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## SF<sub>6</sub> in a xenon matrix: Vibrational energy relaxation

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In this communication, we report preliminary measurements of the vibrational energy relaxation time of SF<sub>6</sub> isolated in solid xenon. This relaxation time, at 7 K, is in the microsecond range.

We have previously shown<sup>1-3</sup> that the choice of the matrix may greatly influence the vibrational lifetimes of trapped molecules, in rotation dominated processes. Therefore, the mechanism of vibrational energy relaxation of a matrix isolated molecule must be very carefully investigated, in order to find, for example, the best conditions for an IR multiphoton dissociation.

Samples of SF<sub>6</sub> in solid xenon ( $M/R=20\,000$  to 100) are studied with the same IR double resonance method as used for CH<sub>3</sub>F,<sup>1</sup> <sup>12</sup>CD<sub>3</sub>F,<sup>2</sup> and <sup>13</sup>CD<sub>3</sub>F.<sup>3</sup> The  $\nu_3$  mode of <sup>32</sup>SF<sub>6</sub> in the 10  $\mu$  region is weakly excited by a Q-switched CO<sub>2</sub> laser (pulse energy about 25  $\mu$ J, 250 ns FWHM). A cw CO<sub>2</sub> laser, weak enough to cause no perturbation of the population of the system even if it is absorbed, is used as a probe. The double resonance signal is then the time dependent transmitted energy of the probe following the exciting pulse.

Figure 1(a) shows a low resolution absorption spectrum of the  $\nu_3$  band of a dilute sample of SF<sub>6</sub> in solid xenon. Two broad peaks are observed at 931.3 and 933 cm<sup>-1</sup> (948 cm<sup>-1</sup> in the gas phase). Actually, these peaks are probably the envelope of a more complicated structure as observed in high resolution spectroscopy.<sup>4-6</sup> The presence of different trapping sites and also a possible removal of the degeneracy of  $\nu_3$  are the proposed explanation of this structure, which shows a striking reversible and irreversible temperature dependence.

We must mention that the double resonance signals are strongly dependent upon the thermal history and the temperature of the sample. Generally, a long lived (in the hundreds of microseconds range) thermal component is observed, superimposed to the population relaxation signal. This thermal effect is due to the change in the frequencies and lineshapes with temperature, consistent with the strong temperature reversible dynamics of the trapping sites of SF<sub>6</sub> observed in solid rare gases.<sup>5,6</sup> In this letter, samples deposited at 37 K and cooled to 6 K are studied, without further annealing. Furthermore, due to the low power of the lasers, no

visible irreversible effect occurs and the double resonance signals remain the same during the whole experiment.

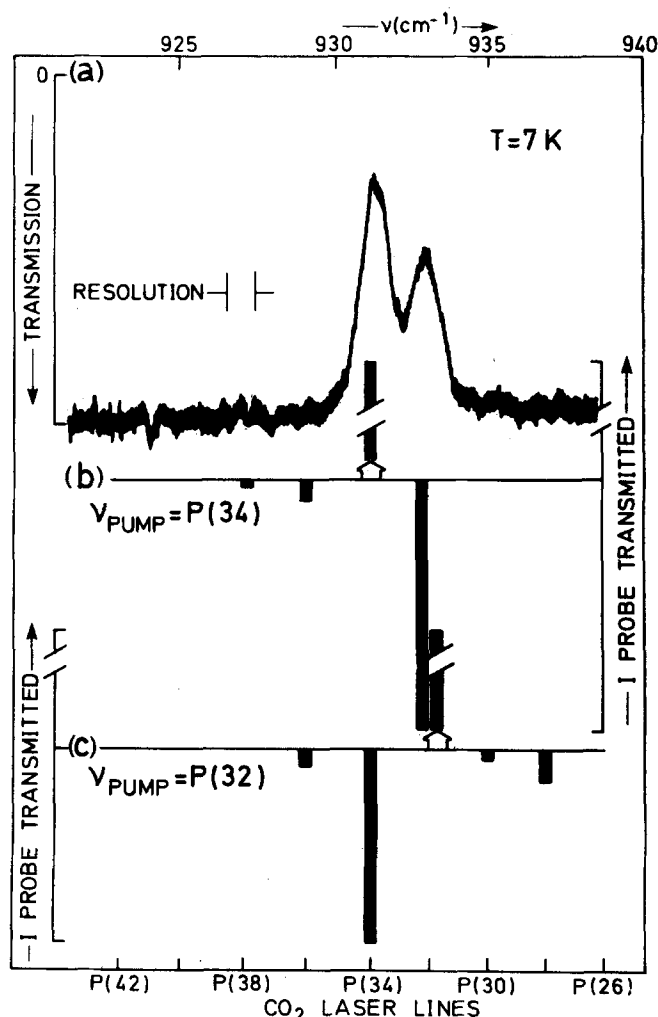


FIG. 1. SF<sub>6</sub> in a xenon matrix: Xe/SF<sub>6</sub>=20 000; deposition: 4 mmol h<sup>-1</sup> at 37 K; sample thickness  $\approx 250 \mu$ . (a) Typical low resolution absorption spectrum in the  $\nu_3$  region at 7 K; (b) initial amplitude of the double resonance signal for different probe laser lines, with the excitation at P(34); (c) same as (b), with the excitation at P(32).

The relative initial amplitudes of the double resonance signals at 7 K are plotted as a function of the probe wave number in Figs. 1(b) and (c).  $P(34)$  and  $P(32)$  laser lines are in coincidence with  $\text{SF}_6$  absorptions. A positive signal corresponds to probing a fundamental absorption, whereas a negative signal corresponds to a hot band. From these observations, two different categories of molecules seem to be involved in the system, one pumped by  $P(34)$  and the second one pumped by  $P(32)$ . Furthermore, no evident energy transfer takes place between these categories during the relaxation process. This is consistent with the absence of any  $V-V$  transfer to the "dimers"<sup>2</sup> (two  $\text{SF}_6$  molecules trapped in neighboring sites), even up to  $M/R=100$ .

On the other hand, the anharmonicity, generally unaffected by the matrix, is  $7\text{ cm}^{-1}$  for  $\nu_3$ , so the transition  $V_3=1 \rightarrow V_3=2$  should be seen with the lines  $P(40)$  or  $P(42)$  of the probe [Fig. 1(b) and (c)]. As no transient absorption is observed at these wave numbers, it may be concluded that  $\nu_3=2$  cannot be populated for an appreciable length of time. Probably, a fast intramolecular  $V-V$  transfer takes place from  $\nu_3=1$  to a lower level  $\nu_i=1$  not identified so far. Then the probed hot bands could be assigned to some  $(\nu_3 + \nu_i) - \nu_i$  transition, where  $\nu_i$  is any vibrational level of  $\text{SF}_6$  lying below  $\nu_3$ . The fast rise time of the hot bands (shorter than the response time of the detection system of 500 ns) supports the above hypothesis.

The best time constant measurements of the repopulation of the fundamental level are achieved here on the positive signal observed with the pump and the probe at  $P(34)$ . At this wave number, the amplitude of the thermal component is weak compared to the relaxation signal. Furthermore, while negative below 15 K, this thermal component becomes positive at higher temperature, which provides an estimate of the subsequent

error. We have been able to fit the relaxation signal with the sum of two exponential functions of approximately equal amplitude: a slow component decaying in  $16 \pm 3\text{ }\mu\text{s}$ , and a faster component decaying in  $5 \pm 1\text{ }\mu\text{s}$ . These two decay times are carefully determined by fitting to the data from time 0 to time  $80\text{ }\mu\text{s}$ . All of the time measurements performed on the  $P(32)$  system and on the hot bands are in agreement with the above results within the accuracy allowed by the strong thermal effects.

In conclusion, laser excited  $\text{SF}_6$  isolated in a xenon matrix shows fast intramolecular  $V-V$  transfer. There is no clear evidence of intermolecular  $V-V$  transfer between the two categories of molecules which seem involved in the system. We are currently engaged in further studies, for different conditions of deposition and annealing and in different matrices, which we expect will give more information about the mechanisms of the vibrational energy transfers. On the other hand, IR absorption spectra of very high optical density samples may provide the assignments of the hot bands involved in the system.

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## Asymptotic form of first-order density matrix for atoms and molecules

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The first-order density matrix of an atom or a molecule is most elegantly written in terms of the natural orbitals  $\psi_i$  and their occupation numbers  $n_i$  as

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_i n_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}') \quad (1)$$

However, as Morell *et al.*<sup>1</sup> have shown, the natural orbitals have the same asymptotic form, i.e.,

$$\psi_i(\mathbf{r}) \sim \psi(\mathbf{r}) \text{ independent of } i. \quad (2)$$

Inserting Eq. (2) into Eq. (1) yields immediately