Competitive energy dynamics in IRMPD of UF6

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The photochemical isotope separation schemes have renewed the detailed investigations of gas phase photochemistry and photochemistry of UF6. One of the schemes is based on massive multiphoton excitation of UF6 using one or more suitable IR laser frequency in 16μm region in its ground electronic state. In the present work we have modelled such Infrared Multiphoton Dissociation (IRMPD) on a rate equation formalism. Using RRKM theory, the multiphoton dissociation rate constants for UF6 with 16 μm laser have been estimated. It is shown that about 50 laser photons, which are 15 photons excess over the dissociation threshold of 3 eV, are required for dissociation of each UF6 molecule. Using the present model, the fluence dependence of dissociation yield has been evaluated and it is found that MPD of UF6 occurs with a threshold fluence of $1 - 1.2 \text{ J cm}^{-2}$. Isotopic selectivity in this model is described as the difference in the rate of laser energy absorption for the two isotopic species. Considering various time scales involving excitation, collisional deactivation and life time of energized 235-UF6 molecule, the extent of selectivity loss has been estimated.

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The demand for enriched uranium as a fuel source in nuclear fission reactors has directed a large amount of research in recent years towards the development of more efficient and economic isotope separation method. Though the idea of selective photochemistry as a means of uranium isotope separation dates back to the Manhattan Project1, only the advent of lasers has stimulated reconsideration of the photochemical process.

Choice of an appropriate molecular form of uranium is an important first step in developing such a process. It is desirable to work with a molecular form which has high vapour pressure to maximize the working density and throughput. Uranium hexafluoride has the highest vapour pressure of any uranium compound and its industrial production and handling have been well developed for existing diffusion and centrifuge methods. It has therefore been automatically a preferred choice for the scheme. The economics of isotope separation have consequently dictated the direction of much of the applied photochemical research2-4 on UF6. We have carried out photochemical investigations on various volatile uranium compounds5-9.

The chief advantage of UF6 for use in LIS schemes is its known spectroscopy, thermal stability and monoisotopy of fluorine. In its 16 μm IR absorption band, the $v_3$ mode has a marked isotope shift of 0.65 cm⁻¹ at 625 cm⁻¹. In the molecular approach schemes of LIS, selective excitation of the desired isotopic species can thus be achieved by a suitable IR laser in 16 μm region. In view of this, two approaches appear to be promising for collecting the desired excited isotopic species. The first approach is based on massive multiphoton excitation of UF6 using one or more IR frequency in its ground electronic state so that the molecule absorbs sufficient energy to unimolecularly dissociate. In the second approach, a limited vibrational selective excitation is followed by an electronic excitation with a suitable UV-visible laser to decompose the excited molecule. The objective of either of these approaches is to maximize selective photodissociation of the desired isotopic species.

The electronic photochemistry of UF6 has been dealt in details earlier5,6,10-14. Presently, we will discuss the vibrational photochemistry of this molecule in the context of Infrared Multiple Photon Dissociation (IRMPD).

Vibrational Photochemistry of UF6

UF6 belonging to O₆ point group has six normal modes of vibration. Out of these only the $v_3$ and $v_4$ modes give rise to rovibronic spectra proper, whereas the remaining modes are manifested in the spectrum by overtone vibrations (Table 1). The reason for this
Table I—Fundamental vibrational frequencies of UF$_6$ (O$_h$ point group)

<table>
<thead>
<tr>
<th>Normal mode (i)</th>
<th>Irreducible representation</th>
<th>Frequency $v_i$ (cm$^{-1}$)</th>
<th>Assignments</th>
<th>Optical activity</th>
<th>Isotope shift (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$A_{1g}$</td>
<td>667.1</td>
<td>$\nu$(U-F)</td>
<td>Raman</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$E_g$</td>
<td>532.5</td>
<td>$\nu$(F-U-F)</td>
<td>Raman</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$F_{1u}$</td>
<td>624.0</td>
<td>$\nu$(U-F)</td>
<td>Raman</td>
<td>0.65</td>
</tr>
<tr>
<td>4</td>
<td>$F_{1g}$</td>
<td>186.2</td>
<td>$\delta$(F-U-F)</td>
<td>Raman</td>
<td>0.16</td>
</tr>
<tr>
<td>5</td>
<td>$F_{2g}$</td>
<td>202.0</td>
<td>$\delta$(F-U-F)</td>
<td>Raman</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$F_{2u}$</td>
<td>142.0</td>
<td>$\delta$(F-U-F)</td>
<td>Raman</td>
<td></td>
</tr>
</tbody>
</table>

Computed frequency parameters (cm$^{-1}$)

$\langle v \rangle = 346.3$

$\langle v^2 \rangle = 405.5$

$v = 285.98$

is that the displacement of the center of gravity of charges occurs only in the $v_3$ and $v_4$ vibrations. The normal vibrational energy states, normalized to zero for the ground state levels, can be described by introducing a dimensionless anharmonicity constant $\chi$ and the quantum number $v : E = hv v [1-\chi(v-1)]$ where $v$ is the frequency required for resonant excitation of the first vibrational level. The anharmonicity shift $\Delta v_{an}$ in the simplest case is related to the anharmonicity coefficient $\chi$ by $\Delta v_{an} = 2\chi v$. Combination of rotational and vibrational transitions resulting in the rotation-vibration spectrum can be displayed in the well known Fortrat diagram. The selection rules valid for changes in vibrational quantum number $v$ and rotational quantum number $J$ are: $\Delta v = \pm 1 ; \Delta J = \pm 1$. It is seen that all normal modes have very low vibrational frequencies and all except one are degenerate (cf Table I). Because of the degeneracy coupled with low frequency many of them will be populated to a large extent even at room temperature. As many vibrational levels are occupied at room temperature, $\Delta v_3 = \pm 1$ and $\Delta v_4 = \pm 1$ transitions can occur not only from ground level but also from many higher vibrational levels which give rise to "hot bands". In real situation, due to anharmonicity shift, none of the transitions will occur at the same frequency and superposition of all these transitions contribute to the overall $v_3$ or $v_4$ absorption band. Nevertheless, the overtone (i.e., $3v_4$) and combination bands (i.e., $v_3 + v_4 + v_6$) are also possible, though the corresponding cross sections are smaller by about four orders of magnitude.

The transitions with $\Delta J = -1, 0, +1$ generate the P, Q and R branches respectively, of the rotation-vibration band, where the central Q-branch is flanked by the broader P and R branches which are lower in intensity. This structure becomes evident in the experimental spectra$^{15}$ at 300 and 228 K as shown in Fig. 1. Lower temperature narrows the rotational band and increases its intensity, as transitions tend to bunch in the lower energy rotational states. At the same time, absorption in the Q-branch is also enhanced. The room temperature absorption spectrum is not resolved in rotational structure because the rotational linewidth is larger than the average spacing between them. Assuming the combined effect of Coriolis coupling and symmetry reduction in vibrating molecule, the average spacing between two rotational levels is given by$^{5,11}$:

$$\Delta v_{av} = 2B (1-\zeta)\langle \rho \rangle / (2J_{max} + 1)$$  \hspace{1cm} (1)

where $\langle \rho \rangle$ is the mean value of the vibrational probability distribution and $J_{max}$ is the J value corresponding to maximum of rotational probability distribution and $\zeta$ is the Coriolis constant and $B$ is the rotational constant. At room temperature, $\Delta v_{av} = 0.12$ MHz, which is much smaller than the expected line broadening due to Doppler effect, $\Delta v_D = 11$ MHz and collisional broadening $\Delta v_C = 4.2$ MHz Torr$^4$.

A significant reduction in the complexity of the spectrum could be obtained by lowering the temperature. At 40 K, only 2.5% of the molecules remain in the excited vibrational levels. As the vapour pressure of UF$_6$ drastically reduces with static cooling (about 0.2 Torr at 228 K), an appreciable working density in the gas phase can only be obtained by dynamic cooling in supersonic molecular beam$^{16}$.
Though there are only a few studies involving the spectral features of the cooled beam, the characteristic information like exact wavelengths, isotope shift, etc., are classified.

The isotope shift of rotation-vibration spectra is caused by the dependence of the vibrational frequency on the reduced mass corresponding to normal vibration. An influence of the central mass atom is expected only for those vibrations which imply motion of the central atom. The isotope effect induces a mutual displacement of two practically identical rotation-vibration bands, where the band corresponding to the lighter isotope lies on the high frequency side (cf Fig. 1). Given the small mutual displacement of the uranium isotope band, the intensity ratio in small signal absorption is a complicated function of frequency, which oscillates around unity several times. The most favourable combination of absolute value and absorption cross-section difference between $^{235}$UF$_6$- and $^{238}$UF$_6$ isotopes can be found within bands of central Q-branch.

Theoretical Modeling of IRMPD of UF$_6$

Energy transfer probability in sensitized dissociation

Before embarking on theoretical modeling on IRMPD of UF$_6$, it is necessary to carry out the MPD process and establish the process parameters. Since the 16 micron laser technology is involved and difficult, we planned to use available CO$_2$ laser (9-11 μm) radiation for affecting the dissociation. However, there is no measurable absorption of CO$_2$ laser by UF$_6$ at room temperature, even through its hot bands (absorption cross section of $5.3 \times 10^{-7}$ torr$^{-1}$ cm$^{-1}$).

Thereby, we innovatively devised experiments using near resonant V-V energy transfer from various sensitizers like SF$_6$, CF$_3$Cl, CF$_2$Cl$_2$, etc. having good absorption in CO$_2$ laser region.

The relative changes in the sample concentrations were monitored by IR-spectrometry where one can easily notice the decrease in UF$_6$ - $v_3$ absorption and appearance of new product peak and they can be used for measuring the cell averaged dissociation yield per pulse. The roles of various experimental parameters like exciting frequency, fluence and pressure of sensitizer/acceptor on the dissociation processes were studied. Overall processes occurring can be summarized as follows:

(i) Multiple photon absorption (MPA) by CF$_2$Cl$_2$:

\[
<\!n\!> \text{hv} \rightarrow \text{CF}_2\text{Cl}_2 \rightarrow \text{CF}_2\text{Cl}_2^* (n \nu_2) \quad \ldots (2)
\]

(ii) Intermode relaxation in CF$_2$Cl$_2$:

\[
\text{CF}_2\text{Cl}_2^* (n \nu_2) \rightarrow \text{CF}_2\text{Cl}_2^* (n \nu_m) \quad \ldots (3)
\]

(iii) Inter species V-V transfer:

\[
\text{CF}_2\text{Cl}_2^* (n \nu_m) + \text{UF}_6 \rightarrow \text{UF}_6^* (n \nu_3) + \text{CF}_2\text{Cl}_2 \quad \ldots (4)
\]

(iv) Multiple photon absorption (MPA) by UF$_6^*$:

\[
<\!m\!> \text{hv} \rightarrow \text{UF}_6^* \rightarrow \text{UF}_6^* \rightarrow \text{UF}_6 + \text{F} \quad \ldots (5)
\]

In dealing with the mechanism of vibrational energy flow in polyatomic molecules whose specific vibrational mode is excited by a laser, it is the general consensus that the intramode V-V dominates the intermode V-V energy transfer. Therefore, a local vibrational quasi-equilibrium distribution is attained within the laser-pumped mode prior to the establishment of the steady state distribution among all the modes. In the final stage of relaxation the V-T/R energy transfer occurs from modes having low fundamental frequencies.

Energy transfer was also verified by looking at infrared fluorescence (IRF) from excited sensitizer.
molecule at 9.6 μm and of UF₆⁺ at 16 μm in a laser excited mixture. It was observed that simultaneously with the increase in number of average photon absorbed, <n>, with UF₆ pressure, there is a decrease in 9.6 μm fluorescence and a growth of 16 μm fluorescence intensity. The observed decrease in 9.6 μm intensity could be understood as the energy was siphoned off to UF₆ from sensitizer via V-V energy transfer, while the increase in 16 μm fluorescence is caused by IRF from such excited UF₆ molecules. The fast rise of 16 μm IRF (< 1 μs limited by the rise time of the detection system) suggested that intermolecular V-V energy transfer from sensitizer to UF₆ is complete within the laser pulse duration.

The efficiency of the energy transfer process was estimated on the basis of long range dipole-dipole interaction. This gave fruitful information about the dissociation mechanism relating the role of the absorption characteristics of the sensitizer and relative energy levels of the sensitizer. The probability for transition from state 1 to state 2 induced by a time-dependent perturbation V(t) in the first order Born approximation is given by:

\[ P_{12} = \frac{\hbar^2}{2} \int V_{12}(t) \exp(i\Delta \omega t) dt \]  

... (6)

where \( V_{12}(t) = < 1 \mid V(t) \mid 2 > \) and \( \Delta \omega \) is the frequency difference.

It is known that the probability will be greatest when \( V_{12}(t) \) has Fourier components at frequency \( \Delta \omega \). For a V-T process where \( \Delta \omega \) is large and the process occurs through the lowest vibrational level, this may be achieved on the repulsive part of the interaction potential where \( V_{12} \) changes rapidly with time. However, in V-V processes, it is possible for \( \Delta \omega \) to be quite small or even zero for a resonant energy transfer. In such cases, the attractive part of the interaction potential may introduce significant Fourier components at frequency \( \Delta \omega \) into \( V(t) \). That such long range dipole-dipole interactions could induce near resonant V-V transfer was first pointed out by Mahan and was subsequently improved by Sharma and Brau.

The non-resonant \( (\Delta \omega \neq 0) \) V-V relaxation probability under the Sharma-Brau cut-off is given by:

\[ < P > = (4\pi^2C^2\Delta \omega / \sqrt{3 \hbar^2 d^2 \nu kT}) \exp(-\mu \nu^2 / 2kT) \]  

... (7)

where \( C = 1/3 \) \([\text{d.m.}]_{1/2} \times [\text{d.m.}]_{1/2} \) and \([\text{d.m.}]_{1/2}\) is the 1→2 vibrational dipole matrix element for molecule A and \( \nu^* \) is given by \( (2d\omega kT)^1/2 \). The above relation gives a behaviour similar to that given by SSH theory i.e. \( \ln < P > = \Delta \omega^{2/3} \). These matrix elements can be determined from measurements of the integrated infrared absorption \( \langle S_m \rangle \) which is related to them by:

\[ \text{d.m.} = 0.3646 \left( \frac{S_m}{\nu} \right)^{1/3} \]  

... (8)

where \( \text{d.m.} \) is in Debye, \( S_m \) in km mole⁻¹ and \( \nu \) is the band centre frequency in cm⁻¹.

From the available spectroscopic and kinetic data, the vibrational energy transfer probabilities were evaluated for UF₆ / sensitizer systems using the above treatment. For one-quantum transfer, the probabilities are given in Table 2 which indicate that energy transfer can occur to UF₆ very efficiently from CF₂Cl₂ and SF₆. The estimated one-quantum transfer probability in the SF₆ / UF₆ system agrees with the value of \( 2.8 \times 10^{-1} \) cm⁻³ s⁻¹ at 300 K reported in the literature.

Therefore, sensitized MPD has been shown to be an effective way of studying system which does not have absorption in the working laser emission range. It may be pointed out that in favourable cases (33/32 in SF₆CI and 13/12 in CF₂Cl system with SF₆ sensitizer) even isotopic selectivity has been demonstrated. However, with the complexity and the small isotope shift of UF₆ molecule it would be extremely difficult to realize such an effect. Once the MPD process for UF₆ has been clearly established, we carried out a theoretical estimate of multiple photon dissociation rate constant and competitive energy dynamics in IRMPD of UF₆.

Unimolecular dissociation rate constant

Following RRKM theory²³, it is assumed that the multiphoton excitation energy of UF₆ molecule is rapidly randomized among all the vibrational modes of the molecule. The energized molecule, having more than sufficient energy for the dissociation to occur, will then reorganize its internal degrees of freedom to become an activated complex (AC). This activated complex has the appropriate critical molecular configuration for the dissociation process to occur readily.
Table 2—Vibrational energy transfer probabilities for various sensizers with UF₆

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Pump/ Transfer mode (cm⁻¹)</th>
<th>Dipole moment (D)</th>
<th>Laser line (cm⁻¹)</th>
<th>Energy defect Δω (cm⁻¹)</th>
<th>C(S/UF₆) (erg/cm³) ×10⁴</th>
<th>Probability &lt;fₚ&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃Cl</td>
<td>v₁</td>
<td>0.226</td>
<td>9R(30)</td>
<td>156</td>
<td>87.40</td>
<td>0.0062</td>
</tr>
<tr>
<td></td>
<td>1105</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>v₂</td>
<td>0.069</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₃Cl₂</td>
<td>v₁</td>
<td>0.183</td>
<td>9R(30)</td>
<td>42</td>
<td>250.80</td>
<td>0.369</td>
</tr>
<tr>
<td></td>
<td>1101</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>v₂</td>
<td>0.198</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF₆</td>
<td>v₃</td>
<td>0.388</td>
<td>10R(20)</td>
<td>10</td>
<td>169.70</td>
<td>0.239</td>
</tr>
<tr>
<td></td>
<td>948</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>v₄</td>
<td>0.0134</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\langle \text{nhv} \rangle \quad K_d(E_v^*) \quad \text{UF}_6 \rightarrow \text{UF}_6^* \rightarrow \text{UF}_6 + F \)

(Energized molecule) (Activated complex)

... (9)

The conversion of the energized molecule to activated complex occurs at a definite rate, \(K_d(E_v^*)\), which is a function of the non-fixed energy available for redistribution with the molecule.

Therefore, molecules with energy \(E_v^*\) will have RRKM unimolecular dissociation rate constant:

\[
K_d(E_v^*) = L^3 (Q_1^*/Q_1) \left[ \hbar N^{D}(E_v^*) \right]^{-1} \sum_{E_v^* = E_v^*} E_v^* \Sigma P(E_v^*) \quad \quad \text{... (10)}
\]

where \(L^3\) = statistical factor taken as 6 representing the number of equivalent paths of dissociation; \((Q_1^*/Q_1)\) = rotational partition functions for the activated complex and the undistorted molecule respectively. Assuming one U-F bond length is doubled in forming the activated complex it is 1.75; \(N^{D}(E_v^*)\) = density of vibrational states at energy \(E_v^*\) and the sum \(\Sigma P(E_v^*)\) is the total number of vibrational states in the activated complex up to energy \(E_v^*\); The internal energy of activated complex is defined as:

\[
E_v^* = E_v^* - E_v^* \quad \text{since an amount of energy } E_v^* \text{ equivalent to the energy barrier between the reactants and products, becomes fixed in the formation of the activated complex.}
\]

Using Whitten–Rabinovitch approximation, \(N^{D}(E_v^*)\) and the sum \(\Sigma P(E_v^*)\) are evaluated with the vibrational frequencies of UF₆ and activated complex. The evaluation of \(\Sigma P(E_v^*)\) depends on what set of vibrational frequencies can be assigned to the activated complex. The AC is assumed to have the configuration where one U-F bond has been stretched and the bond length is doubled. The number of modes in AC is reduced by one since the normal stretching mode of U-F (which is now different from other F-atoms) becomes the reaction coordinate. The vibrational frequencies of AC were determined by first dividing the frequencies of UF₆ into two categories (a) those which are little affected and (b) those most affected by extending the bond. As one bond is stretched and that particular F atom becomes different from the rest, the symmetry point group for AC changes from \(O_h\) to \(C_4v\). From the correlation table, it was possible to assign AC frequencies. The frequencies which are least affected were taken to be 0.95 times the corresponding UF₆ frequencies. The most affected mode frequencies were taken as 0.75 and 0.65 times those of UF₆ to allow adequate range for defining the properties of the AC (Table 3). It would be possible to define the vibrational frequencies of the AC more precisely by comparing with thermal reaction rate data, if available.

Using the data of Tables 1 and 3, the unimolecular dissociation rate constant of uranium hexafluoride was estimated and presented in Table 4. It can be seen that about 15 excess photons over the dissociation threshold \((E_v = 68 \text{ kcal mol}^{-1})\), i.e., about 50 laser photons are required for efficient dissociation \((5 \times 10^7 \text{ s}^{-1})\) of each UF₆ molecule.
Table 3—Vibrational frequencies of the activated complex \((\text{UF}_6^+)\)

<table>
<thead>
<tr>
<th>(\Gamma_{\text{UFS}})</th>
<th>(\Gamma_{\text{UFS+}})</th>
<th>(i)</th>
<th>Assignment</th>
<th>(\nu_i (\text{cm}^{-1}))</th>
<th>(\nu_i (\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_{1_g})</td>
<td>(A_1)</td>
<td>2</td>
<td>(\nu_{\text{sym}}(\text{UF}_4))</td>
<td>633.75(^a)</td>
<td>633.75(^b)</td>
</tr>
<tr>
<td>(E_g)</td>
<td>(A_1)</td>
<td>3</td>
<td>(\delta_{\text{asy}}(\text{UF}_4)) out of plane</td>
<td>346.13(^b)</td>
<td>399.37(^b)</td>
</tr>
<tr>
<td>(B_1)</td>
<td>(A_1)</td>
<td>5</td>
<td>(\nu_{\text{sym}}(\text{UF}_4)) out of plane</td>
<td>505.88(^a)</td>
<td>505.88(^b)</td>
</tr>
<tr>
<td>(F_{1u})</td>
<td>(A_1)</td>
<td>1</td>
<td>(\nu(\text{U-F}))</td>
<td>405.6(^b)</td>
<td>468.0(^b)</td>
</tr>
<tr>
<td>(F_{1u})</td>
<td>(A_1)</td>
<td>4</td>
<td>(\nu(\text{U-F'}))</td>
<td>592.8(^b)</td>
<td>592.8(^b)</td>
</tr>
<tr>
<td>(E)</td>
<td>(A_1)</td>
<td>7</td>
<td>(\nu_{\text{asy}}(\text{UF}_4)) in plane scissoring</td>
<td>191.9(^a)</td>
<td>191.9(^b)</td>
</tr>
<tr>
<td>(B_2)</td>
<td>(A_1)</td>
<td>10</td>
<td>(\delta_{\text{asy}}(\text{UF}_4)) in plane</td>
<td>131.3(^b)</td>
<td>151.5(^b)</td>
</tr>
<tr>
<td>(F_{2u})</td>
<td>(B_1)</td>
<td>6</td>
<td>(\delta_{\text{asy}}(\text{UF}_4)) out of plane</td>
<td>92.3(^b)</td>
<td>106.5(^b)</td>
</tr>
<tr>
<td>(E)</td>
<td>(B_1)</td>
<td>11</td>
<td>(\delta(\text{UF}_4)) rocking</td>
<td>134.9(^b)</td>
<td>134.9(^b)</td>
</tr>
</tbody>
</table>

Computed frequency parameters (cm\(^{-1}\)) for activated complex:

\(< \nu > = 303.38 \quad 315.54\)

\(< \nu^2 > \frac{1}{2} = 360.90 \quad 371.46\)

\(\nu = 244.59 \quad 257.47\)

Table 4—Unimolecular dissociation data of uranium hexafluoride

<table>
<thead>
<tr>
<th>Energy in excess photon (E_{o}^* - E_{o})</th>
<th>Vibrational state density (N(E_{o}^*)/\text{cm}^{-1})</th>
<th>Total no. of vibrational states in activated complex (\Sigma P(E_{o}^*)) case II</th>
<th>Dissociation rate constant (K_i(E_{o}^*) s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>(6.2 \times 10^{14})</td>
<td>(1.8 \times 10^{3})</td>
<td>(9.5 \times 10^{3})</td>
</tr>
<tr>
<td>7</td>
<td>(1.1 \times 10^{15})</td>
<td>(4.2 \times 10^{5})</td>
<td>(1.18 \times 10^{5})</td>
</tr>
<tr>
<td>9</td>
<td>(1.85 \times 10^{15})</td>
<td>(4.4 \times 10^{9})</td>
<td>(8.50 \times 10^{5})</td>
</tr>
<tr>
<td>10</td>
<td>(2.54 \times 10^{15})</td>
<td>(1.6 \times 10^{10})</td>
<td>(1.98 \times 10^{6})</td>
</tr>
<tr>
<td>12</td>
<td>(4.28 \times 10^{15})</td>
<td>(1.13 \times 10^{11})</td>
<td>(8.47 \times 10^{6})</td>
</tr>
<tr>
<td>13</td>
<td>(5.56 \times 10^{15})</td>
<td>(2.82 \times 10^{11})</td>
<td>(1.60 \times 10^{7})</td>
</tr>
<tr>
<td>14</td>
<td>(7.15 \times 10^{15})</td>
<td>(6.53 \times 10^{11})</td>
<td>(2.37 \times 10^{7})</td>
</tr>
<tr>
<td>15</td>
<td>(9.17 \times 10^{15})</td>
<td>(1.44 \times 10^{12})</td>
<td>(4.94 \times 10^{7})</td>
</tr>
</tbody>
</table>

Competitive energy dynamics

The subject of multiple photon excitation of polyatomic molecules by intense IR laser radiation has received much attention over the past years. Following the qualitative picture of the process that has emerged out of numerous experimental and theoretical studies, it is clear that the complete quantum mechanical treatment is extremely complicated and impractical. Due to lack of structural information, i.e., potential surfaces on highly excited polyatomics, the exact nature and coupling strengths of these states are not known. Moreover, even if one is equipped with such information, it is impossible to solve for the dynamics of \(10^{10}\) states interacting with strong laser field. On the other hand, the information which is of real interest is much less detailed than the knowledge of the complete molecular states. In practice, one is interested only in a few molecular
observables and their time evolution on a coarse grained time scale which is much longer than the molecular frequencies, i.e., $10^{13} - 10^{14}$ s. The basic assumption is that, due to enormous complexity of the problem, energy is being randomized completely among all accessible molecular states and the reaction rates are then evaluated.

Presently, we have developed a reaction model on a rate-equation formalism that can be used to explain the experimental data. An energy grained master equation (EGME) is constructed using available spectroscopic, thermodynamic and kinetic properties of UF$_6$ which is solved numerically. The main emphasis of the present work is to show the application of the model to obtain the time evolution of multiple photon levels during the laser pulse and in turn find out the necessary molecular and laser parameters that have to be controlled for achieving reasonably good isotope-selective dissociation. It should be noted that extensive work on URIMIR (unimolecular reactions induced by monochromatic infrared radiation) type of calculation has been done to move forward from simple kinetic approach.

When a system in which molecules are distributed among a series of energy levels with a concentration $n_i$ in i-th energy level is considered, the process by which molecules enter or leave this energy level is shown in Fig. 2. Three processes are included: (i) absorption and emission of laser photons with cross section for optical transition $j \rightarrow i$, $\sigma_{ji}$; (ii) collisional energy transfer; governed by the gas kinetic collision rate constant $\omega$ and collisional transition probability for $j \rightarrow i$, $P_{ji}$; and (iii) dissociation with rate constant $K_i$. The rate equation is given by:

$$\frac{dn_j}{dt} = r_L \sigma_{ji} n_i - r_n n_j + \omega \Sigma n_k - \omega n_j - K_i n_i \quad \ldots \quad (11)$$

where $r$ is laser intensity divided by energy difference between levels $j$ and $i$; and $\sigma_{ji}$ is the emission cross section for the reverse transition $j \rightarrow i$. The dissociation with rate constant $K_i$ can be calculated from RRKM treatment. For levels below the dissociation threshold $E_0$, rate constant $K_i = 0$.

Laser excitation being stochastic process, quickly distributes the population over many levels and one can get the time evolution of multiphoton levels during the exciting laser pulse (Fig. 3). As time proceeds, the population is continuously pumped up in the energy domain and distribution curve shifts towards higher energies. At moderate level of excitation in the dissociative manifold, unimolecular dissociation successfully competes with further pumping and the excitation process becomes life time limited. In general, it has been found that higher laser fluxes will populate higher and higher quantum states in polyatomic molecules within a limited energy spread.
The fluence dependence of dissociation yield has been measured experimentally and it was found that MPD of UF₆ occurs with a threshold of 1-1.2 J cm⁻². In the present model, the dissociation yield is obtained as the fraction of the molecular ensemble which cross the dissociation threshold. Using the rate equation model, the threshold fluence and the dissociation yield were evaluated and they agreed well with the experimental dissociation data of 1 Torr UF₆ as shown in Fig. 4.

![Graph showing fluence dependent dissociation yield of UF₆ at various pressures estimated from rate equation model](image)

**Fig. 4**—Fluence dependent dissociation yield of UF₆ at various pressures estimated from rate equation model (*points are taken from work on decomposition of 1 Torr UF₆ using 16 μm CF₄ laser of ref [26].

Isotopic selectivity in this model is prescribed as the difference in the rate of laser energy absorption for the two isotopic species. Once the selectivity is introduced in the excitation process, it should be maintained provided there is no or minimum collisional deactivation. From the point of view of isotopic selectivity, two parameters, which are of interest, are: (i) what should be the optimum level of energization for UF₆ molecule to dissociate with minimum collisional energy exchange and (ii) what laser fluences are required to achieve this energization. Considering various time scales involving excitation, collisional deactivation and life time of energized 235-UF₆ molecule, the extent of selectivity loss has been estimated. The mean collisional time for 235-UF₆ collisions in 1 Torr natural UF₆ is about 285 ns. The random life time for an energized UF₆ molecule at 15 excess photons is about 10-20 ns. Therefore, within a typical laser pulse of 200 ns with a fluence of about 5-10 J cm⁻², we can expect about 10% loss of 235-UF₆ excited at 13 - 15 excess photons i.e., about a total of 50 laser photons per molecule. Figure 5 shows the lifetimes of the energized molecule and % loss of selectivity as a function of excess energy content of UF₆ molecule.

![Graph showing lifetime of the energized molecule and selectivity loss as a function of excess energy content of UF₆ molecule](image)

**Fig. 5**—Lifetime of the energized molecule and selectivity loss as a function of excess energy content of UF₆ molecule.

**Conclusion**

The photochemical isotope separation schemes have renewed the detailed investigations of gas phase photophysics and photochemistry of UF₆. One attractive scheme involves massive multiphoton excitation of UF₆ using one or more suitable IR laser frequency (16 μm) in its ground electronic state to unimolecularly dissociate. In the present work we have modeled such IRMPD on a rate equation formalism. It includes three processes: (i) absorption and emission of laser photons, (ii) collisional energy transfer and (iii) dissociation. An energy grained master equation is constructed using available spectroscopic, thermodynamic and kinetic properties of UF₆ which is solved numerically.

Important findings can be summarized as follows: Laser excitation being stochastic process, quickly distributes the population over many levels and one can get the time evolution of multiphoton levels during the exciting laser pulse. Using RRKM theory, the multiphoton dissociation rate constants for UF₆ with 16 μm laser has been estimated. It is shown that about 50 laser photons, which is 15 photons excess over the dissociation threshold of 3 eV, are required...
for dissociation of each UF₆ molecule. Fluence
dependence of dissociation yield has been evaluated
and it is found that MPD of UF₆ occurs with a
threshold fluence of 1 - 1.2 J cm⁻². Considering
various time scales involving excitation, collisional
deactivation and life time of energized 235-UF₆
molecule, the extent of selectivity loss has been
estimated.

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