THE COLLISION INDUCED INCREASE IN THE MULTIPLE PHOTON ABSORPTION IN POLYATOMIC MOLECULES

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The results reported herein show that collisions of a nonabsorbing buffer gas with some polyatomic molecules cause an increase in the average number of photons absorbed. The experimental work to date has centered on these effects in SF_6.

Two basic experiments were done. First, to compare the effect of different buffer gases on a single collision basis, the nonabsorbing diluent gas (M) was added to SF_6 (constant pressure of 0.1 torr) at a pressure which gave a mean time between SF_6-M collisions (τ) of 100 ns. The character of M was varied (H_2, D_2, CH_4, He, ..., Xe), but the partial pressure of M was always adjusted to keep τ constant. The CO_2 laser pulse had an initial spike of 180 ns FWHM followed by a 2 μs tail. The energy transmittance through the cell was the quantity measured. Figure 1 shows the results. The high fluence (1 J/cm^2) data show that the nature of the collision partner has no effect on the absorption coefficient. However, at moderate to low fluence levels (100 mJ/cm^2 or smaller) the larger the collision partner (hard sphere collision cross section) the greater the absorption coefficient in SF_6. This trend is similar to the one seen in near-resonant intramolecular V-V exchange in SF_6 [see Knudtson and Flynn, JCP 58, 1467 (1973)].

The second experiment involved the actual diluent pressure dependence of the SF_6 absorption cross section. The SF_6 pressure was set at 0.1 torr and the partial pressure of M was varied from approximately 1 to 100 torr. Again, at the high fluence levels, no effect was observed. However, at the low fluence levels, there was a dramatic increase in the absorption cross section.

For example, at 70 mJ/cm^2, the average number of photons absorbed per molecule in a xenon diluent went from < 3 at 1.5 torr Xe added to more than 12 at 100 torr. Figure 2 shows the results of this experiment for a xenon diluent.

The explanation of this phenomenon is only at the qualitative stage. Rotational relaxation of molecules into states which are depleted by the radiation field seems to be the most plausible at present. However, collision induced intramolecular V-V transfer has not been eliminated from consideration. Both processes are consistent with the results of Fig. 1. On the other hand, at high pressure and for light collision partners, V-T processes are clearly contributing to the increase in the number of photons absorbed.

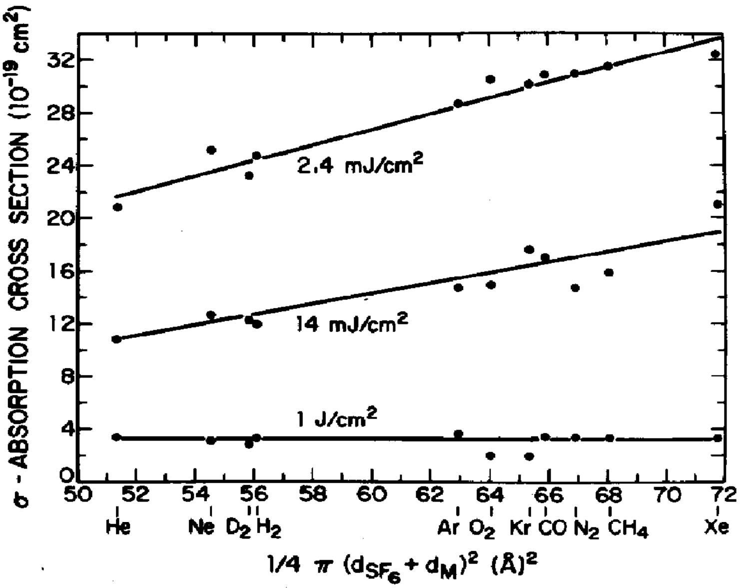

Figure 1. The variation in the cross section for absorption in SF_6 of the P(20) CO_2 laser frequency as a function of the size of the collision partner expressed as 1/4 Π $(d_{SF_6} + d_M)^2$ for three different laser fluence levels. The d_{SF_6} and d_M are Lennard-Jones hard sphere collision diameters.

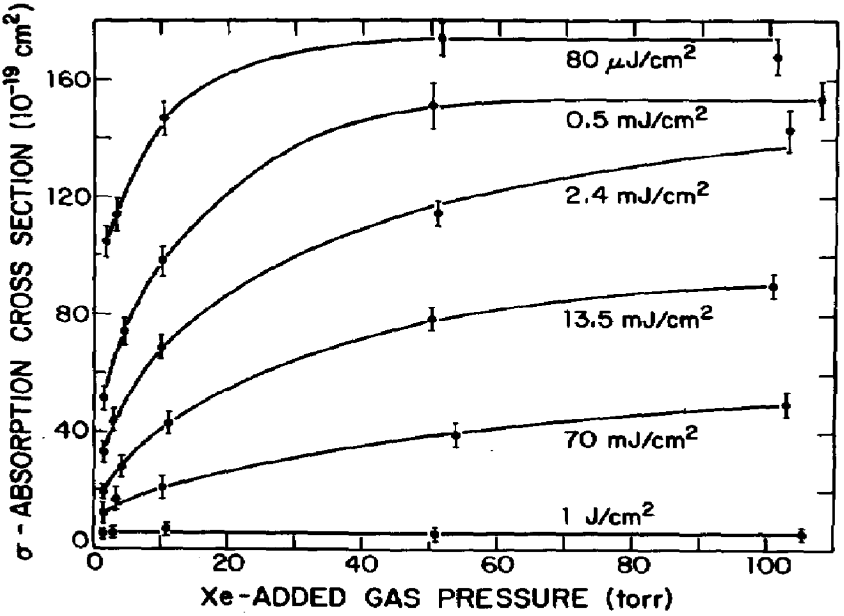

Figure 2. The change in the cross section for absorption in SF_6 of the P(20) CO_2 laser line as the pressure of Xe is increased. (SF_6 pressure = 0.1 torr).