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PHOTOCHEMICAL REMOVAL OF NpF_6 AND PuF_6 FROM UF_6 GAS STREAMS

James V. Beitz and Clayton W. Williams
Chemistry Division, Argonne National Laboratory
Argonne, IL 60439 USA

ABSTRACT

A novel photochemical method of removing reactive fluorides from UF_6 gas has been discovered. This method reduces generated waste to little more than the volume of the removed impurities, minimizes loss of UF_6, and can produce a recyclable by-product, fluorine gas. In our new method, impure UF_6 is exposed to ultraviolet light which dissociates the UF_6 to UF_5 and a fluorine atom. Impurities which chemically react with UF_5 are reduced and form solid compounds easily removed from the gas while UF_5 is converted back to UF_6. Proof-of-concept testing involved UF_6 containing NpF_6 and PuF_6 with CO added as a fluorine atom scavenger. In a single photolysis step, greater than 5000-fold reduction of PuF_6 was demonstrated while reducing NpF_6 by more than 40-fold. This process is likely to remove corrosion and fission product fluorides that are more reactive than UF_6 and has been demonstrated without an added fluorine atom scavenger by periodically removing photogenerated fluorine gas.

DISCLAIMER

INTRODUCTION

Removal of impurities from UF_6 gas is challenging due to the chemically aggressive character of UF_6. When the uranium source material for preparing UF_6 comes from spent nuclear reactor fuel, the metal element impurities likely to be converted to volatile hexafluorides are fission product d-transition metals and the transuranium elements Np and Pu. Because the vapor pressures of several likely impurity hexafluorides are similar to that of UF_6, fractional distillation alone is an impractical purification method. Fractional distillation has been shown to be effective in removing transition metal fluorides whose volatility is much different than that of UF_6 (*1*). Selective fluorination is a method of minimizing formation of transuranic hexafluorides when impure uranium is converted to UF_6 (*2*). Use of sorption beds, and thermal cracking, with (*3*) or without (*4*) added fluorine acceptors, in the case of PuF_6, are additional methods of removing transuranic hexafluorides from UF_6.

In practice, it is difficult to completely suppress fluorination of many impurities and sorption beds ordinarily generate large volumes of radioactive waste for which disposal costs are rapidly rising. An exception occurs when the sorption bed is consumed in use and regenerates the desired product (*5*). Thermal cracking methods do not remove hexafluorides, such as NpF_6, whose thermal stabilities are similar to UF_6. Clearly, new methods of removing impurities from UF_6 are needed. Much of the past work in this area has been related to fluoride volatility processing of spent nuclear fuel which has been review by Schmets (*2*). The conventional solution to generating high purity UF_6 from spent nuclear fuel or targets is removal of troublesome impurities from uranium before it is converted to UF_6. This is achieved by use of solvent extraction (PUREX) processing to remove transuranic elements and fission products capable of forming volatile fluorides. This "solution" has generated large volumes of radioactive waste for which disposal costs are rapidly increasing.

The present work demonstrates, at the proof-of-concept level, a novel method of photochemically removing chemically reactive fluoride impurities from UF_6 gas. This method uses photodissociation of UF_6 to generate lower valent uranium fluoride species. When fluoride impurities react with these uranium fluoride species, the impurities are reduced in valence and form solid compounds easily removed from the gas while UF_6 is regenerated.

RELEVANT PHYSICAL PROPERTIES OF ACTINIDE HEXAFLUORIDES

Reviews of the physical properties of well-characterized actinide hexafluorides, including published vapor pressure and spectral data, are available (see, for example, Ref. (*6*) for UF_6 work, Refs.(*7*) and (*4*) for NpF_6 studies, and Refs. (*7*) and (*8*) for PuF_6 investigations). Both UF_6 and NpF_6 are readily synthesized by heating lower valent

compounds in excess F_2 gas. Special apparatus, incorporating a method of rapid gas cooling, is essential to efficient synthesis of PuF_6 using thermal fluorination of lower valent Pu fluorides or oxides (*9*), but PuF_6 has also been synthesized by photodissociating F_2 gas above solid PuF_4 (*10*). These hexafluorides are volatile solids at ambient temperature and have quite similar vapor pressures (*11,12*). The vapor pressures of actinide hexafluorides are such that they condense quantitatively at 195 K.

THERMODYNAMICS OF ACTINIDE HEXAFLUORIDES

Available thermodynamic data for actinide fluorides have been reviewed (see for example (*13,14,15*). Bond dissociation energies are of particular importance in assessing likely reaction paths in photochemical work. Hildenbrand and co-workers have determined bond dissociation energy values for gaseous uranium fluorides, including UF_6 (*16*), using mass spectrometer. The enthalpy of dimerization of monomeric UF_5 is reported to be comparable to the heat of sublimation of solid UF_5 (*17*). The bond dissociation energy of NpF_6 has not been measured although NpF_6 is thermally stable. PuF_6 is generally regarded as being thermodynamically unstable with respect to formation of F_2 gas and PuF_4 solid (*7*). Nonetheless, PuF_6, once formed, persists at ambient temperature, aside from decomposition induced by radiolysis. It may seem surprizing, therefore, that PuF_6, a thermally unstable compound, has generally been synthesized by thermal fluorination. This is explained by reported data on the equilibrium between $PuF_6(g)$, $PuF_4(s)$ and $F_2(g)$ which indicate that the fraction of Pu present as PuF_6 increases with increasing temperature (*18,19*). Recently, Kleinschmidt reported bond dissociation energies for Pu fluorides, including PuF_6, from appearance potential measurements (*20*). Unfortunately, the enthalpy of formation of PuF_6 that results from these bond dissociation energies does not equal that deduced from studies of the $PuF_6(g) + PuF_4(s) + F_2(g)$ equilibrium. Further studies are evidently needed.

OPTICAL SPECTRA AND ENERGY LEVEL STRUCTURE

Vibrational and optical spectra of many hexafluorides have been reviewed by Weinstock and Goodman (*21*). The optical absorption spectrum of UF_6 has been reported by DePorter and DePorter(*22*) over a wide range of pressure-path length products. The near-ultraviolet bands are predominantly charge transfer bands (*23,24*) and no lower-lying electronic states exist since UF_6 has no occupied 5f electron orbitals. Steindler and co-workers have published the optical absorption spectrum of NpF_6 (*25*) and PuF_6 (*26*) gases from the near infrared through the ultraviolet. The low-lying f-electron states of NpF_6, a $5f^1$ system, have been theoretically modelled by Eisenstein and Pryce (*27*) and others (*23,24*) have considered additional as well. Calculations of the energy levels of PuF_6, a $5f^2$ system, are also available (*23,24,28,29,*). A charge state of NpF_6 doped into solid UF_6 has been identified in a low temperature laser-induced fluorescence study (*30*).

Based on these spectroscopic and thermodynamic studies, Fig 1 shows the energy regions over which observed optical absorption due to low-lying charge transfer and 5f-electron states occur for UF_6, NpF_6, and PuF_6 gases at ambient temperature. Also shown are the reported bond dissociation energies, and associated uncertainties, for UF_6 (*16*) and PuF_6 (*20*). The data shown in Fig 1, together with the reported thermal properties of UF_5 (*6*), NpF_5 (*31*), and the photoproduct resulting from dissociation of PuF_6 (*32*), provide a basis for speculating that photochemical removal of NpF_6 and PuF_6 from a mixture initially containing UF_6, NpF_6, and PuF_6 gases, might be feasible using direct photodissociation of NpF_6 and PuF_6.

The primary disadvantage to removing transuranic hexafluorides by direct photodissociation lies in their very small absorbance when they are present at low concentration in UF_6 gas. Consider UF_6 gas at its ambient temperature vapor pressure containing 1 part-per-million of PuF_6 as an impurity. Based on reported optical absorption spectra (*22,26*), an optical pathlength of over 25 km is required for the PuF_6 to absorbed 90% of incident light in the blue-green spectral region where the photon energy exceeds the bond dissociation energy of PuF_6 but UF_6 has little absorbance. A factor of approximately 10 times longer pathlength is required for NpF_6 to absorb 90% of incident light under the same conditions. Because light is an expensive "reagent" for bringing about chemical change, the most desirable photochemical process would be one in which essentially all photolysis light is efficiently utilized even when the impurities to be removed are present at very low concentration. The photochemical method we report here is such a method.

PHOTOCHEMISTRY OF ACTINIDE HEXAFLUORIDES

Photodissociation of actinide hexafluorides, AnF_6, from low-lying charge transfer states likely proceeds by breaking of a metal-fluorine bond (*33*) and subsequent radical-radical reactions,

$$AnF_6 + h\nu \rightarrow AnF_5 + F$$

$$AnF_5 + (AnF_5)_n \rightarrow (AnF_5)_{n+1}$$

$$F + (AnF_5)_n \rightarrow AnF_6 + (AnF_5)_{n-1}$$

$$F + F + M \rightarrow F_2 + M$$

where M is an inert third body, such as AnF_6, and n is 1 or a larger integer.

PRIOR PHOTOCHEMICAL STUDIES

The photochemistry of uranium compounds has been reviewed by Paine and Kite (*33*). In 1971, workers in France published a brief report of photoreduction of UF_6 (*34*) using ultraviolet light and a wide range of fluorine atom scavengers. Subsequently, Halstead and Eller published a synthesis procedure for generating gram amounts of UF_5 by photolyzing a mixture of UF_6 and CO with a mercury arc lamp (*35*). Jacobs and Becker (*36*) demonstrated that addition of a fluorine atom scavenger, such as CO, was not essential to photoreduction of UF_6. These workers generated circa 50 g of UF_5 by periodically removing accumulated F_2 during ultraviolet arc lamp photolysis of UF_6. Work by Lyman and co-workers (*37*), with direct detection of UF_5, found kinetic rate parameters for UF_5 dimerization and recombination with F atom which are consistent with the observation that arc lamp photolysis of UF_6 readily leads to photoreduction UF_6 and formation of particles of UF_5 solid.

There are few reported photochemical studies of NpF_6 and PuF_6. Photodestruction of NpF_6 and PuF_6 by mercury arc source lamps evidently prevented acquisition of Raman spectra of these molecules until red laser light sources became available (*21*), but no identification of photoproducts or mechanisms was reported. Other workers have reported synthesis of PuF_6 by arc lamp photolysis of F_2 gas above a layer of solid PuF_4 (*10*). Young (*32*) recently reported photodissociating PuF_6 with an arc lamp to a largely amorphous solid, identified as PuF_4. Kim and Campbell have reported that the quantum yield for dissociation of PuF_6 gas at 337 nm is 0.86, falling to 0.17 in presence of added F_2 gas (*38*).

EXPERIMENTAL METHODS

The UF_6 was used in this work had been synthesized from natural abundance uranium. NpF_6 and PuF_6 were synthesized from ANL stocks of ^{237}Np and radiochemically characterized, mixed isotope Pu (0.4070 Ci per g of Pu, 91.4 atom% ^{239}Pu). For each hexafluoride, flowing trap-to-trap distillations were used to remove higher or lower volatility material and the purity of the resulting hexafluoride was confirmed by measurement of its vapor pressure at 273.15 K. A separate metal vacuum line (constructed from monel and nickel fittings) was used for each actinide hexafluoride to avoid cross-contamination. Each vacuum line was equipped with a thermostated, high accuracy, 100 torr full scale, corrosion-resistant capacitance manometer. The photolysis cells consisted of a single crystal sapphire tube (1.27 cm diameter by 30 cm long, plugged at one end) connected to a monel valve by means of a monel compression fitting equipped with polytetrafluoroethylene ferrule (see Figure 2). The internal volume of each sapphire cell assembly (typically 31 cm^3) was measured pycnometrically. Each cell was passivated immediately prior to use. The passivation procedure began with exposure of the cell assembly to small amounts of fluorine, followed by evacuation. The cell was

then filled with mixture of fluorine and oxygen gases, photolyzed with a 450 W medium pressure mercury arc, and evacuated.

Gas mixtures of accurately known composition were prepared by first adding the desired number of moles UF_6 to an evacuated cell based on pressure-volume-temperature measurement and assumed ideal gas behavior. The cell was then transferred to the NpF_6 line, the cell connection to the line passivated by exposure to NpF_6 gas, and the manifold evacuated. The tip of the cell was immersed in liquid nitrogen (to condense the UF_6), NpF_6 gas was introduced to the manifold (whose volume had been measured pycnometrically), and the desired amount of NpF_6 was condensed into the cell. The amount of NpF_6 added was obtained from the difference in manifold pressure before and after admitting NpF_6 to the cell. PuF_6 and CO, when used, were added in the same manner. Prior to beginning photolysis, the bottom of the cell was held slightly above ambient temperature for a period of minutes to ensure convective mixing of the gases.

Two light sources were used during the course of this work. The first was a 75 W high pressure Xe arc lamp and the second was a 200 W high pressure Hg arc lamp. Both lamps were used in a rhodium-coated ellipsodial reflector housing providing circa one-half sphere light collection. A disk of borosilicate glass was used to remove light of wavelengths less than 290 nm and longer wavelength light was minimized by means of a Corning 7-51 optical filter. The amount of gas remaining after photolysis was measured on the PuF_6 gas manifold. The gas species present could be assessed, in part, due to their different volatiles. For example, neither F_2 nor CO condense at 77 K, but most carbonyl fluorides do and the actinide hexafluorides condense quantitatively at 195 K (*11,12*).

The experiment in which gamma counting of the gas mixture was carried out used a NaI(Tl) gamma detector (1.5 mm thick by 25 mm diameter) sensitive primarily to low energy gamma and a single channel analyzer set to maximize the count rate due to the 86 keV line from ^{237}Np. The background count rate, taken after freezing out condensible gases by cooling the bottom end of the sapphire cell to 77 K, was subtracted from the count rate observed with the entire cell at ambient temperature. Addition of PuF_6 to the cell increased the observed count rate due to the small value of the lower limit of the discriminator setting of the single channel analyzer. The gamma detector, shielded by 2.5 cm of lead, was mounted so that it was in close proximity to the upper section of the sapphire tube when the cell assembly was connected to the PuF_6 manifold. The counting geometry remained fixed throughout the experiment.

PHOTOCHEMICAL STUDIES WITH ADDED FLUORINE ATOM SCAVENGER

The initial experiment consisted of photolysis of a mixture of UF_6, NpF_6, PuF_6, and CO gases. Carbon monoxide, $(1.40\pm0.03)\times10^{-5}$ mole, was added as a fluorine atom scavenger to suppress the back reaction of F atoms with UF_5, or deposited impurity

fluorides, and to prevent accumulation of F_2 in the photolysis cell. The amounts of hexafluorides added to the cell are listed in Table 1. A light tan, nearly white, film built up quickly on the walls of the sapphire tube where the filtered light beam from the 75 W Xe arc lamp impinged and a similarly colored powder accumulated at the bottom of the tube. The position of the arc lamp housing with respect to the cell was periodically shifted to minimize attenuation of photolysis light by the film and photolysis was continued until little new film formation was observed. The number of moles of gas remaining after 68 minutes of photolysis that were not condensible at 77 K was found to be $(2.2\pm0.6)\times10^{-6}$ mole and that gas was pumped away. The gas not condensible at 195 K was found to be $(1.54\pm0.09)\times10^{-5}$ mole by repeatedly evacuatin g the manifold and expanding the cell contents into it (i.e. taking "heads"). The gas not condensible at 195 K was pumped away. A measured fraction of the gases condensible at 195 K (the actinide hexafluorides and possibly some carbonyl fluorides) was hydrolyzed in a freeze-pump-thaw degassed 1 M HNO_3 solution contained in a KEL-F tube. The actinide content of this solution was determined by alpha pulse height analysis and inductively coupled plasma atomic emission spectroscopy (ICP/AES). Pu and Np were below the limits of detection, providing evidence that >99.98% of the PuF_6 initially present, and >97.5% of the NpF_6 initially present, had been removed from the gas phase (see Table 1). Prolonged photolysis, however, had reduced the amount of UF_6 remaining in the gas by circa 20%. This success in photochemically removing PuF_6 and NpF_6 from UF_6 prompted a second experiment designed to determine whether the initial photolysis product solid contained are primarily Np and Pu as expected.

The second experiment used similar initial gas concentrations as the first, but the gases were only briefly photolyzed which necessitated analysis of the solid generated by photolysis rather than the gases remaining after photolysis. The photolysis period was circa 1/30th that used in the first experiment. After photolysis, the number of moles of gas had decreased by approximately 3%. The gases were pumped out and the solid remaining in the sapphire tube was dissolved in 1 M HNO_3. The solution was analyzed by alpha pulse height and ICP/AES methods. With respect to actinides, the solution contained primarily plutonium with uranium and neptunium being below the limit of detection. Using the limits of detection for U and Np as upper limits, the actinide content of the photoproduct was <10% U, <29% Np, and >61% Pu. This result is consistent with the first experiment in that the initially-created photoproduct solid contained primarily Pu with lower amounts, or even no, Np or U.

PHOTOLYSIS WITH PERIODIC REMOVAL OF PHOTOGENERATED F_2 AND ON-LINE GAMMA COUNTING.

Photolysis of a mixture of UF_6, NpF_6, and PuF_6 with no added CO was carried out to determine whether use of a fluorine atom scavenger was essential to photochemical removal of transuranic hexafluorides from UF_6 gas. The apparatus shown in Figure 2 was used. This is a non-optimum design for such an experiment because the

arc lamp light interacts with only a fraction of the gas and the resulting photoproduced solid is deposited near the photolysis zone. Because no CO was added to the gas mixture, photolysis was periodically interrupted to permit removal of photogenerated F_2 gas. The amount of fluorine removed was determined by pressure-volume-temperature measurement. The initial amounts of actinide hexafluorides added to the photolysis cell are listed in Table 2. Gamma counting was used to determine the relative amount of low energy gamma emitters (primarily ^{237}Np) in the gas phase. A gamma count of the cell containing UF_6 and NpF_6 gases was obtained when the sample cell was connected to the PuF_6 vacuum line. The observed gamma count of the gas mixture increased 37% after condensing PuF_6 into the cell and warming it to mix the gases. The background count, obtained when the gases were then condensed at the bottom of the cell, was unaltered by addition of the PuF_6. The cell was then warmed to ambient temperature and the mixture of UF_6, NpF_6, and PuF_6 gases were left in the cell for an hour after which a gamma count was again taken, followed by condensation of the gases to check the background count. To within the counting statistical error, no change in observed counts was found. These observations provide evidence of minimal reaction of PuF_6 with the passivated cell surfaces. Photolysis was begun and gamma counting was carried out during photolysis.

Periodically, photolysis was interrupted to permit removal of accumulated photogenerated fluorine gas. This was accomplished by cooling the bottom of the sapphire tube to 77 K, condensing out the hexafluorides. The amount of gas removed was determined by repeatedly evacuating the manifold and expanding the gas content of the cell into the manifold. After removal of F_2, a gamma count was taken to obtain a background value, the cell was warmed to ambient temperature, and a gamma count of the gas was carried out before resuming photolysis. Photolysis was terminated when additional exposure of the gas to ultraviolet light resulted in little decrease in the observed gamma count rate (see Fig 3). The gas remaining after termination of photolysis was hydrolyzed in a freeze-pump-thaw degassed 1 M HNO_3 solution in a KEL-F tube. The alpha content of the resulting solution was determined by scintillation counting. The solid remaining in the sapphire tube was dissolved in 1 M HNO_3 and its alpha content determined by scintillation counting.

In Figure 3, a dashed line has been drawn connecting the data points to aid in identifying trends. While the overall trend is reduction in gas phase gamma count with increasing photolysis time, one aspect of the data deserves comment. The observed reduction in gas phase gamma count immediately after interruption of photolysis to remove accumulated F_2 gas is attributed to incomplete mixing of the gas during photolysis. Because the photolysis zone was near the bottom of the sapphire tube, we would expect depletion of PuF_6 and most NpF_6 in this zone with the result that some UF_5 may have been accumulated. Cooling the bottom of the sapphire tube to 77 K and then warming back to ambient temperature brings the remaining NpF_6 and PuF_6 into contact with such UF_5 with resultant loss of gas gamma activity immediately after removal of F_2. When photolysis resumed, some of the deposited Np and Pu fluorides

may have been re-fluorinated to hexafluorides via reaction with F atoms from photodissociation of UF_6. Such regeneration of transuranic hexafluorides would account for the increase in the gas phase gamma count observed upon resuming photolysis after removal of F_2 from the sample cell.

ANALYSIS OF "PHOTOLYSIS WITH PERIODIC REMOVAL OF F_2 AND ON-LINE GAMMA COUNTING" EXPERIMENT

For our purposes, the alpha activity due to the UF_6 added to cell is negligible. We can relate x, the fraction of the total amount of Pu added to the cell which was deposited in the photoproduct solid and y, the fraction of the total amount of Np added to the cell which was deposited in the photoproduct solid, to the total alpha activity of the photoproduct solid as follows:

$$f_p x + (1-f_p)y = \frac{\alpha_s}{\alpha_t} \qquad (1)$$

where α_t is the total alpha activity present in the cell prior to photolysis, ϕ_p is the fraction of α_t that is due to the PuF_6 content of the gas mixture, and α_s is the alpha activity in the solid remaining in the cell after evacuation. Substituting numerical values gives,

$$0.99045x + 0.00955y = 0.9609 \qquad (2).$$

In addition, g_f, the gamma count rate after photolysis was terminated, is related to g_n, the gamma count rate due to the NpF_6 present in the cell prior to any photolysis, and g_P, the gamma count rate due to PuF_6 present in the cell prior to any photolysis, are related to y by the relationship:

$$y = 1 - \left(\frac{g_f - g_P (1 - x)}{g_n}\right) \qquad (3).$$

Inserting numerical values gives:

$$y = 1 - \left(\frac{307 - 942 (1 - x)}{2564}\right) \qquad (4).$$

Using Equation 4 in substituting for y in Equation 2 and solving for x, gives x = 0.962±0.010, resulting in y = 0.894±0.009. These values, together with the amount of NpF_6 and PuF_6 initially added to the cell, enable determination, by difference, of the amount of transuranic hexafluorides remaining when photolysis was terminated (see

Table 2 for resulting values). Summing the NpF_6 and PuF_6 values together, we find that $(1.41\pm0.015)\times10^{-5}$ moles of transuranic hexafluorides were removed from the gas mixture by photolysis. Taking the difference between 1.588×10^{-4} moles (the total amount of actinide hexafluorides added to the cell) and 1.397×10^{-4} moles (the amount of gas condensible at 195 K upon terminating photolysis), we find that $(1.91\pm0.015)\times10^{-5}$ moles of actinide hexafluoride were removed from the gas mixture by photolysis. Subtracting from this value the amount of transuranic hexafluorides removed by photolysis, we conclude that $(5.0\pm0.3)\times10^{-6}$ moles of UF_6 were removed from the gas mixture by photolysis, which is equivalent to 3.5% of the UF_6 added to the cell. The stated errors are based on evaluation of the effect of counting statistics and systematic errors on the values derived from Equations 1 and 2.

The number of moles of gas not condensible at 77 K (i.e. fluorine), generated by photolysis, was found to be $(1.3\pm0.1)\times10^{-5}$ moles. Photoreduction of NpF_6 generates a solid whose formal stoichiometry is $NpF_{4.75}$ (J. V. Beitz and C. W. Williams, unpublished). Assuming the photoproduct neptunium fluoride has this same stoichiometry, the photoproduct uranium fluoride is UF_5, the photoproduct plutonium fluoride is PuF_4, and the above values for the number moles of each hexafluoride converted to photoproduct, the calculated amount of fluorine generated during photolysis is $(1.38\pm0.015)\times10^{-5}$. This is in good agreement with that found experimentally. We conclude that photolysis with periodic removal of F_2 and on-line gamma counting enabled removal 96% of the PuF_6 (and 89% of the NpF_6) initially added to the cell with conversion of only 3.5% of the UF_6 to a solid compound.

For simplicity, we used a static (i e. non-flowing) gas cell in which the photolysis zone (where fluorine atoms are generated) is in close proximity to accumulating solid photoproduct. This is a distinctly non-optimum experimental arrangement in that photogenerated fluorine atoms may come into contact with the photoproduct solid, react with it, and thereby re-volatilize the actinides in the solid. Removal efficiencies for NpF_6 and PuF_6 comparable with those found in the proof-of-concept experiment, in which CO was used as a fluorine atom scavenger, seem likely to be achievable using a flow system. Such a system would need to incorporate means for rapid removal of both photoproduct solid (by filtration or centrifugation) and F_2 gas (by passing the gas stream through a trap at circa 200 K, to condense actinide hexafluorides, and then through a lower temperature trap to condense F_2).

APPLICABILITY OF PHOTOCHEMICAL REMOVAL TO FISSION PRODUCT d-TRANSITION METAL HEXAFLUORIDES

Studies of the reactions of d- and f-transition metal hexafluorides provide evidence that their chemical reactivities vary as shown in the following series(*39,40,41*):

$$WF_6 < MoF_6 < UF_5 < NpF_6 < PuF_6 < AmF_6$$

$OsF_6 < PuF_6 < RuF_6$

$MoF_6 < TcF_6 < RuF_6 < RhF_6$.

These reactivity series provide a basis for assessing the likelihood of removing d-transition hexafluorides from UF_6 gas using our photochemical method. Hexafluorides more reactive than UF_6 are likely to be removable from UF_6 using our new method. It is therefore probable that AmF_6, RuF_6, and RhF_6 will be photochemically removable from UF_6. Based on preliminary experiments in which TcF_6 has been found to react with solid UF_5 (J. V. Beitz and C. W. Williams, unpublished), prospects are also good for photochemical removal of TcF_6. Some chemically reactive corrosion product fluorides, such as CrF_5, and some volatile fluorides, such as VF_5, arising from metallic impurities in uranium ore, are also likely to be removed using our photochemical technique.

ADVANTAGES AND DISADVANTAGES OF PHOTOCHEMICAL REMOVAL OF IMPURITIES FROM UF_6 GAS

Efficient reduction of the volume of waste generated in removing reactive fluoride impurities from UF_6 gas is the principle advantage of this photochemical separations technique. Potentially, the volume of waste generated need be no more than the volume of the removed impurities since the process does not dilute the radioactive species in aqueous solutions or molten salts. If no fluorine atom scavenger is used, F_2 gas is generated as a by-product which, in a process plant, would be recycled to UF_6 production.

A disadvantage of this new photochemical separations technique for purifying UF_6 is that not all impurities are sufficiently chemically reactive to be removed. Fortunately, non-reactive hexafluorides of d-transition metal fission products are also appreciably more volatile than is UF_6 (*42*) and so should be readily removable by fractional distillation. For example, removal of MoF_6 from UF_6 by fractional distillation has been demonstrated (*1*). Fractional distillation would also be effective in removing those solid impurity fluorides (generated by reaction of gaseous impurities with UF_5) whose vapor pressure is not negligible with respect to UF_6. A combination of photochemical reaction and fractional distillation is particularly attractive when it is necessary to remove all metallic impurities from UF_6.

Accumulation of solid photoproduct on photolysis windows or tubes can be minimized by adjusting the velocity and direction of gas flow, but a mechanical scraper system and periodic removal of adherent particles via photofluorination may be needed in practice. Minimizing loss of U to waste in a process environment likely will require on-line, near real-time, monitoring of impurity levels immediately after the photolysis zone with feedback control of the photolysis light intensity and/or gas flow rate. Radioactivity

monitoring and laser-induced fluorescence (*43*,*44*) are two potential methods for monitoring impurity levels in near real-time.

CONCLUSIONS

A novel photochemical method of removing chemically reactive fluoride impurities from UF_6 gas has been demonstrated using mixtures of UF_6, NpF_6, and PuF_6. Reduction of PuF_6 by a factor of more than 5000, with simultaneous reduction of NpF_6 by more than a factor of 40, has been demonstrated in a single photolysis step using added CO as a fluorine atom scavenger. Similar, but smaller, reductions of PuF_6 and NpF_6 were also found in a non-optimum experimental apparatus in which no fluorine atom scavenger was added and accumulated fluorine gas was periodically removed from the photolysis cell. This mew photochemical method, combined with fractional distillation, can hold the volume of waste generated in purifying UF_6 to little more than the volume of the removed impurities while minimizing loss of UF_6 and generating fluorine gas as a valuable, recyclable, by-product.

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Table 1. Extensive Photolysis of UF_6 + NpF_6 + PuF_6 + CO Gas Mixture Experiment

Species	Added to sample cell (moles)	Present after photolysis (moles)[a]	Fraction of Actinide Hexafluoride Remaining After Photolysis
UF_6	1.47×10^{-4}	1.18×10^{-4}	0.803
NpF_6	7.29×10^{-6}	$<1.67 \times 10^{-7}$	<0.023
PuF_6	7.325×0^{-6}	$<1.1 \times 10^{-9}$	<0.00015

a. Gases remaining after photolysis were hydrolyzed and the resulting solutions analyzed. Uranium value based on ICP/AES measurement. Np and Pu were below alpha pulse height limit of detection. Numerical value shown for Np and Pu is the limit of detection.

Table 2. Photolysis of UF_6 + NpF_6 + PuF_6 Gas Mixture With Periodic Removal of F_2 and On-line Gamma Counting Experiment

Species	Added to sample cell (mole)[a]	Present after photolysis (mole)[a,b]	Fraction of Actinide Hexafluoride Remaining After Photolysis
UF_6	1.436×10^{-4}	1.386×10^{-4}	0.965±0.002
NpF_6	7.86×10^{-6}	8.3×10^{-7}	0.106±0.019
PuF_6	7.345×0^{-6}	2.8×10^{-7}	0.038±0.020

a. Uncertainty: $\pm 3\xi 10^{-7}$ $\phi o \rho$ $Y\Phi_6$, $\pm 1.5 \times 10^{-7}$ mole for PuF_6 and NpF_6.
b. See text for method used to determine amounts of actinide hexafluorides remaining after photolysis.

Figure Captions

Figure 1. Comparison of electronic and thermodynamic properties of actinide hexafluorides based on literature references cited in the text. Energy regions over which electronic states of actinide hexafluorides absorb light are shown shaded with diagonal lines and centers of gravity of 5f electron states are denoted by solid horizontal lines. Reported bond dissociation energies and uncertainties for UF_6 and PuF_6 are shown along with an estimate for NpF_6 which assumes that its bond dissociation limit corresponds to the onset of charge transfer state absorption.

Figure 2. Schematic diagram of photolysis apparatus. The gamma detector was used only in the experiment in which no fluorine atom scavenger was added to mixture of actinide hexafluorides.

Figure 3. Observed gamma count (2 minute counting period) from actinide hexafluoride gas mixture as a function of photolysis time. Data recorded during photolysis are shown as open circles. Data recorded immediately after removal of accumulated fluorine gas are shown as solid squares.

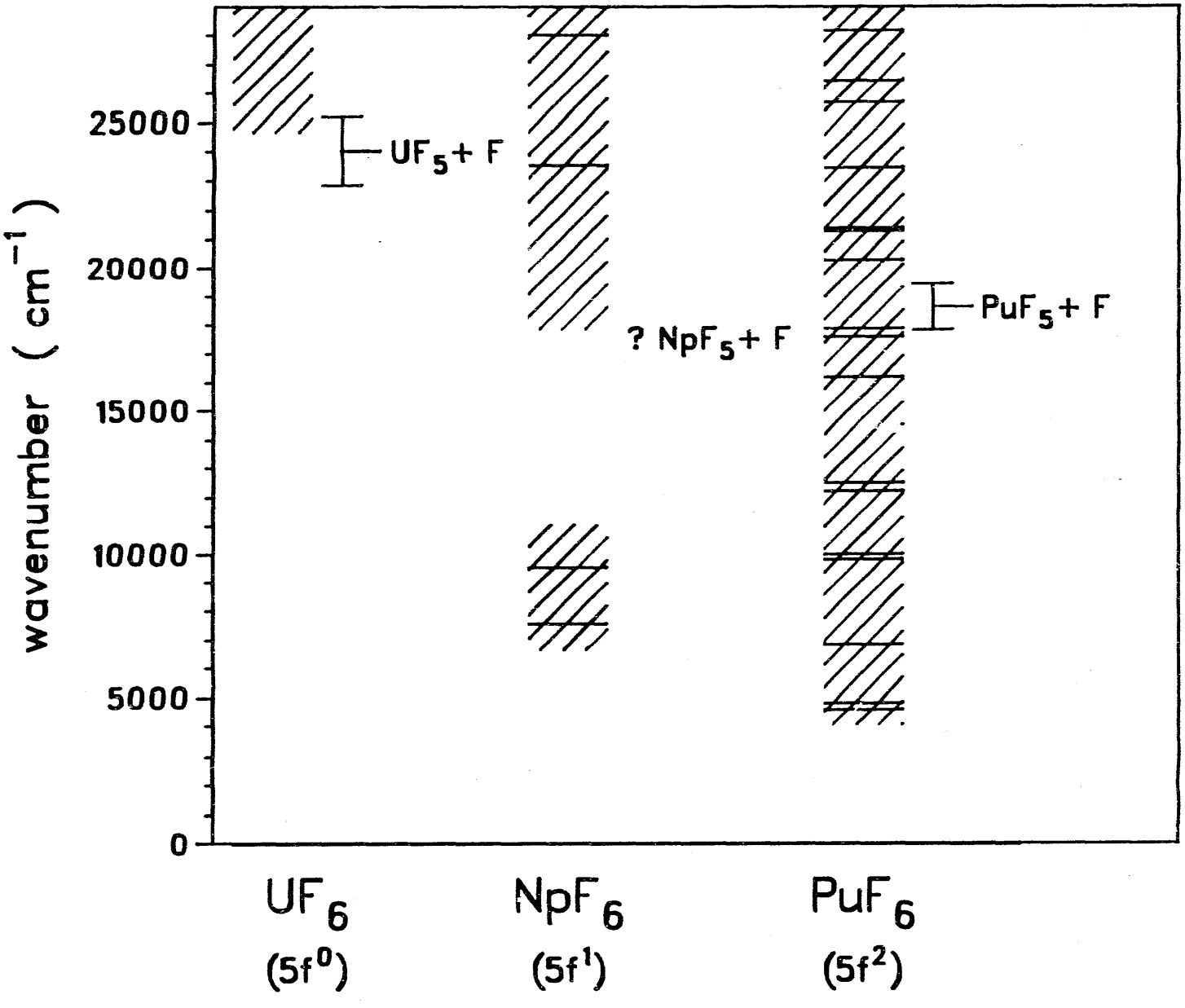
wavenumber (cm^{-1})
25000
20000
15000
10000
5000
0
UF_5 + F
? NpF_5 + F
PuF_5 + F
UF_6
($5f^0$)
NpF_6
($5f^1$)
PuF_6
($5f^2$)

Fig. 1

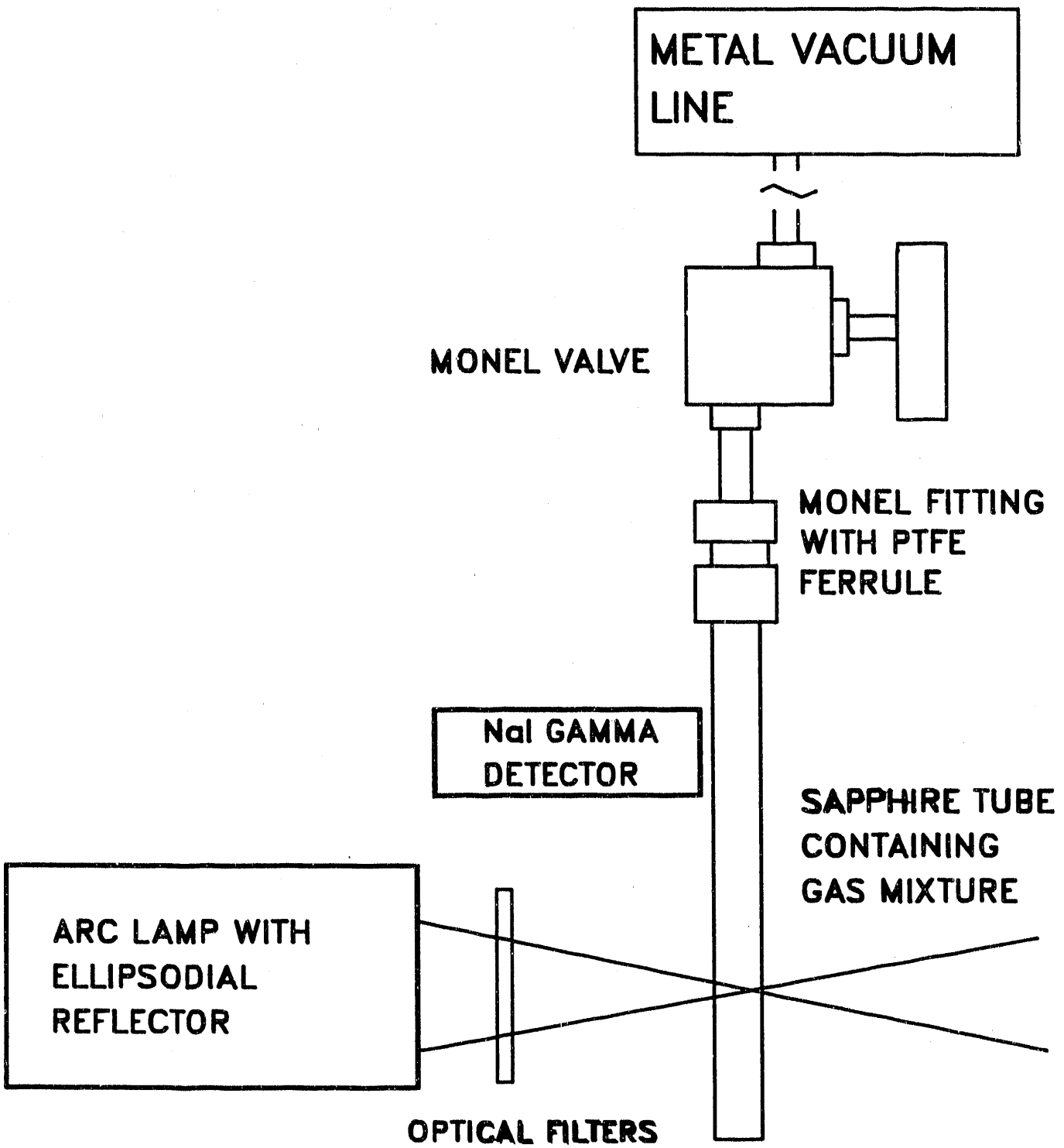
METAL VACUUM LINE
MONEL VALVE
MONEL FITTING WITH PTFE FERRULE
NaI GAMMA DETECTOR
SAPPHIRE TUBE CONTAINING GAS MIXTURE
ARC LAMP WITH ELLIPSODIAL REFLECTOR
OPTICAL FILTERS

Fig. 2

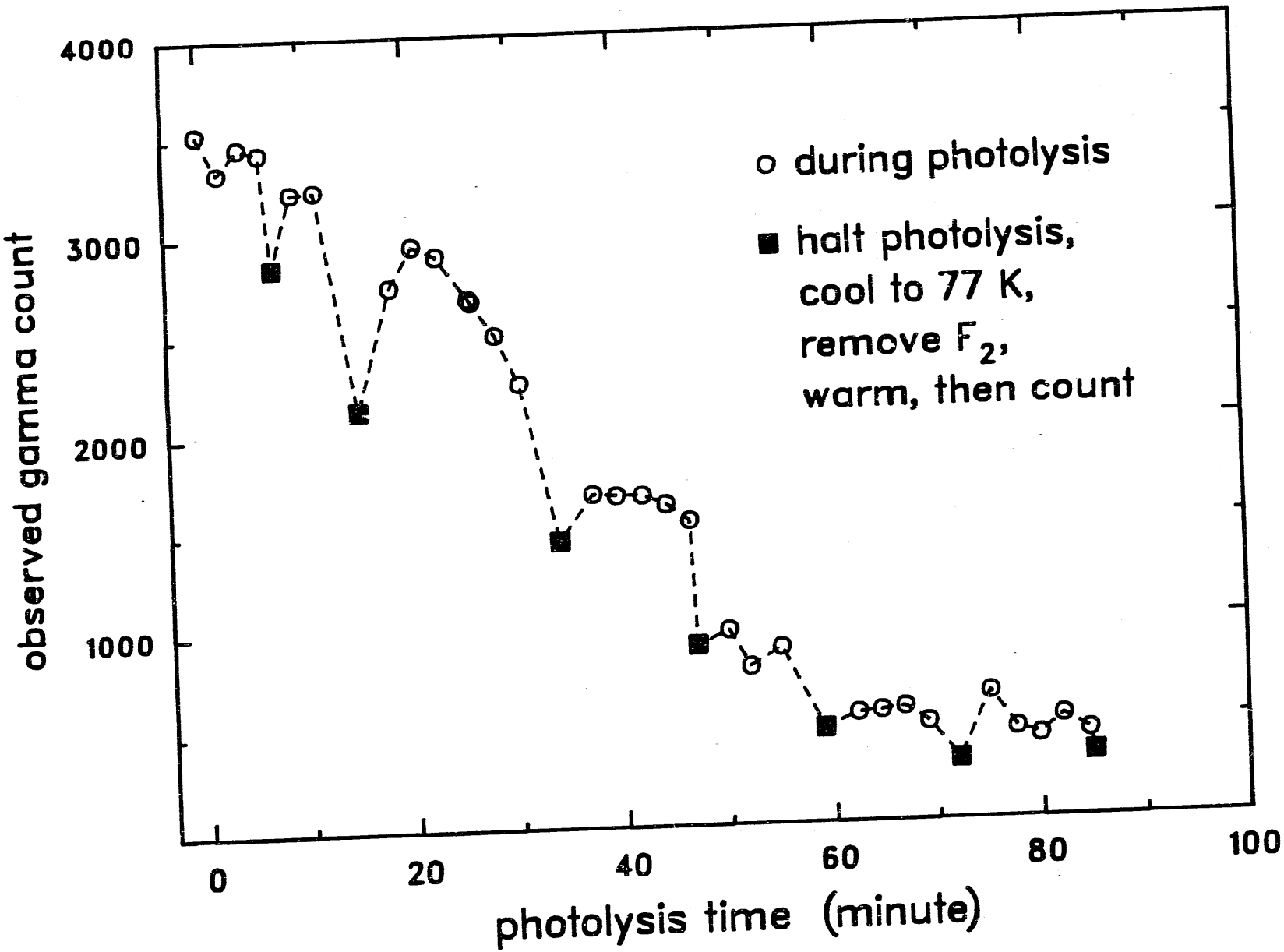
4000
3000
2000
1000
observed gamma count
o during photolysis
■ halt photolysis, cool to 77 K, remove F_2, warm, then count
0
20
40
60
80
100
photolysis time (minute)

Fig. 3

END

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