Appl. Phys. B 40, 39–42 (1986)

Applied Physics B Photophysics and Laser Chemistry

CO_2-Laser-Induced Multiphoton Absorption of CF_2Cl_2

Collisional Effects

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Received 4 February 1985/Accepted 9 November 1985

Abstract. Energy absorption by CF_2Cl_2 from an intense TEA CO_2 laser pulse is measured as a function of the pressure of CF_2Cl_2 and the pressure of Ar bath gas for different laser energy fluences. The fraction of the molecules excited by the laser field and the average energy of the molecular ensemble are determined by a simple experimental method.

PACS: 82.50, 33, 35

In recent years infrared-laser-induced dissociation of CF_2Cl_2 has been extensively investigated. A principal aim of these studies has been to examine the competition between different reaction pathways and the energy partitioning in the resultant primary fragments [1–9]. This molecule has also been of substantial interest in several isotope separation experiments for the production of ^{13}C [10–13] and ^{37}Cl [11–14] enriched products.

In the present paper multiphoton energy absorption by CF_2Cl_2 from TEA CO_2 laser radiation, up to the dissociation threshold, has been studied by calorimetric measurements of energy transmission by the sample. The magnitudes reported are the average excitation level and the gross average absorption cross section of the laser-excited molecules.

For a correct determination of these quantities one should know the fraction of molecules which interact with the laser field (q). This fraction has been measured for some molecules by different methods [15–20]; in this experiment we use the method proposed by Kolomilskii et al. [20], which makes it possible to determine q by saturating the energy absorption when an inert gas is added to the sample.

Experimental

The experimental arrangement is shown in Fig. 1. A home-made TEA CO_2 laser (4 J, 200 ns FWHM, multimode, grating tunable) was used, with power stability of the order of 10%. The laser was operated without He in order to minimize the energy contained in the tail of the pulse. The beam was collimated and intensified by a telescope formed by a CuBe mirror and a Ge lens (AR coated); the homogeneous center region of the spatial energy distribution of the beam was selected with an iris. The beam diameter (9 mm) was obtained by measuring the size of the laser burn pattern on a dark surface.

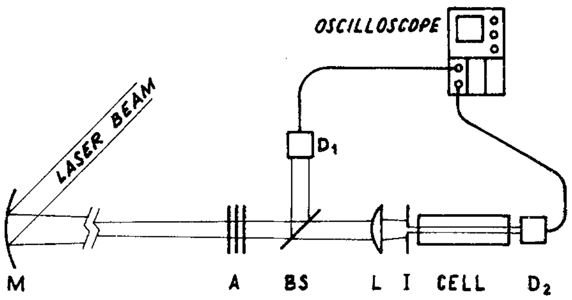

Fig. 1. Experimental set-up. (M: Cu mirror, A: CaF_2 attenuators, BS: NaCl beamsplitter, L: Ge lens, I: iris, D_1 and D_2: pyroelectric detectors)

The samples were transferred to Pyrex glass cells, with 32 mm internal diameter and lengths between 0.05 and 1.3 m, so as to keep the absorbed energy to about 10% of the incident energy. In this way all the molecules along the beam path were exposed to essentially the same conditions of energy fluence: in fact, changes of about 10% in fluence caused variations of the average number of photons absorbed per molecule, which were comprised within experimental error. Nevertheless an energy absorption of about 10% is necessary for minimum precision due to the sensibility of the detection system.

The fluence was varied by using CaF_2 calibrated attenuation flats.

The incident and transmitted energy were measured simultaneously by calibrated pyroelectric detectors (Gen-Tec ED-200 and ED-500, respectively) and a Tektronix 7633 oscilloscope. All the absorption data were obtained by normalizing, averaging five measurements, and corrected by losses in the NaCl cell windows.

CF_2Cl_2 (Matheson, >99.0% purity) and Ar (Matheson, >99.995% purity) were used without further purification. Pressures were monitored on capacitance manometers (MKS Baratron). When mixtures were introduced in the cell, CF_2Cl_2 and Ar were allowed to scramble during 15 min before starting absorption measurements, in order to ensure reproducibility of results.

Discussion

The TEA CO_2 laser was tuned to the $P(36)$ line of the 10.6 μm CO_2 band, coincident with the R branch of the CF_2Cl_2 ν_8 mode (CCl_2 – asymmetric stretching). As can be seen from Fig. 2, the average number $\langle n \rangle$ of photons absorbed per molecule (total number of absorbed laser photons/number of irradiated molecules in the ground state) is constant at a low pressure of CF_2Cl_2 up to about 0.7 Torr; this result can be due to the fact that collisions during the laser pulse are not important, at least within experimental error. The increase of $\langle n \rangle$ with increasing pressure can be explained by two effects: 1) the hole in the Boltzmann distribution of molecules over the rotational levels of the ground vibrational state, created by laser excitation (rotational bottleneck) [21], is filled more quickly by a greater number of collisions during the laser pulse, without modifying the real average excitation level; 2) at the same time a strong intermolecular V–V energy exchange takes place, which not only involves more molecules in the absorption process but also changes the average energy of excited molecules. The average number of photons absorbed per molecule takes a constant value in the range 6 to 30 Torr. CF_2Cl_2 carefully measured at fluences of about 0.5 and 0.3 J/cm² (not shown in Fig. 2); this saturation of $\langle n \rangle$ suggests that all the CF_2Cl_2 molecules in the ground state (38%) become resonant with the field, during a CO_2 laser pulse.

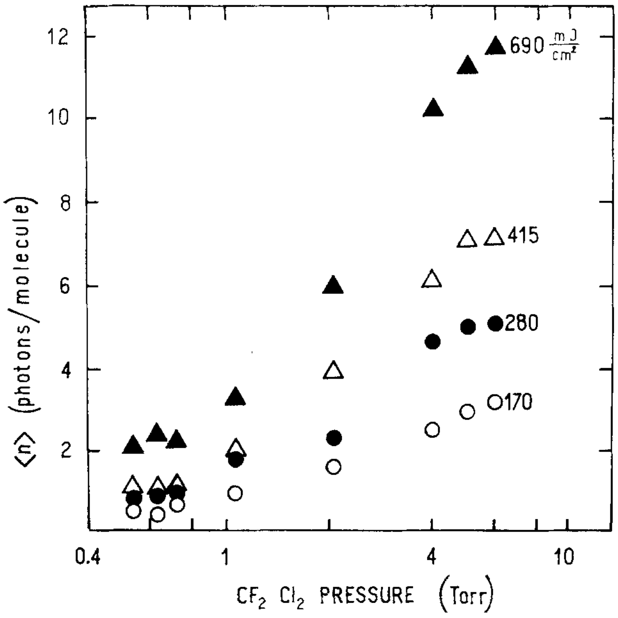

Fig. 2. The average number of photons absorbed per molecule of CF_2Cl_2 as a function of the CF_2Cl_2 pressure, at different laser fluences

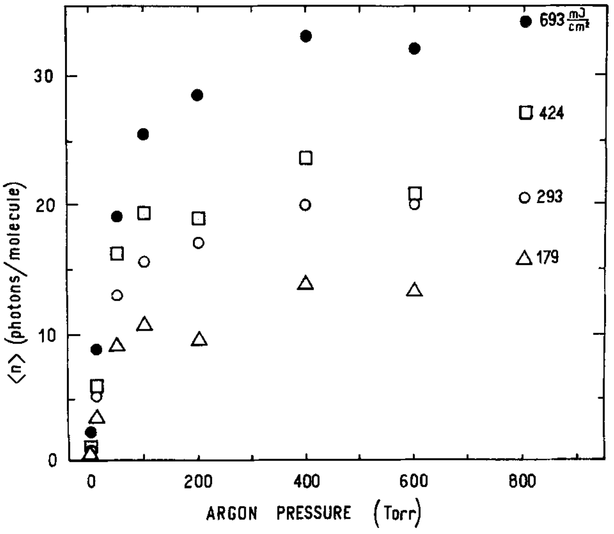

Fig. 3. The average number of photons absorbed per molecule of CF_2Cl_2 as a function of the argon pressure, at different laser fluences. The CF_2Cl_2 pressure is 0.6 Torr

The effect of adding Ar to low pressure CF_2Cl_2 samples is displayed in Fig. 3. The results can be considered collision free, for collisions CF_2Cl_2-CF_2Cl_2, only in the sense discussed above for Fig. 2, as, at the CF_2Cl_2 pressure used only 0.5 collisions take place during the laser pulse. Therefore the increase of $\langle n \rangle$ with increasing inert gas pressure can be associated mainly with multiple filling of the rotational hole during the laser pulse. Similar results have been obtained for several other molecules [22, 23].

Near saturation an important difference distinguishes the experiments described previously: when CF_2Cl_2-CF_2Cl_2 collisions take place a fast intermolecular V–V energy exchange modifies substantially the absorption process which is not affected by V–T relaxation ($P\tau_{V-T} \sim 20\,\mu s$ Torr) [24]; for the experimental conditions of Fig. 3 instead, the only important effect might be V–T deactivation of CF_2Cl_2 by CF_2Cl_2-Ar collisions. Multiphoton V–T relaxation at low pressure of Ar is negligible during the laser pulse (P_{Ar}, $\tau_{V-T} \sim 200\,\mu s$ Torr) [24] and might only influence the absorption at high pressures of inert gas (>100 Torr).

Other collisional effects, such as dephasing of coherences of the lower states and intramolecular energy redistribution, can play a role in IR multiphoton absorption but are considered a perturbation in this experiment.

From the curves of Fig. 3 the time of rotational hole filling can be estimated when collisions with Ar take place (τ_h, at 0.6 Torr CF_2Cl_2) assuming that the hole burned in the original molecular distribution is filled in a pulse period, when an increase of Ar pressure from zero doubles the average number of photons absorbed per molecule [25]. The result obtained is $P_{Ar}\tau_h \cong 1\,\mu s$ Torr. The conventional phenomenological relaxation time constant can be obtained from [26]

$$\tau_r = \tau_h \cdot q/(1-q),$$

where q is the fraction of laser excited molecules. For the conditions of this experiment, this relation gives a typical value $(P\tau_r)_{Ar} = 50$ ns Torr.

The fraction q of the molecules excited by the resonant laser field can be determined directly from Fig. 3, assuming that V–T relaxation does not substantially modify the multiphoton-absorption process; as a result the energy absorbed per molecule, E_{AM}, (or average number of photons absorbed per molecule, $\langle n \rangle$) in pure collisionless CF_2Cl_2 is nearly equal to the energy absorbed when collisions with buffer gas take place.

If saturation implies that all of the molecules in the beam path interact with radiation during the laser pulse, then q might be obtained from the energy absorbed by the sample at $P_{Ar} = 0$ and the energy absorbed at $P_{Ar} = P_{SAT}$ as

$$q = E_{AM} \cdot N/E_{AM} \cdot N_0 = \langle n \rangle_0 / \langle n \rangle_{SAT},$$

where $q = N/N_0$ is defined as the ratio between the number N of excited molecules and the total number of irradiated molecules N_0 with

$$\langle n \rangle_0 = \langle n \rangle \; (P_{Ar} = 0) \quad \text{and}$$

$$\langle n \rangle_{SAT} = \langle n \rangle \; (P_{Ar} = P_{SAT}).$$

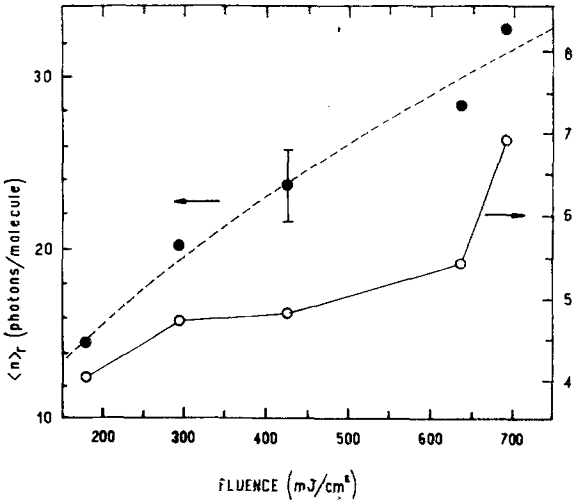

Fig. 4. The real average number of photons absorbed per molecule of CF_2Cl_2 at 0.6 Torr, $\langle n \rangle_r$, vs. laser fluence (*black circles*). The points were fitted to a function ϕ^b. The error bar corresponds to the 90% confidence level. The *white circles* corresponding to the fraction q of absorbing molecules have been arbitrarily joined by a *solid line*

The determination of q by this method is limited by multiphoton V–T relaxation of CF_2Cl_2 in collisions with the buffer at saturation pressures.

Furthermore the real average number of photons absorbed per molecule $\langle n \rangle_r = E_{AM}/h\nu$, where $h\nu$ is the photon energy, is calculated from

$$\langle n \rangle_r = \langle n \rangle_0 / q = \langle n \rangle_{SAT},$$

under the assumption that only molecules in the ground state interact with the laser pulse.

Figure 4 shows $\langle n \rangle_r$ and q as a function of the laser fluence (ϕ) at 0.6 Torr CF_2Cl_2. As can be observed, the $\langle n \rangle_r(\phi)$ results fit well to a relation of the form

$$\langle n \rangle_r = \phi^b, \quad \text{with} \quad b = 0.55.$$

In the fitted curve the dissociation threshold fluence, $\langle n \rangle_r = 28$ infrared photons, corresponds to $0.55\,J/cm^2$.

Taking into account that absorption could be also accomplished by hot bands involving ν_4 and ν_5 [27], the values of $\langle n \rangle$ would be rather lower than those in Fig. 4. Nevertheless, as these hot bands are toward the red edge of the ν_8 fundamental, absorption through these transitions can be neglected like in the approximation used above.

The values of q obtained for CF_2Cl_2 by this method (3 to 7%) are smaller than those reported for several other molecules [21]; this result might be due to a lower small-signal absorption coefficient and to the

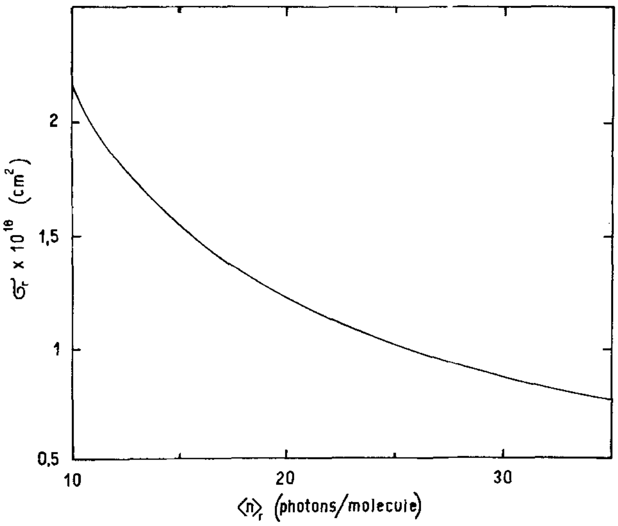

Fig. 5. Dependence of the gross multiphoton cross section on the real average number of photons absorbed per molecule of CF_2Cl_2

fact that the laser line coincides with the blue edge of the ν_8 fundamental.

For a better comprehension of the nonlinear absorption process, the gross multiphoton absorption cross section $\sigma_r = \langle n \rangle_r \cdot h\nu/\phi$ was plotted as a function of the real average energy of the molecular ensemble (Fig. 5). This average cross section takes into account the whole excitation process of the molecules, starting from the ground or thermally populated states and climbing up the internal vibrational manifold. The gross absorption cross section monotonically decreases with increasing vibrational energy, suggesting that the net absorption for a molecule from levels in the quasi-continuum decreases as the vibrational number increases.

Acknowledgements. The authors wish to thank Dr. E.J. Quel for supporting this work, J. Castiglioni and J. Silvestri for technical assistance in the construction of the laser and M. Seifert for his glass works.

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