LIFETIMES OF ELECTRONICALLY EXCITED UF$_6$ IN THE PRESENCE OF INORGANIC QUENCHERS

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Summary

UF$_6$ was excited at 3935 Å by a nitrogen-laser-pumped dye laser and the lifetimes of *UF$_6$ were determined in the presence of selected inorganic gases. The following low pressure quenching rate constants (units of 10^{11} l mol^{-1} s^{-1}) were determined: oxygen, 1.0; helium, 0.0095; argon, 0.0097; hydrogen, 0.013; CO, 0.024; fluorine, 0.016; nitrogen, 0.018; SF$_6$, 0.015. All the gases except oxygen at high pressures give *UF$_6$ lifetimes much longer than those calculated from the low pressure rate constants. The lifetime behavior at high pressures is consistent with a mathematical formulation which predicts that the zero pressure value derived from a high pressure asymptotic extrapolation is independent of the chemical identity of the quenching gas.

1. Introduction

The dynamics and spectroscopy of UF$_6$ excited within the A-band, hereafter denoted *UF$_6$, have been the subject of several recent studies [1 - 11]. The dynamics of *UF$_6$ in UF$_6$ have proved to be rather complicated and have marked deviations from a linear Stern–Volmer behavior at high pressures [4, 5]. At high pressures the lifetimes are longer than those predicted from the low pressure Stern–Volmer rate constants. Similar deviations from a linear Stern–Volmer relation have been observed experimentally in the intermediate molecule SO$_2$ [12, 13]. Rudolph and Stricker [12] and Su *et al.* [13] fit these results to a mathematical formulation based on Freed's recent paper [14] on the saturation at high pressures of collisionally induced intersystem crossings. We were interested in investigating the dynamics of *UF$_6$ with various inorganics to see whether these quenchers produce a saturation of lifetimes (via physical quenching) and to examine the possibility of any rapid chemical quenching reactions. We report here our findings with regard to these items of interest.

2. Experimental

The vacuum system is constructed primarily of aluminum, Monel metal and nickel. Pressure is monitored with various MKS Baratron pressure sensors. The UF_6 is excited at 3935 Å with a Molectron nitrogen-laser-pumped dye laser operating with Pilot "386" dye. Its bandwidth is approximately 0.15 Å with the grating-output mirror cavity employed and its wavelength is determined with a Spex 1 m monochromator. The laser beam enters and leaves the fluorescence cell through Suprasil windows. The emission is viewed perpendicular to the laser beam through a dielectric interference filter with a central wavelength of 4225 Å and a full width at half maximum of 200 Å. It is detected by an RCA C31034 photomultiplier tube which is followed by a Pacific Photometric Model 2A44 preamplifier. The resultant signal is displayed on a Tektronix 7844 oscilloscope where about 20 - 80 shots are photographically superimposed. The observed decays were exponential for our experimental conditions.

Fluorine, helium, argon, hydrogen, nitrogen, SF_6 and CO were obtained commercially. SF_6 was 99.6% pure and the other gases were at least 99.99% pure. UF_6 was supplied in-house and was properly handled to render it free of contaminants.

3. Results

Stern–Volmer plots of the oxygen and helium data are shown in Fig. 1. The pressure of UF_6 is 3.00 Torr in all the quenching data reported in this study. Note how effective oxygen is in quenching $^*UF_6$ relative to helium. Figures 2 - 4 give Stern–Volmer plots for the quenchers hydrogen, argon, CO, fluorine, nitrogen and SF_6. These quenchers are all relatively ineffective compared with oxygen. The striking feature is the pronounced non-linear behavior shown in these figures. The helium data also show this non-
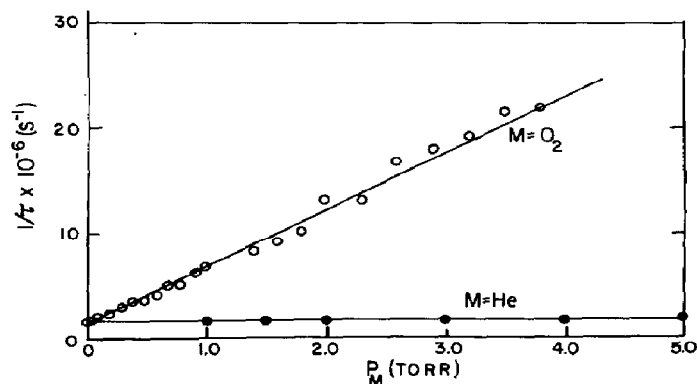

Fig. 1. Stern–Volmer plots for oxygen (open circles) and helium (solid circles): P_{UF_6} = 3.00 Torr; excitation λ = 3935 Å.
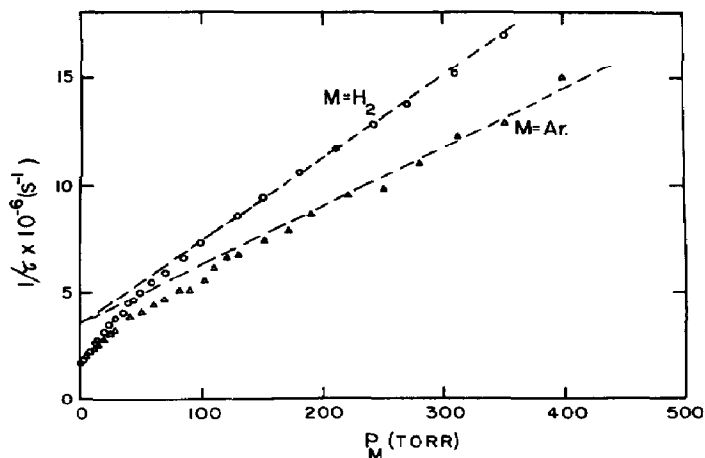
Fig. 2. Stern–Volmer plots of hydrogen (circles) and argon (triangles): P_{UF_6} = 3.00 Torr; excitation λ = 3935 Å. The broken lines represent the high pressure asymptotic fit. The convergence for hydrogen and argon at P_M = 0 should be noted.
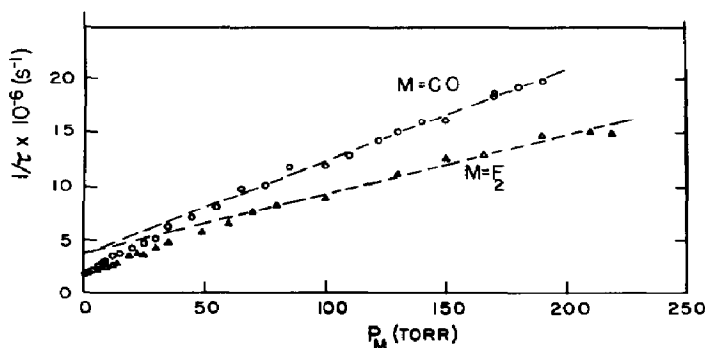

Fig. 3. Stern–Volmer plots for CO (circles) and fluorine (triangles): P_{UF_6} = 3.00 Torr; excitation λ = 3935 Å. The broken lines represent the high pressure asymptotic fit. The convergence for CO and fluorine at P_M = 0 should be noted.

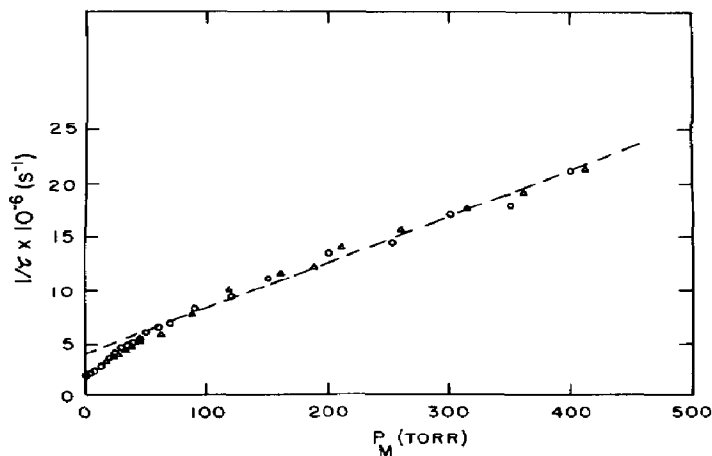
Fig. 4. Stern–Volmer plots for nitrogen (circles) and SF_6 (triangles): P_{UF_6} = 3.00 Torr; excitation λ = 3935 Å. The broken line represents the high pressure asymptotic fit. Both nitrogen and SF_6 share the same asymptotic line.

linearity, although the plot in Fig. 1 does not go to sufficiently high pressures to display it.

All the Stern–Volmer plots are linear at low pressures. The rate constants derived from the slopes of the low pressure linear regions are listed in Table 1. In Figs. 2 - 4 many low pressure points were omitted for the sake of clarity in display, but all the data were utilized in determining the slopes. The broken lines in Figs. 2 - 4 are the asymptotes of the high pressure data. The rate constants derived from the slopes of these lines are also tabulated in Table 1.

TABLE 1

Rate constants at 25 °C for quenching of $^*UF_6$ by various quenchers M^a

M	Rate constants (10^{11} l mol^{-1} s^{-1})	
	Low pressure region ($k_M^c + k_M^P$)	High pressure asymptote (k_M^c)
O_2	1.0	—
He	0.0095	0.0044
Ar	0.0097	0.0041
H_2	0.013	0.0073
CO	0.024	0.016
F_2	0.016	0.010
N_2	0.018	0.0080
SF_6	0.015	0.0080

^{a}Excitation λ = 3935 Å and $P(UF_6)$ = 3.00 Torr for the quenching experiments.

4. Discussion

Let us first examine the quenching data for oxygen. Oxygen did not show any saturation effects; however, the maximum pressure of oxygen added was only 3.8 Torr. No additional oxygen was added since we could not experimentally determine shorter lifetimes with any reasonable degree of accuracy. The quenching rate constant of 1.0×10^{11} l mol^{-1} s^{-1} is near gas kinetic and thus some very efficient quenching channel must be available. It should be noted that $^*UF_6$ (excited at 3935 Å) has two unpaired spins [10] and thus the ground state $O_2(^3\Sigma^-)$ molecule can quench $^*UF_6$ without violating the conservation of total spin angular momentum to produce the UF_6 ground state singlet and $O_2(^1\Delta)$. Another possibility is that there could be available a very rapid chemical reaction channel between oxygen and $^*UF_6$. Our present data do not allow us to distinguish between these two possibilities.

We now focus our attention on interpreting the non-linear Stern–Volmer kinetics of the other inorganic quenchers. Freed's theory [14] on the pressure saturation of lifetimes was developed for small and intermediate molecules and it deals with the high pressure saturation of collisionally

induced intersystem crossings. We recognize that UF_6 is neither a small nor an intermediate molecule in terms of non-radiative transition theory. However, there are some aspects of the mathematical formulation of Su *et al.* [13], who applied Freed's theory [14] to lifetime saturation in SO_2, that yield results strikingly similar to our data for UF_6. The most noteworthy of these is that the asymptotic line at high pressures extrapolates to a zero pressure value which is independent of the chemical identity of the quenching gas. Our present knowledge of the spectroscopy of $^*UF_6$ and the relative importance of chemical and physical quenching do not make it judicious for us to undertake extensive computational work which may be of limited value in relation to its proper physical interpretation. However, the comment earlier regarding the extrapolation of the asymptotes to zero pressure does merit some attention at this time.

According to the mathematical formulation of Su *et al.* [13] we write the following equations to show the variation in lifetime as a function of pressure:

$$1/\tau_{obs} = 1/\tau_c + 1/\tau_p + 1/\tau_0 \tag{1}$$

$$\frac{1}{\tau_{obs}} = \Sigma_i k_i^c p_i + \frac{\Sigma_i k_i^p P_i}{1 + \Sigma_i \alpha_i P_i} + k_{uni} \tag{2}$$

where τ_{obs} is the observed lifetime; $1/\tau_0 = k_{uni}$ the collision-free decay rate constant, k_i^c the chemical quenching constant of the ith quencher, k_i^p the physical quenching constant of the ith quencher, P_i the pressure of the ith quencher and α_i an experimental constant which depends on the ith quencher. It should be noted that implicit in Freed's theory [14] is that

$$K = k_i^p/\alpha_i \tag{3}$$

where K will be unique to the UF_6 molecule.

In fact, it should be noted that at high pressure the physical quenching part of eqn. (2) reduces to

$$\frac{\Sigma_i k^p P_i}{\Sigma_i \alpha_i P_i} = \frac{\Sigma_i K \alpha_i P_i}{\Sigma_i \alpha_i P_i} = K \tag{4}$$

Thus, at high pressures eqn. (2) may be written as

$$1/\tau_{obs} = \Sigma_i k_i^c P_i + K \tag{5}$$

where k_{uni} has also vanished because of its minor contribution at high pressure. Equation (4) defines the asymptotic broken lines shown in Figs. 2 - 4. It defines the condition of total saturation of physical quenching (*i.e.* no pressure dependence) and permits the pressure dependence of $1/\tau_{obs}$ to be contained only in the chemical quenching terms. For our conditions of 3.00 Torr UF_6 (constant during quenching experiments) the term $\Sigma_i k_i^c P_i$ is represented by

$$k_{UF_6}^c (3.00) + k_M^c P_M \tag{6}$$

Since $k_{UF_6}^c$ (3.00) is a constant, say C_0, we can write eqn. (5) for our experimental conditions as

$$1/\tau_{obs} = C_0 + k_M^c P_M + K \tag{7}$$

Equation (7) indicates that when the asymptotic plots of our high pressure data are extrapolated to $P_M = 0$ then the intercept value $1/\tau_{obs} = C_0 + K$. This implies that extrapolated $1/\tau_{obs}$ at $P_M = 0$ will be independent of the chemical identity of M. Figures 2 - 4 show that this relation is obeyed within experimental error for argon, hydrogen, CO, fluorine, nitrogen and SF$_6$. The results for $C_0 + K$, including our value for helium (not given in graphical display), are presented in Table 2. From our earlier work on UF$_6$ self-quenching, we could not assess the relative magnitudes of $k_{UF_6}^c$ and $k_{UF_6}^p$; thus C_0 remains unevaluated. The fact that the observed intercept values are nearly identical is in agreement with a mathematical formulation of the saturation phenomenon suggested theoretically by Freed [14] for small to intermediate molecules.

TABLE 2

$K + C_0$ values for quenchers M determined at $P_M = 0$[a]

M	$K + C_0(10^6 \text{ s}^{-1})$
He	3.6
Ar	3.6
H$_2$	3.6
CO	3.7
F$_2$	3.7
N$_2$	3.9
SF$_6$	3.9

[a]P_{UF_6} = 3.00 Torr.

Equation (7) indicates that the slopes of the high pressure asymptotes (listed in Table 1) are simply the chemical quenching rate constants. There are no favorable chemical reaction channels involving the formation of chemical bonds with most of the quenchers studied. The reaction which these rate constants most probably represent is the collisionally induced dissociation reaction

$$*UF_6 + M \rightarrow UF_5 + F + M \tag{8}$$

It should be noted that the *UF$_6$ molecules excited at 3935 Å and room temperature have more than enough energy to dissociate to UF$_5$ and F [15]. Collisions could facilitate the dissociation process for those *UF$_6$ molecules which would normally relax back down to the ground electronic state. It should be noted that the monatomic gases have the lowest rate constants as might be expected. The chemical quenching rate constant for CO is largest, possibly because of the affinity of the CO for fluorine atoms. The rate for

SF_6 is no faster than that of the inert diatomics, despite its increased size. However, the role of molecular complexity may be masked in this case owing to $F-F$ repulsive interactions.

The slopes from the low pressure region, listed in Table 1, represent the sum of the physical (saturable) and chemical (unsaturable) quenching rate constants. By subtracting the chemical quenching rate constants, as determined from the high pressure asymptotes, from these low pressure slopes we find that the physical quenching rate constants for the molecules hydrogen, argon, CO, fluorine, nitrogen and SF_6 are all between $(0.5 - 1.0) \times 10^9$ l mol^{-1} s^{-1}.

In conclusion, we see that the dynamical behavior of the $^*UF_6-M$ systems show qualitative agreement with a mathematical formulation of the saturation phenomenon suggested theoretically by Freed [14]. We hope to do further experiments to elucidate better this most interesting observation.

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