- 5. D/H: $2000<\beta<20,000$, (IA, IB, IC, ID) collisions increase β . T/H: $\beta>10^4$ with buffer gas, β increases at low temperatures, D can be removed

- from a T/D/H mixture with Cl₂ 10R(12) line. Two-colour MPD studied. (17,28-40)
6. Self-focussing or defocussing depending on wavelength (41)
7. Non-toxic, make-up <12 kg CHF₃/kg D₂O, stable, easily handled; Pumping plus recompression costs estimated higher than GS process for single laser MPD (12,42)

2. Chloroform (CHCl₃)

1. T/D: S(0)=6500 to 12000, NL, S(15)>500. D/H: S(ϕ) obtained with Cl₃, Cl₂ (43-45)
2. For H₂O requires catalyst, faster than CHF₃ not known for CH₄ (46)
3. $f(\phi)=3.8\exp(-13.4/\phi)$, P=1.3 kPa; function of P (48,49)
4. Primary Products: HCl, CCl₂ (45)
5. T/D: 165< β <2200(IC) for 200 p.p.m., 6400 for 5 p.p.m. High β for two-colour excitation (42,50)

3. Difluoromethane (CH₂F₂)

1. D/H: S(0.2)=1800, S(23) = 350 near 954 cm⁻¹ (12)
3. D/H: depends on P, $f(\phi)=(\phi/20)^3$, $\phi<20$ at highest P studied (12)
4. Primary Products: HF + CHF (12)
5. D/H: 1800< β <3500 (ID) (12)
7. Laser energy requirements 51 GJ_t/kg for heavy water production, makeup 13 kg CH₂F₂/kg D₂O (12)

4. Chlorodifluoromethane (CHClF₂)

1. D/H: S(ϕ) for Cl₂ 10R(28) 10R(34), and 9P(30) to 9P(42) (51-53)
2. Suggestion of two step exchange with water and HCl at 425°C (52)
4. Primary Products: HCl + CH₂ (54-56)
5. Suggestion that $\beta>10^4$ (IC) possible for D/H (52)

5. Dichlorofluoromethane (CHCl₂F)

1. D/H: S(ϕ) high for 920 - 960 cm⁻¹. S(0)=4000 for T = 200 K, Cl₂ 10P(38) (51,57,60,61)
2. Quantitative at 100°C, NaOH/DMSO catalyst. Faster than fluoroform, hydrolysis slower (51,58)
3. $f(\phi)=\exp(-13/\phi)$ (60)
4. Primary channel: HCl + CHCl (54)
5. D/H: $\beta>10^4$ when Br₂ added; 24000 at natural abundance, (51,58,60)
6. Solubility 6.6 times that of fluoroform. (60)

C. Haloethanes

1. 2,2-Dichloro-1,1,1-trifluoroethane

1. D/H: Near 944 cm⁻¹, S(0) = 100, S(10) = 40 (12)
2. Rapid base catalysed exchange with H₂O, hydrolysis slow (62)
4. Observed products: HCl, CF₂CFH, CF₂CHCl (62,63)
5. D/H: $\beta=1400$ (IA) for $\phi=10$ J/cm² (62)
7. Laser energy requirements 1TJ_t/kg D₂O (62)

2. 2-Chloro-1,1,1,2-tetrafluoroethane

3. Tritiated molecule undergoes MPD at lower fluences than fluoroform (64)
4. Primary products: HCl + C₂F₄ (65)
5. T/H: $\beta=600$ (64)
7. High pressure selectivity can be achieved for 2 ns pulses (65)

3. Pentafluoroethane

1. T/H: S(ϕ) high for Cl₂ 10P(20) line. T/D: S(ϕ) high for 10P(34) line (66,67)
4. T distributed among several free radical products. Both HF elimination and C-C bond breaking seen (66-68)
5. T/H: $\beta>500$ (IA, IC) T/D: $\beta=3000$ (IC). Cooling improves β (66,68)

4. 2-Bromo-1,1,1,2-tetrafluoroethane

1. D/H: S(ϕ) high 900 and 1000 cm⁻¹. T/H: S(ϕ) high for 930 to 908 cm⁻¹ with NL (69)
2. Exchanges with water with NaOH/DMSO catalyst (69)
3. For tritiated molecule at 931 cm⁻¹, $f(\phi)=(13.1/\phi)^5$, ~20% of the "critical fluence" of CTF₃ (69)
5. T/H: $\beta>2700$ (IA) (69)

D. Halopropanes

1. n-Heptafluoropropane

1. T/H: S(ϕ) high for C12 10P(38) line (70)
2. Base catalysed with DMSU, rapid (70)
3. MPD "critical fluence" 31% that of fluoroform (70)
4. Observed Products: C_2F_4 , C_2F_6 , C_2HF_5 (70)
5. T/H: $\beta=3.4$ (IA) for tight focus, much higher for mildly focussed (70)

2. i-Heptafluoropropane

1. T/H: S(ϕ) high for C12 10R(30) line. Expected to be much higher for C13 (70)
2. Very rapid for base catalysed conditions (70)
3. MPD "Critical fluence" 11% that of fluoroform (70)
4. Observed Products similar to n-heptafluoropropane (70)
5. T/H: $\beta>1400$ (IA) for C12 10R(30) line. Higher for C13 laser (70)

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Multiphoton dissociation of UF_6 at $\lambda = 16 \mu\text{m}$ in supersonic jets

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Introduction

The multiple photon excitation of UF_6 at $16 \mu\text{m}$ has been studied in a number of laboratories, in view of its potential applications in uranium enrichment, using various schemes: IR+UV /1/, IR+IR /2/. Because of the small isotope shift: 0.61 cm^{-1} , on the ν_3 line at 627 cm^{-1} , adiabatic cooling of UF_6 at temperatures lower than 120 K , is required to get UF_6 , with a simplified IR spectrum, at reasonably high molecular densities in the order of 10^{15} cm^{-3} .

In a more fundamental point of view, it is interesting to investigate the multiple photon phenomena in UF_6 at low temperatures where it is prepared in a rather well defined vibrational state (at 100 K , 30 % of the molecules are in the fundamental vibrational state, a value to be compared with 4% at 300 K). If it is known that the multiple photon absorption changes markedly between 100 and 300 K /3/, till now, little has been published on the effects of temperature on UF_6 dissociation.

For the vibrational excitation of UF_6 , several types of $16 \mu\text{m}$ lasers have been used during the past five years: optically pumped CF_4 laser /4/, optical parametric oscillators /1,3/, stimulated Raman emission in para- H_2 pumped by a CO_2 laser /2/. The Raman source offer the possibility to generate a second beam at $16 \mu\text{m}$ by four-wave mixing /5,6/, using a second CO_2 laser pump with no energy or linewidth requirements on this pump.

We report results on two-frequency multiphoton dissociation of UF_6 cooled at 90 K in a supersonic expansion of Ar as the carrier gas, using a Raman source pumped by two TEA line-tunable CO_2 lasers. Additional data were obtained on multiphoton absorption of UF_6 at low and ambient temperatures, and on vibrational relaxation of UF_6 .

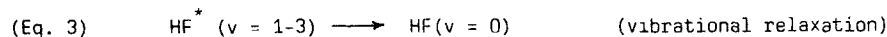
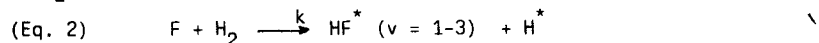
Diagnostic of dissociation

HF^* fluorescence has been used many times as a diagnostic of UF_6 dissociation since the first publication by Tsee and Wittig /7/.

The unimolecular dissociation of UF_6 :



occurs at a significant rate for $\eta = 55$ photons absorbed in the molecule /8/. If UF_6 is excited in the presence of H_2 , a series of reactions takes place; among them the basic ones are:



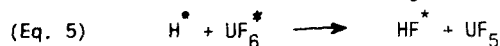
IR fluorescence emission of HF^* at $2.2 - 2.9 \mu\text{m}$, is observed, that has the time evolution of $[\text{HF}^*]$:

$$\text{(Eq. 4)} \quad [\text{HF}^*] = [\text{F}]_0 \cdot \frac{\tau_2}{\tau_2 - \tau_1} \cdot [\exp(-t/\tau_2) - \exp(-t/\tau_1)]$$

$$\text{where } \tau_1^{-1} = k \cdot [\text{H}_2] \quad \tau_2^{-1} = \tau_1$$

From the absolute value and the temporal shape of the fluorescence signal, the initial concentration $[\text{F}]_0$ and, as a consequence, the number of dissociated UF_6 molecules can be determined.

The above analysis is simplified and does not take into account neither secondary reactions related to the unimolecular dissociation of UF_6 , such as:



nor the bimolecular reaction of H_2 with UF_6^* molecules excited under the unimolecular dissociation threshold ($\eta < 55$):

