

# Collisionless Intramolecular Vibrational Relaxation<sup>1</sup> in SF<sub>6</sub>

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## 1. Introduction

There has always been great interest in the limits of applicability of statistical mechanics. For example the point is often made that statistical concepts describe macroscopic systems very well. On the other hand, a tiny dynamical system such as a single isolated molecule may behave in a non-ergodic manner.

While the question of ergodicity may seem highly theoretical, it has rather direct experimental consequences. Consider, for concreteness, the resonant excitation [1] of the  $\nu_3$  vibrational mode in SF<sub>6</sub> by an ultra-short infrared laser pulse. As a result of the energy deposition, the fundamental absorption spectrum will experience an anharmonic shift. There are two possibilities for the spectral shift:

(1) For energy localized within the  $\nu_3$  mode the anharmonic shift will be  $\sim 5 \text{ cm}^{-1}$  per  $1000 \text{ cm}^{-1}$ . This *self*-anharmonicity is known from the overtone spectrum [2] of the  $\nu_3$  mode.

(2) For energy randomly distributed in all the modes the anharmonic shift will be  $2.6 \text{ cm}^{-1}$  per  $1000 \text{ cm}^{-1}$ . This *cross*-anharmonicity is determined from the temperature shift of the fundamental  $\nu_3$  spectrum.

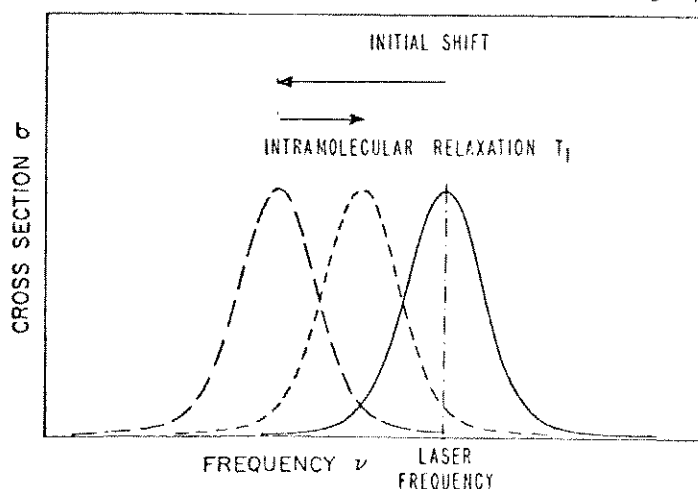


Fig.1 Behavior of the  $\nu_3$  spectrum under infrared pumping by a powerful ultrashort CO<sub>2</sub> pulse

<sup>1</sup>Research supported by Joint Services Electronics Program and Office of Naval Research.

Therefore, we may anticipate the behavior shown in Fig.1. An ultrashort infrared pulse will initially deposit energy in the  $\nu_3$  mode, causing a large anharmonic shift. Subsequently, the energy may randomize among all the vibrational modes, causing the ir spectrum to shift part way back to the original position. Time resolved vibrational spectroscopy can monitor the amount of energy deposited, its distribution among the modes and can provide an operational monitor for ergodicity. The anharmonic shifts in effect measure the probability distribution of the molecule in its phase space, thereby testing for ergodicity and the rate at which it sets in.

The redistribution of energy from a driven mode should be regarded as a  $T_1$ -type relaxation process [4], where the rest of the molecule acts as a heat bath.

In the experiments described below,  $SF_6$  gas is pumped by a powerful picosecond  $CO_2$  laser pulse. The drop in absorption cross-section which results should not be regarded as a true 2-level saturation effect. Instead the absorption saturation is best interpreted as due to a shift off resonance of the absorption spectrum as indicated in Fig.1. We may hope to see a strong absorption saturation effect when the  $\nu_3$  mode is initially excited, followed by a partial recovery of absorption as the vibrational energy is redistributed among the modes.

## 2. Experiment

In this series of experiments the time resolved saturation and partial recovery of absorption is probed at the same wavelength as the pump beam. The full saturation spectrum may be obtained by a simple extension of the techniques employed here.

The experimental apparatus is illustrated in Fig.2. A single mode Tachisto TEA  $CO_2$  laser is followed by a plasma shutter [5] which truncates the laser pulse. The beam then passes through an optical free induction decay [6] cell which generates the 30 psec pulses. This light source is employed in a standard [7] picosecond pump and probe arrangement, the time delay being supplied by a translation stage. The probe pulse were observed with a Ge: Au detector and averaged with a boxcar integrator.

In one of the experiments a comparison was made between the behavior of heated and unheated  $SF_6$ . Rather than using an oven, the pre-heating was accomplished by means of the truncated optical pulse from the plasma shutter. An optical delay of 32 nsec after the heating pulse allowed collisional equilibration before the picosecond pump and probe pulses arrived. The irradiation sequence experienced by the molecules is shown in the insert of Fig.2. However, most of the experiments were performed at room temperature with the pre-heating beam not in use.

## 3. Collisional Effects

In this type of experiment it is important to separate out collisional effects and to operate in a pressure regime where they are negligible. Figure 3 shows a series of pump probe saturation scans which were performed at three different  $SF_6$  gas pressures. The graphs show a strong absorption saturation followed, as anticipated, by a partial recovery on a rapid collisionless time scale and then a slow pressure dependent recovery. The pressure dependent recovery time constant is  $13.5 \pm 3$  nsec-torr. This

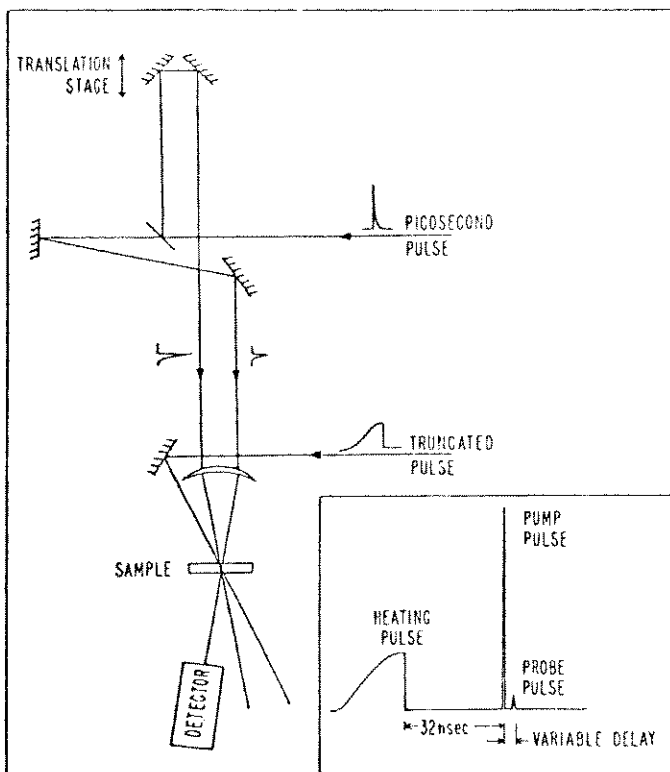


Fig.2 Experimental setup. The sequence of pulses arriving at the sample is shown in the insert

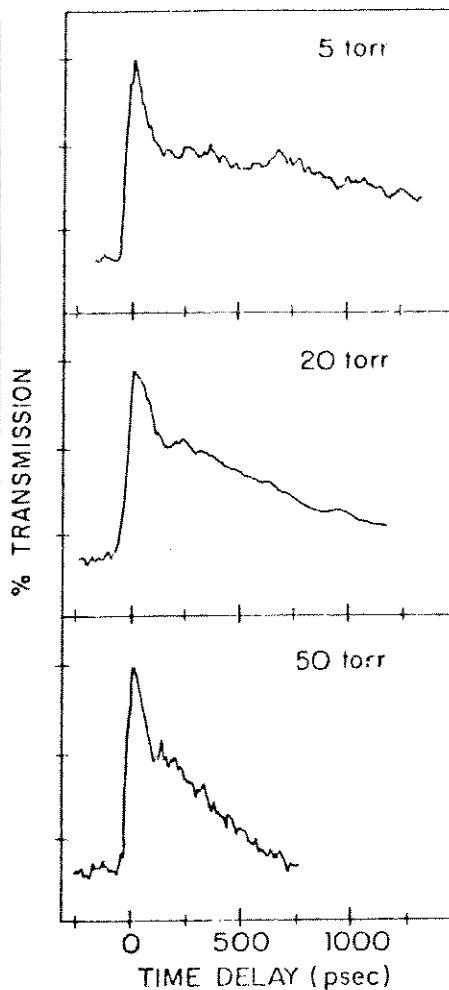


Fig.3 Recovery of saturation is shown for three gas cell pressures. 50 psec pulses at  $66 \text{ MW/cm}^2$  were used

corresponds to a very large gas kinetic cross-section and sets the limit for true collisionless operation of our experiments.

Previous workers [8,9], who observed a saturation recovery in the nanosecond regime, speculated that they might be seeing collisionless effects. The improved time resolution in our experiments shows that those effects were most likely collisional in nature. Deutsch and Brueck [10] have seen some interesting effects even on a microsecond time scale. It is clear from our measured pressure-time constant that their observations were firmly in the collision dominated time scale.

#### 4. Results and Discussion

Our main results are shown in Figs.4 and 5. They were taken at a sufficiently low pressure so that collisional effects can be neglected. Figure 4 compares the saturation recovery in  $\text{SF}_6$  with that observed in the saturable

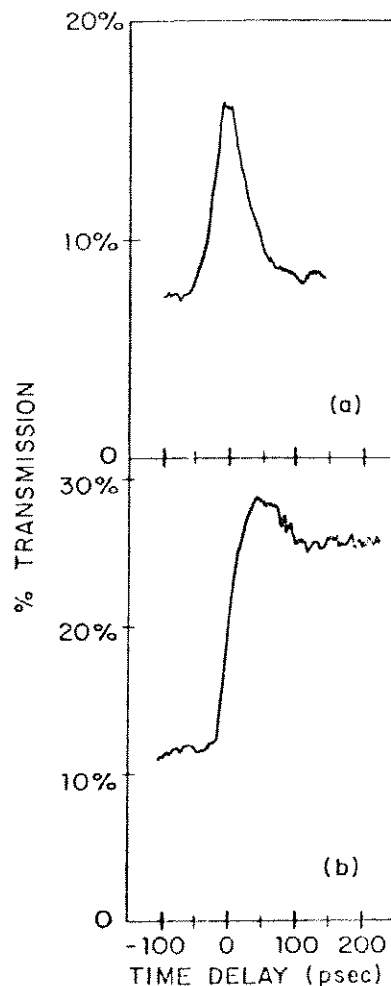


Fig.4 Saturation recovery scans for (a) p-Ge at an intensity of  $150 \text{ MW/cm}^2$ , (b) 20 torr of  $\text{SF}_6$  at  $0.3 \text{ GW/cm}^2$ . 30 psec pulses were employed in these scans

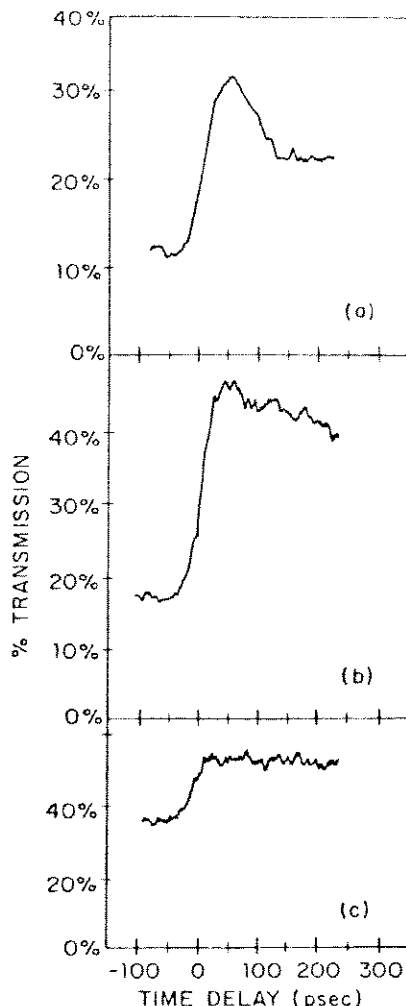


Fig.5 Saturation recovery scans to show the disappearance of the initial fast component as the internal vibrational energy of the  $\text{SF}_6$  molecules is increased. See text for explanations of each curve

absorber p-Ge [11]. The saturation recovery time in p-Ge had been shown to be  $\leq 1$  psec which is essentially instantaneous on the time scale of our experiments. Therefore, Fig.4(a) is a type of pulse autocorrelation scan and it enables us to fix an accurate zero of time delay.

The saturation recovery of  $\text{SF}_6$  under three different conditions of excitation is shown in Fig.5. The scan in Fig.5(a), which resembles those of Figs.3 and 4(b), was taken under conditions where on the average,  $\leq 1000 \text{ cm}^{-1}$  of energy was deposited per molecule by the pump pulse [12]. In Fig.5(b), the pump power was increased so that the average energy deposited per molecule was  $\approx 3000 \text{ cm}^{-1}$ . It can be seen that a steady state was reached

within the 50 psec duration of the laser pulse, and the fast recovery component is absent. In Fig.5(c) the experiment was repeated [13] in SF<sub>6</sub> preheated to 650°K, a temperature at which the average internal vibrational energy is equivalent to ~3500 cm<sup>-1</sup>. Once more, a steady state is reached within 50 psec and the fast recovery component is absent.

The spectral shifts depicted in Fig.1 may result not only from the internal redistribution of energy, but also from the loss of molecular energy due to adiabatic decay of level populations which follow the decaying laser pulse. This loss of internal energy simply reduces the anharmonic shift. We interpret the fast recovery component which is seen in Figs.3,4(b) and 5(a) as due to the adiabatic decay of level populations in an energy region where the vibrational level density is relatively sparse [14]. It is readily seen from Fig.4 that the fast recovery component roughly follows the autocorrelation function.

On the other hand, Figs.5(b) and (c) are typical of experiments on molecules with >3000 cm<sup>-1</sup> excitation. This is the so-called quasi-continuum regime [15] where the vibrational level density is very high. In these cases, there is no fast recovery component and the saturation approaches steady state during the laser pulse duration.

In either of the above cases, the saturation level achieves a final steady state during or immediately following the laser pulse. The conclusion seems inescapable therefore that the intramolecular damping occurs within 30 psec. The proper interpretation of this point requires a clear conceptual picture of intramolecular damping.

Ignoring spontaneous emission, dissociation, and collisional effects, the energy levels of the exact vibrational Hamiltonian, though they may be very dense, are rigorously discrete. A molecule with energy localized in a given mode is inherently nonstationary due to anharmonicity and must be described as a coherent superposition of discrete stationary states of differing energies. Therefore the lineshape of intramolecular damping is best regarded as the *envelope* function of those discrete levels which contribute to the nonstationary superposition. The reciprocal of the width of that envelope function is the intramolecular damping time.

## 5. Conclusion

The experimental conclusion is that the linewidth of the envelope function of such a nonstationary state must be greater than the reciprocal of 30 psec. If the envelope function were any narrower, then the decay of the coherent superposition would produce temporal structure on a time scale longer than the pulse duration. Thus the redistribution of energy from the driven normal mode must occur within an upper limit of 30 psec.

A lower limit of 1 psec may be determined from the absorption linewidth [3] of heated SF<sub>6</sub> which is never much greater than ~20 cm<sup>-1</sup>. Therefore, the intramolecular relaxation time must fall within the limits 1 psec < T<sub>1</sub> < 30 psec.

Although the final steady state is achieved very rapidly, this experiment does not establish that the final state is necessarily exactly ergodic. Indeed, no one individual measurement [16] is sufficient for this purpose. The accessible vibrational phase space contains thousands of cells and

therefore thousands of different experiments would be required to show that each cell is occupied with equal probability.

### References

1. For a review, see N. Bloembergen and E. Yablonovitch, *Phys. Today* 31, No. 5, 23 (May 1978).
2. R.S. McDowell, J.P. Aldridge and R.F. Holland, *J. Phys. Chem.* 80, 1203 (1976); H. Kildal, *J. Chem. Phys.* 67, 1287 (1977).
3. A.V. Nowak and J.L. Lyman, *J. Quant. Spectr. Rad. Transf.*, 15, 1945 (1975); J.F. Bott, *Appl. Phys. Lett.* 32, 624 (1978).
4. E. Yablonovitch, *Opt. Lett.* 1, 87 (1977).
5. H.S. Kwok and E. Yablonovitch, *Appl. Phys. Lett.* 30, 158 (1977).
6. E. Yablonovitch and J. Goldhar, *Appl. Phys. Lett.* 25, 580 (1974).
7. S.L. Shapiro (ed.): *Ultrashort Light Pulses*, Topics in Applied Physics, Vol.18 (Springer, Berlin, Heidelberg, New York 1977).
8. D.S. Frankel, Jr., *J. Chem. Phys.* 65, 1696 (1976).
9. R.S. Taylor, T.A. Znotin, E.A. Ballik and B.K. Garside, *J. Appl. Phys.* 48, 4435 (1977).
10. T.F. Deutsch and S.R.J. Brueck, to be published.
11. F. Keilmann, *Appl. Phys.* 14, 29 (1977).
12. The measured energy deposited with pump pulses of varying duration in the picosecond range will be discussed in a forthcoming paper. H.S. Kwok and E. Yablonovitch, to be published.
13. The scan in Fig.5(c) was actually taken with the P(28) line of the CO<sub>2</sub> laser since the  $\nu_3$  resonance was temperature shifted by preheating. All other scans were made at P(20).
14. The usual condition for adiabatic decay of a given level population in  $\Delta\omega/\Delta\omega_L \gg 1$  where  $\Delta\omega$  is the frequency mismatch and  $\Delta\omega_L$  is the laser linewidth.
15. J.G. Black, E. Yablonovitch, N. Bloembergen and S. Mukamel, *Phys. Rev. Lett.* 38, 1131 (1977).
16. The anharmonic shift observed by W. Fuss, J. Hartmann, and W.E. Schmid, *Appl. Phys.* 15, 297 (1978), is consistent with the deposited energy being distributed among all the modes rather than localized in  $\nu_3$ .