

## **Infrared multiphoton induced chemistry : competitive energy dynamics of excitation and dissociation in SF<sub>6</sub>**

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### **1. Introduction**

The dissociation of polyatomic molecules by intense resonantly absorbed IR laser radiation has been the subject of much recent study, particularly since the phenomenon was identified to be isotopically selective (Letokhov 1976, Aldridge 1976). Though several understandings have been brought forward concerning the mechanisms of this multiphoton dissociation (Bloembergen 1975, Letokhov 1976), these do not yet permit either quantitative interpretation or prediction.

The isotopically selective dissociation of SF<sub>6</sub> was reported in 1975 (Ambertzunian 1975). The choice of SF<sub>6</sub> is based on a number of its advantageous features. SF<sub>6</sub> is very stable upto 1500°K. The dissociation by IR laser appears to be almost irreversible. Only two isotopic species <sup>32</sup>SF<sub>6</sub> (95.0%) and <sup>34</sup>SF<sub>6</sub> (4.2%) exist and isotopic shift of 17 cm<sup>-1</sup> ( $\nu_3$  fundamental of <sup>32</sup>SF<sub>6</sub>: 947 cm<sup>-1</sup> and that of <sup>34</sup>SF<sub>6</sub>: 930 cm<sup>-1</sup>) is convenient to work with CO<sub>2</sub> laser.

The work reported here was intended primarily to identify the role of simple collisional partner with the vibrationally excited SF<sub>6</sub> molecules. The unimolecular dissociation rate constant was calculated using RRKM rate theory. Evaluation of rate constant using detailed RRKM computation was made. It was found that the multiphoton results and lifetime were consistent with a statistical model for the unimolecular decomposition of SF<sub>6</sub> with an assumed energisation of 8-9 photons (22 KCal mole<sup>-1</sup>) above the dissociation threshold.

### **2. Theory**

The gas mixture of interest is placed in a closed absorption cell having entrance and exit windows for the reaction. To achieve high intensity, the laser pulse

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is focussed so that the waist of the beam is within the gas volume. This mode of irradiation is necessary because interesting multiphoton phenomenon occurs at radiation fluxes which are above the damage threshold of the windows. In order to obtain a decomposition yield which can be measured accurately, it is necessary to irradiate the target gas with a sequence of laser pulses. After this, either the number of molecules which have decomposed or relative abundances of isotopic species or both are determined by one means or other.

The region where the laser 'fluence' (energy/area) is strong enough to produce dissociation occupies a small volume near the mirror's focus. The reaction volume,  $V_R$ , is a small fraction of the total cell volume  $V_T$ . The no. of  $SF_6$  molecules,  $N_1$ , remained after one pulse is given by :

$$N_1 = N_0[1 - V_R/V_T] \quad (1)$$

where  $(V_R/V_T)$  is the fraction that decomposes and  $N_0$  is the initial no. of molecules. Hence for 'n' no. of pulses :

$$N_n = N_0[1 - V_R/V_T]^n$$

which can be written as :

$$N_n = N_0 \exp \left[ - \frac{V_R}{V_T} \right] n \quad (2)$$

because  $[V_R/V_T]$  is very small. The ratio  $(V_R/V_T)$  termed as "decomposition Co-efficient per pulse" is denoted by ' $\alpha$ '.

To relate the reaction volume  $V_R$  to a threshold fluence it is necessary to calculate the volume of an 'isofluence surface' in a region near focus. Assuming the laser pulse as gaussian beam and using the so called 'dog-bone' geometry of irradiation (Figure 1) (Keefer 1976), the threshold fluence is related to reaction volume by equation (3)

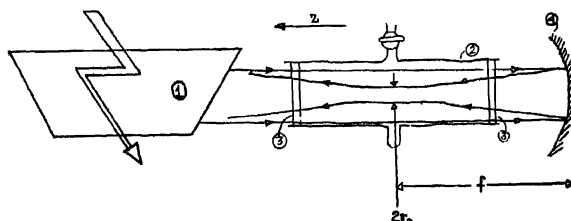
$$\phi_R = \left[ \frac{8}{9} \pi^{\frac{1}{2}} \right]^{2/3} \cdot \phi [f/V_R]^{2/3} \quad (3)$$

Hence, the reaction volume  $V_R$  increases linearly with the  $f$ /number and with the 3/2 power of total laser energy per pulse.

### 3. Experimental

A series of experiments were performed to determine the threshold fluence for the neat  $SF_6$  decomposition. Then oxygen was used as a quencher at different pressures. The  $CO_2$  laser used was helical one and delivered 250 mJ per pulse. The laser cavity was not tuned and therefore emitted on the highest gain line, the  $P(20)$  line which was confirmed by analysing the output beam by spectrum

analyser (Optical Engg. Inc). Each pulse consisted of an initial intense pulse of about 200 ns followed by a long less intense tail upto few  $\mu$ S.



**Figure 1.** Schematic diagram of experimental set up  
 (1) TEA—CO<sub>2</sub> laser (2) Pyrex Cell (3) KCl-windows (4) Gold-coated concave mirror  
 $2r_0$  = laser spot size at the beam-waist  
 $f$  = focal length of the mirror

A pyrex glass cell (80 mm long by 50 mm dia.) fitted with polished KCl windows was filled with 0.33 torr of SF<sub>6</sub> and the laser pulse was focussed in the middle of the cell by a gold coated concave mirror of focal length 10 cm. The SF<sub>6</sub> was used without further purification (Union Carbide Corp., Linde Divn 99% pure). Typically 1000 shots were given to each mixture at a rate of 25 ppm. The amount of SF<sub>6</sub> decomposed in an experiment was determined from IR-spectrum taken before and after irradiation using Perkin Elmer 577 Grating IR Spectrometer.

#### 4. Results

The decomposition Co-efficient per pulse ' $\alpha$ ' is calculated for neat SF<sub>6</sub> and SF<sub>6</sub>/O<sub>2</sub> mixtures at fixed SF<sub>6</sub> partial pressure, by measuring the absorbance of SF<sub>6</sub> at 947 cm<sup>-1</sup> before and after irradiation from equation (2) we have :

$$\alpha = \frac{1}{n} \ln \frac{N_0}{N_n} = \frac{1}{n} \ln \frac{A_0}{A_n}$$

where

$A_0$  = absorbance before irradiation and

$A_n$  = absorbance after irradiation by  $n$  (= 1000) pulses.

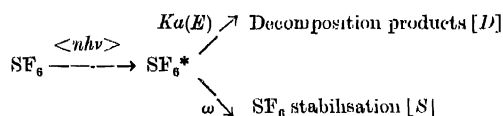
From results given in table 1, it is clear that ' $\alpha$ ' increases with lowering pressure of O<sub>2</sub> and a 'plateau' is obtained, as the pressure of O<sub>2</sub> approached zero.;

Threshold fluence using equation (3) for  $f$ /number 10, found to be 4.4 J/cm<sup>2</sup> which when translated with respect to pulse width of 200 ns gave 22 MW/cm<sup>2</sup> as threshold intensity for neat SF<sub>6</sub> decomposition.

Table 1. Variation of  $\alpha$  with  $O_2$ -pressure [Pressure of  $SF_6=0.33$  torr]

Press of $O_2$ (torr)	$\alpha \times 10^4$	$[\alpha_{SF_6}/\alpha_{SF_6-O_2}]$
0	4.6	—
0.10	4.43	1.038
0.25	4.42	1.04
0.58	4.34	1.06
1.00	3.66	1.25
2.00	3.03	1.52
5.00	2.15	2.14
10.00	1.28	3.59
47.00	0.40	11.5

From the unimolecular rate theory the process can be visualised as follows :



According to this scheme, energized molecule  $SF_6^*$  at energy  $E$  can form decomposition products with a rate constant  $Ka(E)$  or be deenergized to stable molecules. On the strong collision assumption, the first order rate constant for deenergisation is equal to the collision frequency  $\omega = K(\text{collision}) \times P_{O_2}$  where  $P_{O_2}$  = Oxygen pressure and  $K(\text{collision})$  is given by

$$K(\text{collision}) = \sigma_{SF_6/O_2}^2 \left[ \frac{8\pi RT}{\mu_{SF_6/O_2}} \right]^{1/2} \quad (4)$$

where collision diameter  $\sigma = 4.5$  Å corresponding to Lennard Jones hard Sphere Collision diameters and  $\mu =$  reduced mass of  $SF_6/O_2 = 26.25$  gm mol<sup>-1</sup>. Let the fraction of molecules which are energised per unit time into the energy range between  $E$  and  $E+dE$  is  $f(E)dE$ . The fraction of  $SF_6^*$  decomposing by path  $D$  compared with those stabilised by path  $S$  is  $Ka(E)/[Ka(E)+\omega]$

Hence the fraction of molecules in the energy range  $E$  to  $E+dE$  decomposing to products is therefore  $\{Ka(E)/[Ka(E)+\omega]\{f(E)dE\}$ . The total number of molecules decomposing per unit time  $D$ , at all energies above the critical energy  $E_0$ , is given by

$$D = \int_{E_0}^{\infty} \frac{Ka(E)}{[Ka(E)+\omega]} f(E)dE. \quad (5)$$

The total rate of stabilisation,  $S$ , is given by a similar integral with  $Ka(E)$  in the numerator replaced by  $\omega$ .

In a strictly monoenergetic system the experimental ratio  $D/S$  is equal to  $Ka/\omega$ . Where there is a distribution of energies, an average rate constant  $\langle Ka \rangle$  for all energies above  $E_0$  is similarly defined by (6)

$$\frac{\langle Ka \rangle}{\omega} = \frac{D}{S} = \frac{\text{No. of molecules decomposing per unit time}}{\text{No. of molecules being stabilised per unit time}} \quad (6)$$

Utilising equation (5) and equivalent expression for stabilisation, the result is obtained for  $\langle Ka \rangle$ .

$$\langle Ka \rangle = \omega \times \frac{\int_{E_0}^{\infty} \{Ka(E)/[Ka(E)+\omega]\}f(E)dE}{\int_{E_0}^{\infty} \{\omega/[Ka(E)+\omega]\}f(E)dE} \quad (7)$$

At high pressure  $\omega \gg Ka(E)$ , the average rate constant becomes

$$\langle Ka \rangle_{\infty} \approx \langle Ka(E) \rangle. \quad (8)$$

Similarly, at low pressure  $\omega \ll Ka(E)$  and corresponding rate constant is given by

$$\langle Ka \rangle_0 \approx \langle 1/Ka(E) \rangle^{-1} \quad (9)$$

If the vibrationally excited  $SF_6$  molecules are produced in virtually monoenergetic manner, the ratio  $\langle Ka \rangle_{\infty}/\langle Ka \rangle_0$  will approximate unity. If there is a spread of energies, the less excited molecules contribute more heavily towards (9) so that  $\langle Ka \rangle$  falls as the pressure is reduced and  $\langle Ka \rangle_{\infty}/\langle Ka \rangle_0 > 1$ . The ratio is therefore a measure of the spread in energies of the  $SF_6^*$  species and may be related to energy distribution function  $f(E)$ .

The above treatment can be applied to the experimental results. The decomposed and stabilised fractions of the multiphoton excited  $SF_6$  at different  $O_2$ -pressures are evaluated in the following manner. In the absence of  $O_2$ , all the m.p. excited volume  $V_{exc}$  is assumed to decompose i.e.  $V_{exc} = [(V_R)_{O_2=0}]$ . For the same laser irradiation conditions, the excitation volume  $V_{exc}$  remains the same for neat  $SF_6$  and  $SF_6/O_2$  mixtures, but the reaction volume  $V_R$  for the latter decreases, as reflected in the lowering of ' $\alpha$ '-values with increasing  $O_2$ -pressure. Taking  $V_R$  as measure of the net decomposition  $D$  and  $[V_{exc} - V_R]$  as measure of stabilization ' $S$ ' the average rate constants  $\langle Ka \rangle$  are tabulated in table 2 using equation (6):

$$\frac{\langle Ka \rangle}{\omega} = \frac{D}{S} = \frac{V_R}{[V_{exc} - V_R]} = \frac{\alpha_{SF_6/O_2}}{|\alpha_{SF_6} - \alpha_{SF_6/O_2}|}$$

From the plot of  $\langle Ka \rangle$  Vs  $PO_2$  (Figure 2) it is found that  $\langle Ka \rangle$  is independent of oxygen pressure which indicated the multiphoton excitation provided to  $SF_6$  is essentially monoenergetic in nature, and yields an average rate constant  $3.9 \times 10^7 \text{ sec}^{-1}$ .

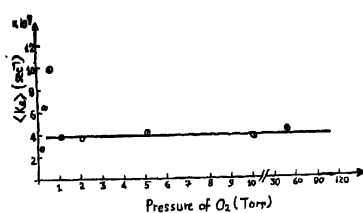


Figure 2. Plot of  $\langle Ka \rangle$  with pressure of  $O_2$ . The value of  $\langle Ka \rangle / \langle Ka \rangle_0$  of unity is indicated by the straight line

Table 2. Evaluation of dissociation rate constants  $\langle Ka \rangle$

$PO_2(\text{torr})$	$[D/s]$	$\omega_{O_2}(\text{Sec}^{-2})$	$\langle Ka \rangle (\text{Sec}^{-1})$
0.10	4.43/0.17	$1.01 \times 10^6$	$2.63 \times 10^7$
0.25	4.42/0.18	$2.52 \times 10^6$	$6.21 \times 10^7$
0.58	4.34/0.26	$5.86 \times 10^6$	$9.78 \times 10^7$
1.00	3.66/0.94	$1.01 \times 10^7$	$3.93 \times 10^7$
2.00	3.03/1.67	$2.02 \times 10^7$	$3.89 \times 10^7$
5.00	2.15/2.45	$5.05 \times 10^7$	$4.43 \times 10^7$
10.00	1.28/3.32	$1.01 \times 10^8$	$3.89 \times 10^7$
47.00	0.4/4.2	$4.74 \times 10^8$	$4.52 \times 10^7$

### 5. Evaluation of $Ka$ using RRKM theory

Using RRKM unimolecular reaction rate theory the correlation between rate constant and the energy excess in terms of photons above the dissociation threshold can be made.

The unimolecular rate constant, for molecules with energy  $Ev^*$ ,  $Ka(Ev^*)$  is given by (Robinson 1972)

$$Ka(Ev^*) = L^{\ddagger} \cdot \frac{Q_1^{\ddagger}}{Q_1} \cdot \frac{1}{hN^*(Ev^*)} \sum_{E_v^{\ddagger}=0}^{E_v^*} P(E_v^{\ddagger}) \quad (10)$$

The superscript asterisk designated an energised molecule that is, one that has sufficient energy for unimolecular reaction to occur. The function  $Ka(Ev^*)$  is

derived by calculating from statistical considerations the rate at which energised molecules (\*) pass through an activated complex (†). The internal energy of the activated complex is defined as :

$$E_{v^\ddagger} = E_{v^*} - E_0 \quad (11)$$

where  $E_0$  = Energy barrier between reactants and products. It will be assumed that  $E_0$  is just the bond strength of S-F bond (Benson 1978) = 90 KCal/mole. Other parameters of equation (10) are as follows :

$L^\ddagger$  = Statistical factor or the no. of equivalent paths for the reaction which is 6 for  $\text{SF}_6$  dissociation.

$Q_1^\ddagger$  and  $Q_1$  = Rotational partition functions for activated complex and undistorted molecules respectively. These partition functions were calculated by assuming that the activated complex was obtained from  $\text{SF}_6$  by doubling one S-F bond which gives  $Q_1^\ddagger/Q_1 = 1.75$

$N^*(E_{v^*})$  = The density of vibrational states of  $E_{v^*}$  which is given by :

$$N^*(E_{v^*}) = \frac{(E_{v^*} + aE_z)^{S-1}}{(S-1)! \prod_{i=1}^S h\nu_i} \left[ 1 - \beta \frac{dW(E')}{dE'} \right] \quad (12)$$

where  $\nu_i$  = set of fundamental vibrational frequencies

$E_z$  = total zero point vib. energy for all 'S' normal modes of the molecule.

=  $\frac{1}{2} \sum_{i=1}^S h\nu_i$  where  $S = 15$  for  $\text{SF}_6$

$a$  = Empirical parameter chosen to give best approximation to the direct count method.  $a$  can have a value between zero and unity. When  $a$  is plotted against 'reduced energy'  $E' = E_{v^*}/E_z$ , it approaches unity at higher energies and values for different molecule lie in a fairly narrow band. The position in this band of the curve for a molecule is found empirically to depend only on the distribution of molecular vibration frequencies. The dispersion of frequencies can be measured by ' $\beta$ ' which is known as 'modified frequency dispersion parameter' and is given by  $\beta = \frac{(S-1)}{S} \frac{\langle \nu^2 \rangle}{\langle \nu \rangle^2}$  in which  $\langle \nu \rangle$  and  $\langle \nu^2 \rangle$  are the mean and mean square frequencies of the molecule. A simple analytical relationship between  $a$ ,  $\beta$  and  $E'$  was achieved by the expression  $a = 1 - \beta W(E')$  where  $W(E')$  is a unique function of  $E'$  and described adequately by .

$$\begin{aligned} W &= (5.00E' + 2.73E'^{0.6} + 3.51)^{-1} \text{ for } 0.1 < E' < 1.0 \\ &= \exp[-2.4191E'^{0.25}] \text{ for } E' > 1.0. \end{aligned} \quad (13)$$

The above treatment known as 'Whitten-Rabinovitch' approximation gives the vibrational state density,  $N^*(E\nu^*)$  as a function of  $E\nu^*$

$P(E\nu^\dagger)$  = no. of vibrational quantum states in the activated complex at energy  $E\nu^\dagger$ . And the sum  $\sum_{E\nu^\dagger=0}^{E\nu^\dagger} P(E\nu^\dagger)$  is the total no. of vibrational states in the activated complex upto  $E\nu^\dagger$  which is given by similar expression :

$$\sum_{E\nu^\dagger=0}^{E\nu^\dagger} P(E\nu^\dagger) = \frac{(E\nu^\dagger + aE_2^\dagger)^S}{S! \prod_{i=1}^S h\nu_i^\dagger} \quad (14)$$

For  $SF_6^\ddagger$ , the no. of normal modes ' $S$ ' becomes 14 since one mode becomes the reaction coordinate. The vibrational frequencies of the  $SF_6^\ddagger$  the activated complex, were determined by first dividing the frequencies into two categories : those most affected by extending one S-F bond and those least affected by extending the bond (Lyman 1977). As one bond is extended the symmetry point group changes from  $O_h$  to  $C_{3v}$ , which is the same as for the molecule  $SF_6Cl$ . In this paper, the frequencies most influenced by bond extension were taken to be 0.60 times the corresponding frequency in  $SF_6$  and those least affected to be 0.90 times that of  $SF_6$ .

The fundamental vibrational frequencies for  $SF_6$  and  $SF_6^\ddagger$  are given in tables (3) and (4).

**Table 3.**  $SF_6(O_h$  point group) fundamental vibrational frequencies [Mc Dowell 1976]

$i$	$\Gamma_i$	$\nu_i(\text{cm}^{-1})$
1	$A_{1g}$	774
2	$E_g$	642 $\langle \nu \rangle = 623.0 \text{ cm}^{-1}$
3	$F_{1u}$	948 $\langle \nu^2 \rangle^{1/2} = 654.9 \text{ cm}^{-1}$
4	$F_{1g}$	615 $\tilde{\nu} = 591.0 \text{ cm}^{-1}$
5	$F_{2g}$	523
6	$F_{2u}$	346

Table 5 was given for vibrational state density  $N^*(E\nu^*)$ , the  $\sum_{E\nu^\dagger=0}^{E\nu^\dagger} P(E\nu^\dagger)$  and rate constant  $Ka(E\nu^*)$  for no. excess photon 4-10. The experimental life-time of 25 ns which corresponds to theoretical estimate of energy excess  $[E\nu^* - E_0]$  in excess photons between 8 and 9 which is consistent with statistical model of RRKM theory.



**Table 4.** Activated complex (SF<sub>6</sub>†) fundamental vibrational frequencies

$\Gamma_{SF_6}$	$\Gamma_{SF_6^\ddagger}$	$\nu$	$\nu_i^\ddagger$ (cm <sup>-1</sup> )
A <sub>1g</sub>	A <sub>1</sub>	2	696.6 <sup>a</sup>
E <sub>g</sub>	A <sub>1</sub>	3	385.2 <sup>b</sup> <math>\langle \nu^+ \rangle = 407.9 \text{ cm}^{-1}</math>
	B <sub>1</sub>	5	577.8 <sup>a</sup> <math>\langle \nu^{12} \rangle^\ddagger = 535.54 \text{ cm}^{-1}</math>
F <sub>1u</sub>	A <sub>1</sub>	1	568.8 <sup>b</sup>
	E	8	853.2 <sup>a</sup> <math>\bar{\nu}^\ddagger = 458.87 \text{ cm}^{-1}</math>
F <sub>1u</sub>	A <sub>1</sub>	4	Reaction coordinate
	E	9	553.5 <sup>a</sup>
F <sub>2g</sub>	B <sub>2</sub>	7	470.7 <sup>a</sup>
	E	10	313.8 <sup>b</sup>
F <sub>2u</sub>	B <sub>1</sub>	6	207.6 <sup>b</sup>
	E	11	311.4 <sup>a</sup>

a  $\nu(SF_6) \times 0.90$  see table 3b  $\nu(SF_6) \times 0.60$ **Table 5.** RRKM Unimolecular rate constants and lifetimes

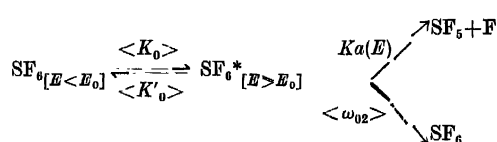
Energy [E <sub>v</sub> * - E <sub>0</sub> ] in excess photons	N*(E <sub>v</sub> *)	$\frac{E_{v,\ddagger}}{\sum_{E_{v,\ddagger}=0} p(E_{v,\ddagger})}$	Ka(E <sub>v</sub> *)(sec <sup>-1</sup> )	τ(ns)
4	7.91 × 10 <sup>11</sup>	3.81 × 10 <sup>5</sup>	1.52 × 10 <sup>5</sup>	6578
5	1.09 × 10 <sup>12</sup>	2.445 × 10 <sup>6</sup>	7.065 × 10 <sup>5</sup>	1415
6	1.51 × 10 <sup>12</sup>	1.24 × 10 <sup>7</sup>	2.58 × 10 <sup>6</sup>	387
7	2.07 × 10 <sup>12</sup>	5.27 × 10 <sup>7</sup>	8.02 × 10 <sup>6</sup>	124
8	2.81 × 10 <sup>12</sup>	1.942 × 10 <sup>8</sup>	2.177 × 10 <sup>7</sup>	46
9	3.799 × 10 <sup>12</sup>	6.374 × 10 <sup>8</sup>	5.28 × 10 <sup>7</sup>	19
10	5.095 × 10 <sup>12</sup>	1.903 × 10 <sup>9</sup>	1.176 × 10 <sup>8</sup>	8.5

## 6. Discussions

Quite a few models have been proposed for multiphoton excitation and dissociation. The following possible mechanisms to overcome anharmonic detuning at several successive transitions of the excited vibrational mode have been considered in previous works: (a) power broadening (Bloembergen 1975, Akulin 1975), (b) rotational anharmonicity compensation (Ambartzmian 1976) and (c) multiphoton transitions (Bloembergen 1976, Larsen 1976). Treating multiphoton excitation process as a series of incoherent one photon transitions among a set

of equally spaced energy levels, a few authors (Grant 1978, Lyman 1977, Quack 1978) have gained an insight into time evolution of the multiphoton levels during the laser pulse. More recently, correlations with collisional deactivation by various gases are being attempted (Bado 1978).

In this paper, we have followed a simple two level system for preliminary analysis of our collisional results with oxygen. Although the laser excitation process may go through various levels, all energy levels below the activation energy,  $E_0 = 90$  KCal/mole, are treated as unexcited  $SF_6$ , and all higher energy levels which can contribute to decomposition as essentially a monoenergetic level  $SF_6^*$ . Although very coarse and approximate, this simplified treatment may give a mean excitation rate and a mean decomposition rate.



With this scheme, the rate equations are

$$\frac{d[SF_6^*]}{dt} = K_0[SF_6] - [K_0' + \omega_{02} + K_a(E)][SF_6^*] \tag{15}$$

$$\frac{d[SF_6]}{dt} = -K_a[SF_6] + (K_0' + \omega_{02})[SF_6^*]. \tag{16}$$

The fraction dissociated during the laser pulse  $\tau$  is given by

$$\left[ \frac{D}{D+S} \right] = \frac{K_0 K_a(E)}{(m_2 - m_1)} \left[ \frac{1}{m_1} (1 - e^{-m_1 \tau}) - \frac{1}{m_2} (1 - e^{-m_2 \tau}) \right] \tag{17}$$

where

$$m_{1,2} = \frac{1}{2} \{ [K_0 + K_0' + \omega_{02} + K_a(E)] \mp \sqrt{[K_0 + K_0' + \omega_{02} + K_a(E)]^2 - 4K_0 K_a(E)} \}$$

when  $m_2 \gg m_1$  and  $[K_0 + K_0' + \omega_{02} + K_a(E)]^2 \gg 4K_0 K_a(E)$ .

$$\left[ \frac{D}{D+S} \right] = [1 - e^{-m_1 \tau}] \tag{18}$$

and

$$m_1 \equiv \frac{K_0 K_a}{K_0 + K_0' + \omega_{02} + K_a} \tag{19}$$

From experimental values of  $[D/(D+S)]$ ,  $m_1$ 's have been evaluated using equation (18). A plot of  $[m_1^{-1}]V_sP_0$  was found to be linear (cf. Figure 3) for  $P_{O_2} > 1$  torr

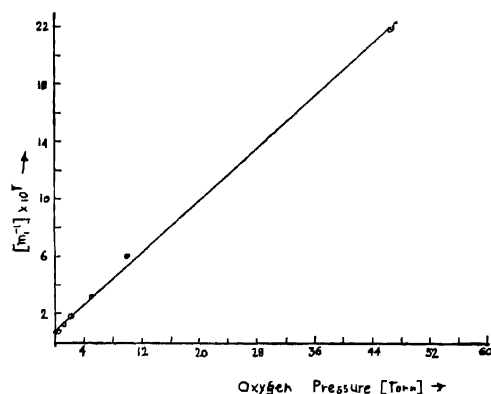


Figure 3. Plot of  $[m_1^{-1}]$  with pressure of  $O_2$ . From the slope and intercept of the plot, the value of  $\langle K_0 \rangle$  or  $\langle Ka \rangle$  was found to be at least  $1.05 \times 10^7$

where the above approximation appears to be valid. From the intercept of the plot and using equation (19) we obtain :

$$\frac{K_0 + K_0' + Ka}{K_0 Ka} = 0.95 \times 10^{-7}$$

Which can be cast as :

$$K_0 = 1.05 \times 10^7 \left[ 1 + \frac{K_0'}{Ka} + \frac{K_0}{Ka} \right] \text{ and similarly for } Ka.$$

Depending on the relative values of  $K_0$ ,  $Ka$  and  $K_0'$ , the actual values of  $K_0$  and  $Ka$  can be found out. But from the above relation, we obtain  $K_0$  and  $Ka > 1.05 \times 10^7$ .

$K_a$  value self consistent with the earlier section is about  $4 \times 10^7$  indicating that the laser excitation gives some 7 to 9 photon excess. Since the mean excitation rate,  $K_0$  is  $\sim 1 \times 10^7$ , a mean excitation cross section is evaluated to be  $1 \times 10^{-20} \text{ cm}^2$  for our threshold laser flux of  $4.4 \text{ J cm}^{-2}$  in the irradiated zone. Such value, although obtained by an approximate treatment, is consistent with a cross section value of  $\sim 10^{-20}$  for this level obtained by Grant (Grant 1978).

The collisional deactivation from such a level as 8 photon excess does not, however, imply a large energy transfer in collisions with oxygen. What is implied in this model is that even limited energy transfer will bring the molecule to a lower photon level, the dissociation rate of which is too small to contribute. (Vide Table 5).

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