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Quenching of the 1.0 and 2.3 μm excited electronic states of PuF_6 at room temperature by selected rare gases and small polyatomic molecules^{a)}

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The quenching rate constants k_q for the following rare gases and small molecules (He , Ar , Xe , H_2 , D_2 , N_2 , O_2 , F_2 , Cl_2 , HF , CO , CO_2 , CH_4 , CHF_3 , CF_4 , NO_2F , SOF_4 , SF_6 , and UF_6) are reported in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for both the 1.0 and 2.3 μm excited electronic states of PuF_6 (see Table I). The self-quenching rate constants for PuF_6 at room temperature are $k_q(1.0 \mu\text{m}) = 1.12 \pm 0.01 \times 10^{-12}$ and $k_q(2.3 \mu\text{m}) = 5.01 \pm 0.11 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The magnitude of the quenching rate constants for most all of the gases considered above suggest that the dominant process in the collisional deexcitation of excited state PuF_6^* (1.0 or 2.3 μm) molecules at room temperature is physical quenching (i.e., E-T or electronic-to-translational collisional energy transfer). Our data also indicate that E-V (electronic-to-vibrational) energy transfer is responsible for the efficient quenching of electronically excited PuF_6 by H_2 , HF , CH_4 , and CHF_3 . There is also evidence from our data that the efficient quenching of the excited states of PuF_6 by ground state PuF_6 molecules proceeds via resonant energy transfer.

I. INTRODUCTION

The photodynamics of the actinide hexafluoride molecules UF_6 , NpF_6 , and PuF_6 has been the subject of a number of investigations. The pressure dependence of the lifetime of the excited A state of UF_6 has been measured by Rice *et al.*¹ The collision-free lifetime τ_0 for UF_6 was reported to be $\geq 56 \mu\text{s}$. Wampler *et al.*²⁻⁵ also measured the quenching rate constants for the excited A state of UF_6 by alkanes, inorganics, and halomethanes. By contrast, the available data on the photodynamics of NpF_6 and PuF_6 is less extensive. Beitz *et al.*⁶ reported the first observation of laser-induced fluorescence from electronically excited states of NpF_6 and PuF_6 in the gas phase at room temperature. The fluorescence was observed to peak at 2.3 μm when PuF_6 was photoexcited at 0.532 and 1.064 μm , respectively, and independent of PuF_6 gas pressure. In this same study, the measured fluorescence lifetime of NpF_6 was also found to be independent of gas pressure. Barefield II *et al.*⁷ have measured the lifetimes of both the 1.0 and 2.3 μm excited electronic states of PuF_6 at room temperature and found that both states exhibit pressure dependence. The collision-free lifetimes τ_0 for the 1.0 and 2.3 μm states are $663 \pm 2 \text{ ns}$ and $218 \pm 5 \mu\text{s}$, respectively. In our experiments, PuF_6 was photoexcited in the 800 nm region.

We began a study of the quenching dynamics of the 1.0 and 2.3 μm electronic states of PuF_6 to see if we could find evidence for quenching via electronic-to-translational (E-T), electronic-to-electronic (E-E), or electronic-to-vibrational energy transfer. The quenching dynamics of the 2.3 μm excited electronic state should be especially interesting since the energy of this state is in the range of molecular vibrational frequencies for small hydrogen containing molecules (H_2 , HF , CH_4 , etc.).⁸ There have been a number of energy trans-

fer investigations reported in the literature for E-V process between atoms and molecules.⁹ To our knowledge, very little data is available on E-V type energy transfer processes where both the donor and acceptor species are *molecules*. The resonance or near resonance of the 2.3 μm excited electronic state of PuF_6 with the molecular vibrational frequencies of small hydrogen containing molecules provides an opportunity to investigate E-V type energy transfer processes where both species are molecules.

II. EXPERIMENTAL

The essential features of our experimental apparatus have been previously described.^{7,10} Therefore, only a brief description will be given here. The 1 μm fluorescence signal is imaged onto the surface of a dry-ice cooled RCA 7102 S-1 photomultiplier tube by an aluminum mirror and a 10 cm focal length CaF_2 lens. A 1 μm broadband interference filter and an AR-coated GaAs window are used for spectral discrimination. The 2.3 μm fluorescence signal is imaged onto the surface of an LN_2 -cooled InSb detector (Infrared Associates) by a copper mirror and a 10 cm focal length lens. An AR-coated Ge window was used to block wavelengths, shorter than 1.5 μm . For lifetime measurements, the fluorescence signals are amplified, digitized (by appropriate Tektronix 7912AD/7612 D transient digitizers) and processed by a PDP 11/34 minicomputer. Using our present data collecting system, both the 1.0 and 2.3 μm fluorescence signals can be acquired simultaneously for processing. In all of our quenching experiments, except those with HF , the pressure of PuF_6 was maintained at 10 Torr and the appropriate increment of quenching gas pressure was added to the LIF cell. In the HF experiments, the PuF_6 pressure was 20 Torr.

The following quenching gases F_2 , Ar , Xe , Cl_2 , HF , SF_6 , CF_4 , CH_4 , CO , CO_2 , and HCl were obtained from the Matheson gas company. The minimum stated purity for this set of gases was 99.9%. The D_2 gas was obtained from Union Carbide's Nuclear Division (Oak Ridge). The quoted purity of the D_2 gas was 99.5%. The He gas that was 99.99% pure was obtained from the Bureau of Mines. The N_2 gas (99.5% pure)

^{a)} work performed under the auspices of the U. S. Department of Energy. A brief account of this work was presented at the 1984 International Chemical Congress of Pacific Basin Societies, Dec. 16-21, 1984, Honolulu, Hawaii.

^{b)} Chemistry Division, Mail Stop J 567.

^{c)} MST Division, Mail Stop E 505.

was obtained from Airco Industrial gases. The UF_6 gas was obtained from the Union Carbide-Oak Ridge Gaseous Diffusion Plant (99.98%). PuF_6 gas was synthesized in our laboratory by high temperature fluorination of PuF_4 . Samples of PuF_6 and UF_6 were purified by trap-to-trap distillation at dry-ice temperature until no significant levels of volatile impurities were detectable using a Nicolet MX-1 FT-IR spectrometer. The SOF_4 and NO_2F gases were synthesized here at Los Alamos by Gary Eller (group INC-4). The CHF_3 was obtained from the Matheson gas company. The sample of CHF_3 used in our quenching experiments was purified at the ICON facility here at Los Alamos National Laboratory.

III. RESULTS AND DISCUSSION

A. Monatomic gases (He, Ar, and Xe)

The quenching data for He, Ar, and Xe are displayed in Fig. 1 for both the 1.0 and 2.3 μm excited electronic states of PuF_6 . The quenching rate constants (see Table I) for the 1 μm excited state are all similar considering the scatter and the resulting poor linear least-squares fit of the data. We also note that this set of rate constants is approximately four orders of magnitude smaller than the corresponding self-quenching rate for the 1 μm state, i.e., 10^{-16} compared to $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In a similar manner, the quenching rate constants (see Table I) in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the 2.3 μm excited electronic state are approximately two orders-of-magnitude smaller (10^{-17}) than the corresponding self-quenching rate for the 2.3 μm state (10^{-15}). Unlike the quenching rate constants obtained for the 1.0 μm excited state, the corresponding rate constants for the 2.3 μm state were determined with a high degree of precision

(i.e., the rate constants were determined from slopes which were larger than the statistical uncertainty in the linear least-square fit of the reciprocal lifetime vs pressure data). Thus, for the 2.3 μm state, the quenching rate constants for He, Ar, and Xe show a statistically significant mass dependence. The magnitude of the quenching rate constants for both the 1.0 and 2.3 μm excited electronic states of PuF_6 by He, Ar, and Xe compared to the corresponding self-quenching rates suggests that the main channel of collisional deactivation by He, Ar, and Xe is simple physical quenching (or E-T energy transfer).

B. Diatomic gases (H_2 , D_2 , N_2 , O_2 , F_2 , Cl_2 , HF , HCl , and CO)

For the quenching of the 1.0 and 2.3 μm excited electronic states of PuF_6 by diatomic gases, only a representative set of data (i.e., Cl_2 , O_2 , and F_2) is shown in Fig. 2. The quenching rate constants (Table I) for the collisional deactivation of the 1.0 μm excited state by D_2 , N_2 , O_2 , F_2 , Cl_2 , and CO are all approximately $10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The quenching rate constants for this set of molecules are approximately three orders of magnitude smaller than the self-quenching rate constant for the 1 μm state ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The notable exceptions are the quenching rate constants for the 1 μm state by H_2 and HF . The quenching rate constants for HF and H_2 are only approximately one and two orders of magnitude, respectively, smaller than the self-quenching rate for the 1 μm state. Again, since the quenching rate constants for the 1 μm state by H_2 , D_2 , N_2 , O_2 , F_2 , Cl_2 , HF , and CO are much smaller than the corresponding self-quenching rate constant, we attribute the collisional deactivation of the excited 1 μm state by this set of diatomics to E-T energy transfer.

A similar trend was noted in the quenching rate constants for the 2.3 μm excited electronic state by D_2 , N_2 , O_2 , F_2 , Cl_2 , and CO . The rate constants (Table I) for this set of gases are approximately an order of magnitude smaller than the self-quenching rate constant for the 2.3 μm state. We therefore attribute the quenching of the 2.3 μm state by this set of gases to E-T energy transfer.

The rate constants for the quenching of the 2.3 μm excited electronic state of PuF_6 by H_2 , D_2 ,¹⁴ and HF ^{13,15} have been submitted for publication. In both of these studies, we showed via detailed theoretical analysis that the large quenching rates observed for H_2 and HF on the 2.3 μm excited electronic state in PuF_6 was due to near-resonant electronic-to-vibrational energy transfer. This observation was in agreement with what has been predicted theoretically¹¹ and experimentally observed¹² for a number of atom-molecule systems [i.e., resonant E-V energy transfer (quenching) rates are large when the electronic energy level of the donor (atom) and the vibrational energy level of the acceptor (molecule) are at or near resonance].

In our diatomic quenching experiments with Cl_2 and HCl we observed evidence for chemical reaction. For Cl_2 , the rate of chemical reaction was small and we were able to separate the rate of quenching and the rate of chemical reaction. However, the rate of reaction with HCl was very rapid and we therefore could not measure a quenching rate for either the 1.0 or the 2.3 μm excited states of PuF_6 . A com-

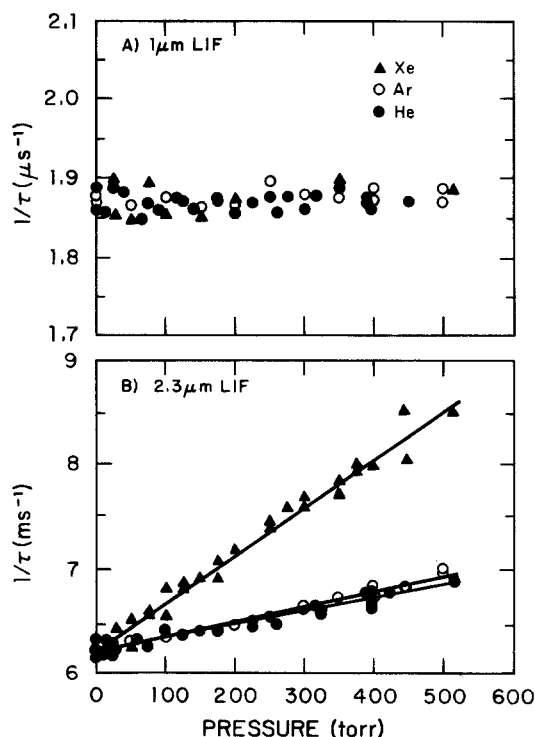


FIG. 1. Quenching data for the collisional deactivation of the 1.0 and 2.3 μm excited electronic states of PuF_6 by He, Ar, and Xe. For visual clarity, all of the data points used to determine the quenching rate constants are not shown. Figures 3 and 4 are displayed with this same consideration.

TABLE I. Summary of room temperature (25 °C) quenching rate constants for reactions of the type PuF₆* + M $\xrightarrow{k_q}$ PuF₆ + M in units of cm³ molecule⁻¹ s⁻¹.

M	$k_q(1.0\ \mu\text{m LIF})$	$k_q(2.3\ \mu\text{m LIF})$	Max, P_M of data (Torr) ^a	Number of ^b data points	type ^c
PuF ₆	$(1.12 \pm 0.01) \times 10^{-12}$	$(5.01 \pm 0.11) \times 10^{-15}$	72(74)	83(75)	Resonant energy transfer
He	$(2 \pm 5) \times 10^{-16}$	$(3.9 \pm 0.2) \times 10^{-17}$	450(517)	26(34)	E-T
Ar	$(5.2 \pm 4.5) \times 10^{-16}$	$(4.4 \pm 0.2) \times 10^{-17}$	500	16	E-T
Xe	$(8 \pm 13) \times 10^{-16}$	$(1.42 \pm 0.04) \times 10^{-16}$	513	15(34)	E-T
		Not single			
H ₂	$(4.8 \pm 0.3) \times 10^{-14}$	exponential decay ^d	65	33(31)	E-T, E-V
D ₂	$(3.7 \pm 1.7) \times 10^{-15}$	$(8.7 \pm 0.3) \times 10^{-16}$	105	38(27)	E-T
N ₂	$(1.7 \pm 0.7) \times 10^{-15}$	$(2.3 \pm 0.1) \times 10^{-16}$	301	68(65)	E-T
O ₂	$(4.0 \pm 0.8) \times 10^{-15}$	$(1.22 \pm 0.04) \times 10^{-16}$	290	40(44)	E-T
F ₂	$(4.9 \pm 1.0) \times 10^{-15}$	$(3.30 \pm 0.05) \times 10^{-16}$	290	26(31)	E-T
Cl ₂	$(1.3 \pm 0.2) \times 10^{-14}$	$(6.1 \pm 0.2) \times 10^{-16}$	103	16	E-T
HCl—Spontaneous reaction to form HF—no measurement possible—					
HF	$(4.9 \pm 1.9) \times 10^{-13}$	$(3.24 \pm 0.93) \times 10^{-13e}$	4	13(14)	E-T, E-V
CO	$(1.3 \pm 1.4) \times 10^{-15}$	$(2.8 \pm 0.1) \times 10^{-16}$	170	31(36)	E-T
CO ₂	$(1.4 \pm 0.1) \times 10^{-14}$	$(1.02 \pm 0.01) \times 10^{-15}$	199	37	E-T
CH ₄	$(2.0 \pm 0.3) \times 10^{-14}$	$(1.95 \pm 0.03) \times 10^{-14}$	85	19	E-T, E-V
CHF ₃	$(1.7 \pm 0.2) \times 10^{-14}$	$(7.4 \pm 0.3) \times 10^{-15}$	200(175)	33(28)	E-T, E-V
CF ₄	$(3.4 \pm 1.0) \times 10^{-15}$	$(2.88 \pm 0.06) \times 10^{-16}$	299	28(34)	E-T
NO ₂ F	$(4.1 \pm 5.0) \times 10^{-15}$	$(1.37 \pm 0.08) \times 10^{-15}$	105	16(18)	E-T
SOF ₄	$(1.2 \pm 0.5) \times 10^{-14}$	$(1.24 \pm 0.09) \times 10^{-15}$	51	19	E-T
SF ₆	$(4.0 \pm 1.6) \times 10^{-15}$	$(1.40 \pm 0.02) \times 10^{-16}$	145	24	E-T
UF ₆	$(9.9 \pm 2.2) \times 10^{-15}$	$(6.5 \pm 0.3) \times 10^{-16}$	114	59	E-T

^a In cases where the maximum pressure for the 1.0 and 2.3 μm state are not the same, the maximum pressure for the 2.3 μm state data is shown in parentheses.^b In cases where the number of data points are not the same for the 1.0 and 2.3 μm states, the number of data points for the 2.3 μm state is shown in parentheses.^c In cases where the collisional deactivation rate type is not the same for both the 1.0 and 2.3 μm state, the 2.3 μm state rate type is included second.^d Theoretical analysis of the H₂ data for the 2.3 μm state yield k (E-V) = $(2.05 \pm 0.30) \times 10^{-14}$ and k (E-T) = $(3.1 \pm 0.5) \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹. (See Ref. 14.)^e The Stearn–Volmer plot for the 2.3 μm state was not linear. This E-V rate constant was determined via a nonlinear least-squares fit of the quenching data. (See Ref. 13.)

plete product analysis was not pursued; however, FT–IR spectroscopy of our PuF₆ + HCl gas mixture showed that one product of the reaction was HF.

C. Carbon containing polyatomics (CO₂, CH₄, CHF₃, and CF₄)

The quenching rate constants (Table I) for the collisional deactivation of the 1 μm excited electronic state of PuF₆ by CO₂, CH₄, CHF₃, and CF₄ are nearly constant (i.e., approximately 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹). The quenching rate constants for this set of gases are a couple of orders of magnitude smaller than the corresponding self-quenching rate for the 1 μm state. We again attribute the collisional deactivation of the 1 μm excited state by CO₂, CH₄, CHF₃ and CF₄ to E-T energy transfer.

The data for the quenching of the 2.3 μm excited state of PuF₆ by CO₂, CH₄, CHF₃ and CF₄ is shown in Fig. 3. We note from Table I that there is a large increase in the quenching rate constant in the CF₄, CHF₃, CH₄ series with the quenching rate constant for CO₂ having an intermediate value. The fundamental vibrational frequencies for CH₄ in wave numbers (cm⁻¹) are ν_1 (2914), ν_2 (1526), ν_3 (3020), and ν_4 (1306), respectively. Of the many combination and overtone bands allowed for this T_d molecule, four significantly overlap the 2.3 μm broadband fluorescence from excited state PuF₆. The four near-resonant combination bands in wave numbers are $\nu_2 + 2\nu_4 = 4133$, $\nu_1 + \nu_4 = 4216$, $\nu_3 + \nu_4 = 4313.2$, and $\nu_2 + \nu_3 = 4546$, respectively.¹⁶ Again the efficient quenching of the 2.3 μm excited state by CH₄ is

attributed to near-resonant E-V energy transfer in agreement with previous theoretical predictions¹¹ and experimental observations.^{12,13,14} Identical binary combinations of vibrational bands in wave numbers for CF₄ are $\nu_2 + 2\nu_4 = 1699$, $\nu_1 + \nu_4 = 1541$, $\nu_3 + \nu_4 = 1913$, and $\nu_2 + \nu_3 = 1716$, respectively.¹⁷ Thus, there are no apparent near E-V resonances for the quenching of the 2.3 μm excited state by CF₄ and the quenching rate is down by a couple of orders of magnitude compared to the corresponding quenching rate constant for CH₄. Of the possible combination bands for CHF₃, the only one that has significant overlap with the broadband fluorescence from the 2.3 μm excited state is $\nu_1 + \nu_2 = 4153$ cm⁻¹.¹⁸ It is interesting that one near-resonant E-V channel in a polyatomic like CHF₃ gives rise to a quenching rate constant that is faster than the self-quenching rate constant for the 2.3 μm excited state. There also appears to be a significant dependence on the density of near resonant E-V energy transfer channels since the quenching rate for CH₄ is a factor of 2 faster than the corresponding rate for CHF₃. The quenching rate for the 2.3 μm excited state by CO₂ is a factor of 5 smaller than the self-quenching rate for the 2.3 μm state (Table I). The quenching rate constants for the collisional deactivation of the 2.3 μm excited state of PuF₆ by both CF₄ and CO₂ is therefore attributed to E-T energy transfer.

D. NO₂F and SOF₄ polyatomic gases

The quenching rate constants (Table I) for the collisional deactivation of both the 1.0 and 2.3 μm excited electronic

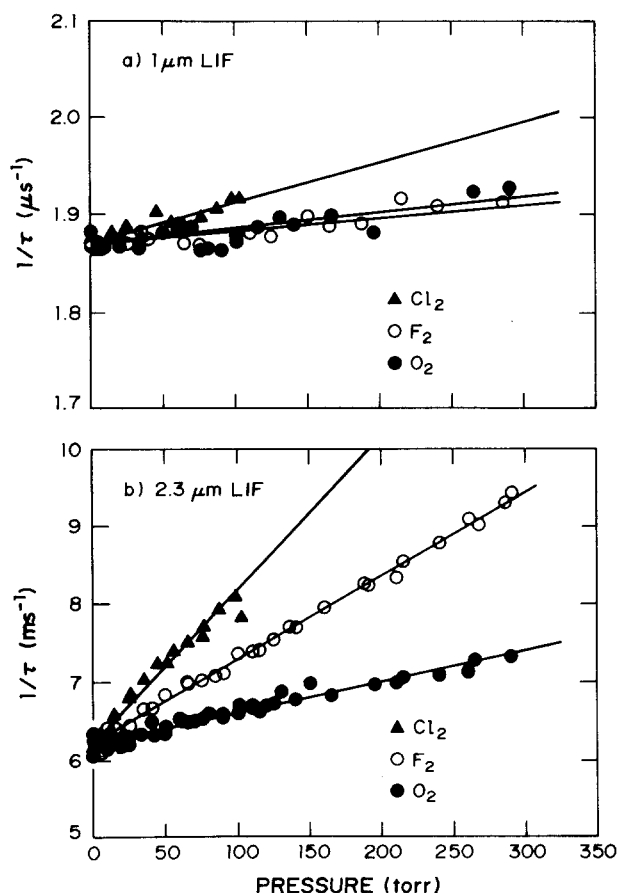


FIG. 2. A display of the quenching data for the 1.0 and 2.3 μm excited electronic states of PuF₆ by Cl₂, O₂, and F₂.

states in PuF₆ by NO₂F and SOF₄ are smaller than the corresponding self-quenching rate constant for both excited states. The magnitude of the quenching rates constants by NO₂F and SOF₄ on both the 1.0 and 2.3 excited electronic states of PuF₆ suggest that the main pathway for collisional deactivation by NO₂F and SOF₄ is E-T energy transfer.

E. Hexafluorides (SF₆, UF₆, and PuF₆)

The quenching data for the collisional deactivation of the 1.0 and 2.3 μm excited electronic states of PuF₆ by SF₆,

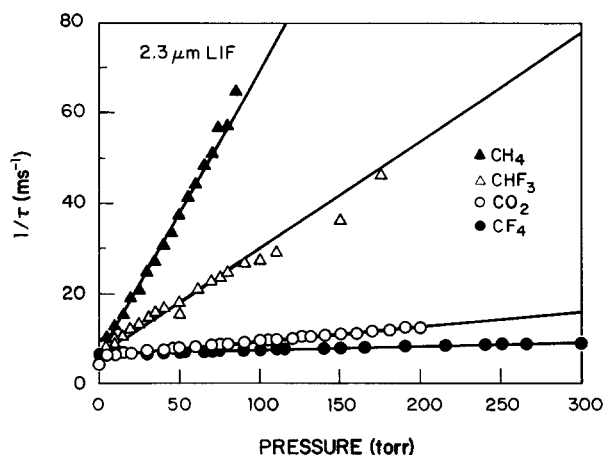


FIG. 3. Quenching data for the collisional deactivation of the 2.3 μm excited electronic state of PuF₆ by CO₂, CH₄, CHF₃, and CF₄.

UF₆, and ground state PuF₆ molecules are displayed in Fig. 4.¹⁹ From Table I, we note that the quenching rate constants for the collisional deactivation of the 1 μm state by SF₆ and UF₆ are approximately three orders of magnitude ($10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) smaller than the corresponding self-quenching rate constant ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the 1 μm excited state. Similarly, for the 2.3 μm excited state the quenching rate constants for SF₆ and UF₆ are approximately an order of magnitude smaller than the self-quenching rate constant ($10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the 2.3 μm state. Again, we believe that the quenching of the 1.0 and 2.3 μm excited states of PuF₆ by SF₆ and UF₆ proceeds via E-T energy transfer. It is interesting to note from Table I that the most efficient collisions that deactivate the 1 μm excited state are collisions with ground state PuF₆ molecules. Since ground state PuF₆ molecules are in perfect resonance with the 1 μm excited state, we attribute the efficient quenching of the 1 μm excited state by ground state PuF₆ molecules to resonant energy transfer. The trend for the 2.3 μm excited state is similar to the one observed for the 1.0 μm excited state. We again believe that the efficient quenching of the 2.3 μm excited electronic state by ground state PuF₆ molecules is due to resonant energy transfer. There are four important exceptions for the quenching of the 2.3 μm excited electronic state. The quenching rate constants for the collisional deactivation of the 2.3 μm excited state by H₂, HF, CH₄, and CHF₃ are all faster than the self-quenching rate constant for the 2.3 μm state. We are not sure at this time why the E-V quenching rate constants for H₂, CH₄, and CHF₃ are faster than the resonant energy transfer (self-quenching) rate constant for the 2.3 μm excited electronic state.

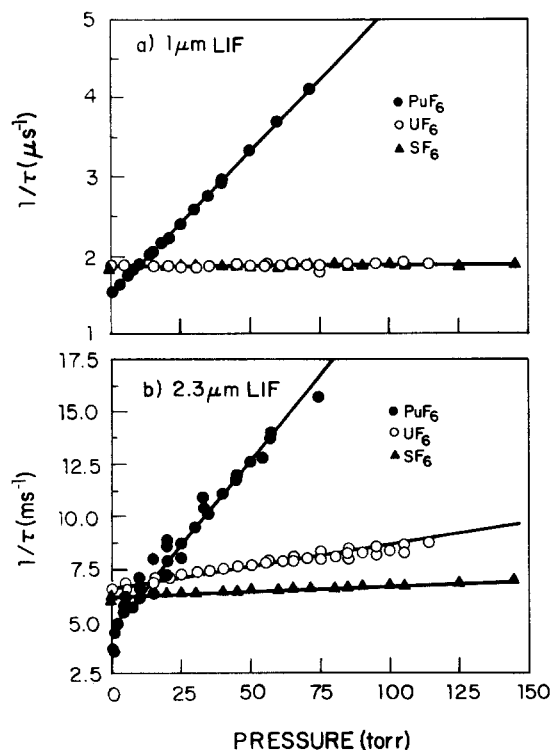


FIG. 4. Quenching data for the collisional deactivation of the 1.0 and 2.3 μm excited electronic states of PuF₆ by SF₆, UF₆, and PuF₆.

IV. CONCLUSIONS

We have studied the collisional deactivation of the 1.0 and 2.3 μm excited electronic states of PuF₆ at room temperature by a number of rare gases and small molecules. The molecules and rare gases studied have a variety of structures and internal degrees of freedom, i.e., from simple monatomic gases to O_h hexafluorides type molecules. Our data indicate that the degrees of freedom or the complex structure of the polyatomic molecules do not play an important role in the effective deactivation of the excited states of PuF₆ (both the 1.0 and 2.3 μm states). For example, the quenching rate constants for the deactivation of the excited states of PuF₆ by D₂, F₂, CF₄, SF₆, and UF₆ are of the same order of magnitude for both states (i.e., $10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the 1 μm state and $10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the 2.3 μm state).

For the 1 μm excited state in PuF₆ collisional deactivation proceeds via simple physical quenching since the quenching rate constants for all the molecules studied are approximately of the same order of magnitude ($10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). H₂ and HF are much more efficient quenchers of the 1 μm excited state in PuF₆. We are not sure why this is so but a high rotational level of $V=2$, for both molecules, might provide possible resonant energy transfer channels for the collision deactivation of the 1 μm state. This would lead to a fast energy transfer rate. The most efficient quenchers for the 1 μm excited state in PuF₆ is ground state PuF₆ molecules. We attribute this efficient quenching rate to resonant energy transfer from the 1 μm excited state.

The most effective quenchers of the 2.3 μm excited electronic state in PuF₆ are H₂, HF, CH₄, CHF₃ and ground state PuF₆ molecules. We have shown via theoretical analysis of the H₂ and HF quenching data that E-V energy transfer is responsible for the accelerated quenching rate of the 2.3 μm excited electronic state by H₂ and HF.^{13,14} As discussed in Sec. III C, there are near-resonant vibrational energy channels available for both CH₄ and CHF₃. The collisional deactivation of the 2.3 μm excited state by CH₄ and CHF₃ also proceeds primarily by near resonant E-V energy transfer. Finally, the efficient quenching of the excited 2.3 μm state by ground state PuF₆ molecules proceeds via resonant energy transfer.

Again, our data indicate that the single most important parameter in the collisional deactivation of the 1.0 μm and 2.3 μm excited electronic states in PuF₆ by the molecules

studied is the availability of a resonant E-E or near resonant E-V energy transfer channel.

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- ¹W. W. Rice, R. C. Oldenberg, P. J. Wantuck, J. J. Tiee, and F. B. Wampler, *J. Chem. Phys.* **73**, 3560 (1980).
- ²F. B. Wampler, W. W. Rice, and R. C. Oldenberg, *Int. J. Chem. Kinet.* **11**, 275 (1979).
- ³F. B. Wampler, R. C. Oldenberg, and W. W. Rice, *Chem. Phys. Lett.* **54**, 560 (1978).
- ⁴F. B. Wampler, R. C. Oldenberg, and W. W. Rice, *J. Photochem.* **9**, 473 (1978).
- ⁵F. B. Wampler, R. C. Oldenberg, and W. W. Rice, *J. Photochem.* **11**, 369 (1979).
- ⁶J. V. Beitz, C. W. Williams, and W. T. Carnall, *J. Chem. Phys.* **76**, 2756 (1982).
- ⁷J. E. Barefield II, W. W. Rice, J. J. Tiee, and R. T. Walters, *J. Chem. Phys.* **79**, 2621 (1983); W. W. Rice and J. E. Barefield II, *ibid.* **82**, 2553 (1985).
- ⁸G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1950).
- ⁹J. T. Yardley, *Introduction to Molecular Energy Transfer* (Academic, New York, 1980), pp. 205-241.
- ¹⁰J. E. Barefield II and W. W. Rice, *Rev. Sci. Instrum.* (submitted).
- ¹¹W. M. Huo, *J. Chem. Phys.* **66**, 3572 (1977); W. M. Huo and M. A. Dillon, *ibid.* **66**, 3588 (1977).
- ¹²J. R. Neely, G. S. Hurst, E. B. Wagner, and M. C. Payne, *J. Chem. Phys.* **63**, 2717 (1975); E. H. Fink, D. Wallach, and C. B. Moore, *ibid.* **56**, 3608 (1972); G. Karl, P. Kruus, and J. C. Polanyi, *ibid.* **46**, 224 (1967); A. T. Pritt, Jr. and R. D. Coombe, *ibid.* **65**, 2096 (1976).
- ¹³W. W. Rice, J. E. Barefield II, and R. T. Pack, *Chem. Phys. Lett.* (submitted).
- ¹⁴W. W. Rice, J. E. Barefield II, and R. T. Pack, *J. Chem. Phys.* **82**, 58 (1985).
- ¹⁵W. W. Rice and J. E. Barefield II, accepted for presentation at the 1984 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, Dec. 16-21, 1984.
- ¹⁶G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1950), pp. 308-309.
- ¹⁷T. Shimanouchi, *Tables of Molecular Vibrational Frequencies, Consolidated Volume I*, Natl. Stand. Ref. Data Ser. Natl. Bur. Stand. No. **39**, (U. S. GPO, Washington, D. C., 1972).
- ¹⁸G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1950), pp. 313-322.
- ¹⁹The vertical scales for the 1.0 and 2.3 μm LIF have been chosen to best display the near PuF₆ data. Since the self-quenching rate constants for the 1.0 and 2.3 μm excited states are much larger than the corresponding quenching rate constants for SF₆ and UF₆, the apparent scatter in the PuF₆ data appear to be larger than the scatter in the UF₆ and SF₆ data (when plotted on the same scale). However, the actual standard deviations in the measurements are listed in Table I.