

IR MULTIPLE-PHOTON EXCITATION IN CDF₃ PROBED BY A PULSED OPTOACOUSTIC TECHNIQUE

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Summary

A pulsed optoacoustic (OA) technique for measuring energy absorbed by weakly absorbing molecules at low pressure is described. The multiple-photon excitation behaviour in fluoroform-*d* (CDF₃) was examined via the OA technique in order to elucidate the dependence of the absorption cross-section on various experimental parameters. Measurements of absorbed energy in neat CDF₃ and in mixtures with argon provided information regarding laser fluence and pressure regimes, this being required to optimize the multiple-photon excitation and dissociation processes.

1. Introduction

The nature and characteristics of the photophysical and photochemical processes induced by IR multiple-photon excitation (MPE) of polyatomic molecules have triggered extensive experimental and theoretical investigations concerning the nature of the excitation and subsequent multiple-photon dissociation (MPD) process. Both quantum mechanical and classical models have been used to describe the processes. The dissociation process has been studied experimentally as a function of laser frequency, fluence, pulse duration and gas pressure [1, 2]. Measurements of dissociation rates are time consuming and provide little information regarding the absorption process at energy densities below the dissociation threshold. However, conventional energy absorption measurements by the transmission technique are difficult to perform in the case of weakly absorbing systems at low gas pressures. The pulsed optoacoustic (OA) technique [3] is a simple and powerful tool for rapid measurement of such small absorption. In the present work, we have examined the potential of this technique and its application in parametric studies of MPE and MPD in fluoroform-*d* (CDF₃) systems.

2. Principles

The absorption cross-section σ can be measured by the transmission technique utilizing a parallel laser beam [1]. By measuring both incident and

transmitted radiant energies (E_{in} and E_{out} respectively), σ can be obtained from the Beer-Lambert law:

$$\sigma = \frac{1}{NL} \ln\left(\frac{E_{in}}{E_{out}}\right) \quad (1)$$

where N is the number density of the absorption and L is the optical path length. However, this technique suffers from the following two limitations [4].

(a) The small absorptions (corresponding to $\sigma NL \approx 10^{-4} - 10^{-5}$) often associated with MPE studies (i.e. $E_{in}/E_{out} \approx 1$) necessitate very precise energy measurements, and these are almost impossible with current instrumentation.

(b) It is very difficult to obtain the high fluence required for MPE in a sufficiently long parallel beam configuration. The optical material damage problem associated with such beams makes their use impossible.

But with the use of the OA technique, such problems can be eliminated conveniently. The interaction of the laser pulse with the absorber raises some of the molecules to a vibrationally excited state along its path. This vibrational energy eventually degrades to translational energy through V-T relaxation. This heating initiates an outward travelling pressure wave which is detected by the microphone and the resulting electrical signal is recorded.

Thus a cross-section is obtained from the OA technique which is a direct measure of the absorbed energy ($E_{abs} = E_{in} - E_{out}$) by utilizing the appropriate form of eqn. (1):

$$\sigma \approx \frac{1}{NL_M} \frac{E_{abs}}{E_{in}} \quad (2)$$

where the approximation applies for small absorptions. A modern microphone (a parallel plate condenser) conveniently measures $E_{abs} \approx 10^{-2} - 10^{-6}$ J so that a very small cross-section can be readily measured for a large range of E_{in} . The quantity L_M is the length of the absorber viewed by the microphone (of length L_M), and this is fairly small (a few millimetres). With appropriate focusing optics, a high fluence can be generated over this small distance at the centre of the measuring cell. Therefore, the problem associated with high fluence and material damage can be eliminated.

Approximating the acoustic source as an infinite line source along the cylindrical axis, the process of wave propagation can be derived from the equation of mass, momentum and energy conservation, neglecting the molecular diffusion effects [5]. The pressure wave propagates as a linear acoustic wave according to the equation

$$\nabla^2 P - C^{-2} \frac{\partial^2 P}{\partial t^2} = - \frac{\gamma - 1}{C^2} \frac{\partial H}{\partial t} \quad (3)$$

where $H(r,t)$ is the rate of heat deposition per unit volume, $P(r,t)$ is the

departure from ambient pressure in the wave, C is the velocity of sound and γ is the ratio of the specific heats for the gas. The amplitude P is proportional to the amplitude of the driving term $\partial H/\partial t$. Increasing the total thermal energy input per unit volume (given by $\int H dt$) increases H proportionately, because the evolution of H which depends on collision occurs on a fixed time scale if the pressure in the cell is kept constant. By the linearity of eqn. (3), P will also increase in proportion to the thermal energy. Since the microphone is a parallel plate condenser, the displacement of the diaphragm of the microphone, resulting in the voltage signal V , will be proportional to P . Therefore it follows that

$$E_{\text{abs}} = KV \quad (4)$$

where K is a calibration factor which is specific to the cell and microphone combination. Although it is independent of laser intensity, it may depend on the nature and pressure of the absorber.

The acoustic pulse originating from the irradiated region in front of the microphone arrives first and initiates the observed response. Next there are signals due to absorptions at the entrance and exit windows which are observed over a longer time scale which depends on the distance of the windows from the microphone. A third category of signals arises from the reflections and cell resonances. Therefore, the microphone response to the acoustic impulse generated via vibrational relaxation subsequent to the MPE process resembles a damped sine wave. A variety of procedures have been used in the literature to characterize an OA signal: the integrated area of the first half-cycle [3, 4], the height of the first peak [7] and the peak-to-trough height of the first cycle [6].

We have found that extreme care has to be taken to make sure that vibrational relaxation is complete within the microphone-response time (about 75 μs) for any reliable investigation to be performed. In such a case, the height of the first peak is most indicative of the energy E_{abs} absorbed by the system. This requirement was investigated after studying the strong correlation between the peak-trough asymmetry and the vibrational relaxation rate of the system, which had been observed by Seder and Weitz [8].

3. Experimental details

The non-resonant aluminium OA cell had an overall length of 10 cm and a radius of 1.5 cm. A Knowles BT-1759 electret microphone (sensitivity, 1 mV μbar^{-1}) was centrally mounted at about 1 cm from the long axis of the cell. This broad band subminiature (7.92 mm \times 5.59 mm \times 2.28 mm) condenser microphone exhibits a relatively flat response across most of the audible frequency range. The microphone response was measured to be linear when the microphone-integral amplifier combination was biased to 1.5 V.

All the investigations were performed with the collimated (cross-sectional area, 0.7 cm^2) unfocused output of a Lumonics 103-2 TEA CO_2 laser. The output pulse consisted of a gain-switched spike of 100 ns (full width at half-maximum) containing approximately two thirds of the pulse energy followed by a tail of about $1 \mu\text{s}$ (full width). Extreme care was taken to maintain a constant beam geometry, position and direction through the cell [9]. The laser fluence was varied by attenuating the beam with appropriate thicknesses of polythene sheet. The microphone output was recorded by a Biomation 8100 transient recorder and transferred to a signal averager (Nicolet 1170) for repetitive measurements. The output of the averager was either displayed on an oscilloscope and photographed or plotted using a $Y-T$ chart recorder.

A commercial sample of CDF_3 (Merck, Sharp and Dohme; atom fraction $D \approx 98\%$) was used after purification by trap-to-trap distillation. Argon (Airco, purity better than 99%) was used as received. Typically, 16 - 64 pulses were used in each experiment. A scheme of the experimental arrangement is shown in Fig. 1.

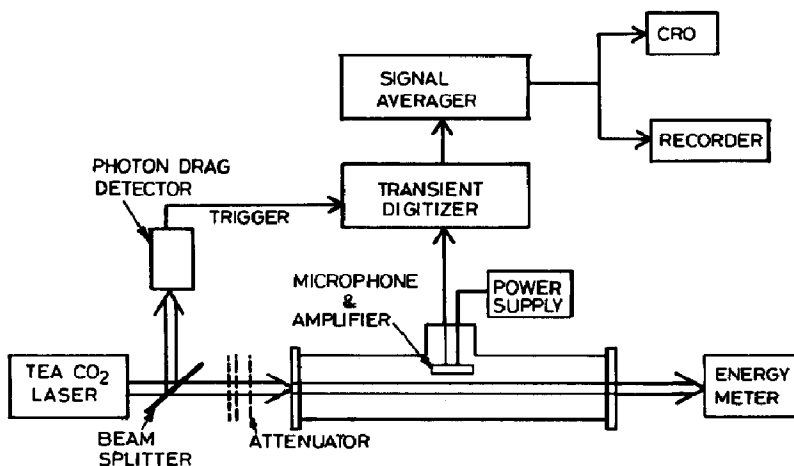


Fig. 1. Scheme of the experimental set-up.

4. Results and discussion

The IR absorption band of CDF_3 (cf. Fig. 4(d) below) has strong P and R branch peaks at 10.21 and $10.31 \mu\text{m}$ resulting from the C-D wagging (ν_5) mode, which can be resonantly pumped by a CO_2 laser. A typical OA signal is shown in Fig. 2 for 10 R(26) excitation of 2 Torr CDF_3 . To ascertain that the first peak does indeed come from the irradiated volume in front of the microphone, the microphone was translated perpendicularly to the cell axis. The distance of the microphone from the beam (i.e. the cell axis) was plotted *versus* the arrival time of the first peak (cf. Fig. 3). How-

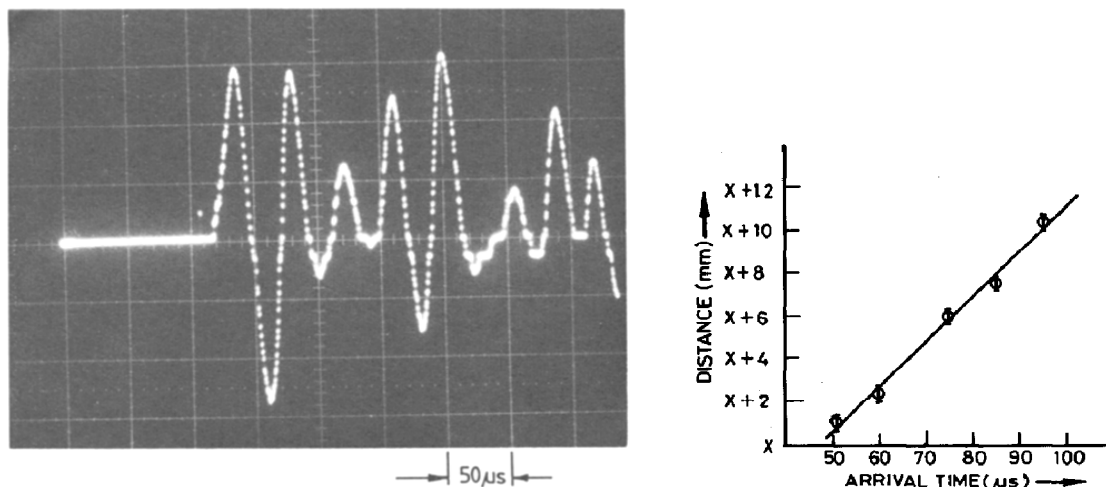


Fig. 2. A typical OA signal (10 R(26) excitation of 2 Torr CDF_3 with 10 mJ cm^{-2} fluence).

Fig. 3. Dependence of the arrival time of the OA signal for CDF_3 ($P = 2$ Torr) as a function of the distance between microphone and laser beam axis (X is an arbitrary position; the slope of the line is $(2.25 \pm 0.2) \times 10^4 \text{ cm s}^{-1}$).

ever, as suggested by Chin *et al.* [4] such a plot can be used to measure the velocity of sound in an absorber gas in neat form or in a mixture with other gases. As the first peak comes from the irradiated volume viewed by the microphone, the slope of the line ($2.25 \times 10^4 \text{ cm s}^{-1}$) represented the velocity of sound in CDF_3 , which agrees well with our estimated value of $2.04 \times 10^4 \text{ cm s}^{-1}$.

4.1. Multiple-photon excitation and dissociation spectra

The wavelength and fluence dependence of MPE for 2 Torr CDF_3 are shown in Fig. 4. It can be seen that the MPE spectrum of CDF_3 appears to follow the small signal absorption spectrum but with some apparent broadening as the fluence increases. Addition of argon to the system improves the energy absorption for a given fluence (compare the spectra in Figs. 4(a) and 4(b)). Generally, for polyatomic molecules such as SF_6 , it has been observed that the MPE spectrum shifts to lower frequencies (known as a "red shift") relative to the small signal absorption spectrum and this shift also increases as the fluence is increased. This red shift has been interpreted as arising from the anharmonicity of the pumped mode. High fluence absorption involves excitation up several rungs of the anharmonic ladder with the resonant frequency quickly becoming mismatched. A somewhat lower frequency that matches an intermediate transition, rather than $\nu = 1 \leftarrow 0$ (low fluence absorption spectrum), is optimum because it averages the mismatch over many levels. This lack of red shift in CDF_3 probably indicates that anharmonicity does not play any important role in the

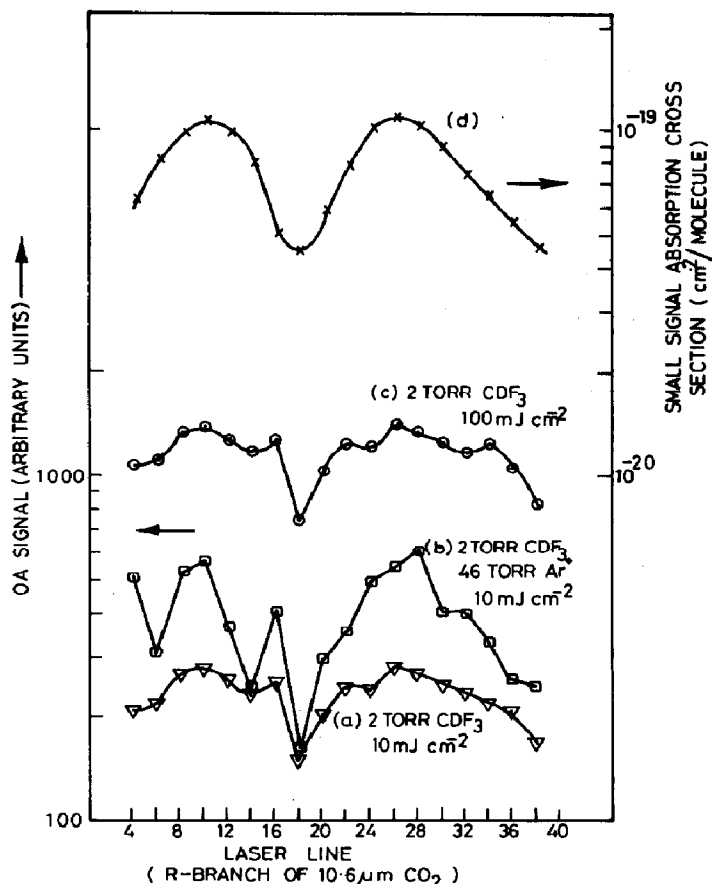


Fig. 4. Wavelength and fluence dependence of MPE for neat CDF_3 and $\text{CDF}_3\text{-Ar}$. For comparison, the small signal absorption in CDF_3 is also shown (top trace).

pumping of the ν_5 mode of CDF_3 , since this has a very small anharmonicity constant ($X_{55} = -0.25 \text{ cm}^{-1}$ compared with $X_{33}(\text{SF}_6) = -2.8 \text{ cm}^{-1}$) [10, 11].

As expected, there was no red shift even in the MPD spectrum of CDF_3 . The MPD spectrum was investigated by irradiating a static sample with a predetermined number of pulses using a focused CO_2 laser beam of requisite fluence and monitoring the CDF_3 decomposition by IR spectrometry. In general, IR spectrometry, gas chromatography and mass spectrometry are utilized in MPD studies, but we have also used the pulsed OA technique. The experimental arrangement is modified to suit the decomposition studies. At first the OA signal is recorded with any particular exciting CO_2 laser line in an unfocused beam of low fluence. Then the fluence is increased by means of a focusing lens to initiate the dissociation. After a predetermined number of dissociating pulses, the OA signal is again recorded under conditions identical with those of the previous measurements. The decrease in OA signal provides information on the MPD process. By this technique, the MPD "action spectrum" can be quickly generated. Such measurements agreed well

with the results of static cell photolysis followed by conventional IR spectrometry.

4.2. Effect of buffer gas

The OA signal was monitored as a function of bath-gas (argon) pressure at the exciting wavelength (10 R(10)) with a fluence level of 10 mJ cm^{-2} . The CDF_3 pressure was kept constant at 2 Torr for all experiments. The signal increases with increasing pressure in the low pressure region and then decreases with a further increase in bath-gas pressure (*cf.* Fig. 5). Similar behaviour was found in MPD studies of CDF_3 [12] and also of similar molecules [2], which can be explained qualitatively in terms of competition between rotational hole filling and collisional deactivation. Rotational hole filling is the process by which collisions repopulate rotational levels, which have been depopulated by interaction with the laser pulse, thereby increasing the number of molecules which can interact with the laser pulse. In Fig. 5, the initial increase is due to the dominance of rotational hole filling at low argon pressures. Collisional deactivation is the process by which energy is removed from vibrationally excited molecules. It occurs primarily via V-T, V-R and V-V relaxation processes. The efficiency with which energy is removed depends on the collision partner. The decrease in signal at high argon pressures is due to the dominance of collisional deactivation and the pressure at which the curve turnover reflects the competition between the rotational relaxation process, which promotes excitation, and V-T relaxation, which reduces the excitation efficiency.

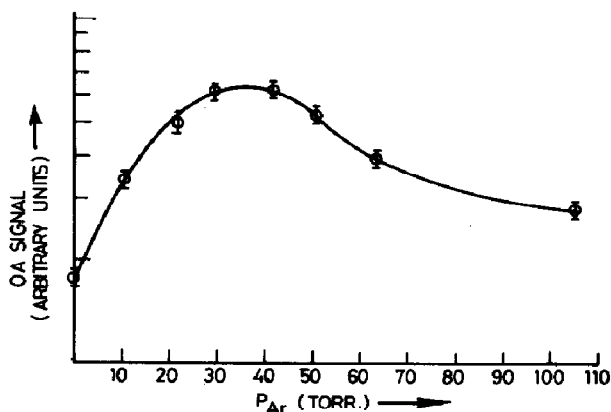


Fig. 5. Pressure dependence of MPE in 2 Torr CDF_3 buffered with various amounts of argon (fluence at exciting 10 R(10) line, 10 mJ cm^{-2}).

4.3. Effect of fluence

Fluence-dependent measurement of energy absorption in the system can lead to information on the multiple-photon absorption cross-section σ . Unlike the small signal absorption cross-section, which is independent of fluence, σ is a monotonically decreasing function of fluence Φ . The cross-section $\sigma(\Phi)$ can be determined by integrating the expression

$$\frac{d\Phi}{\Phi} = -\sigma(\Phi)N dZ \quad (5)$$

where N is the number density and Z is the optical path coordinate, provided the functional dependence of σ on Φ is known. Assuming a power-law-dependent model [13], where $\sigma(\Phi)$ is given by

$$\sigma(\Phi) = \text{constant} \times \Phi^{-q} \quad (0 \leq q < 1) \quad (6)$$

the energy absorption by the system behaves as $E_{\text{abs}} \propto \Phi^{1-q}$. The value $q = 0$ corresponds to the well-known Beer's law (eqn. (1)) and σ (independent of Φ) becomes the small signal absorption cross-section. Figures 6 and 7 represent such parametric studies for CDF_3 (about 2 Torr) and a CDF_3 -Ar (2:20 Torr) mixture using two different exciting laser lines corresponding to the P and R branch maxima of its ν_5 mode. As can be seen from the figures, energy absorption occurs very efficiently in the mixture with argon compared with neat CDF_3 and the slope increases from 0.8 to 0.9. The deviation

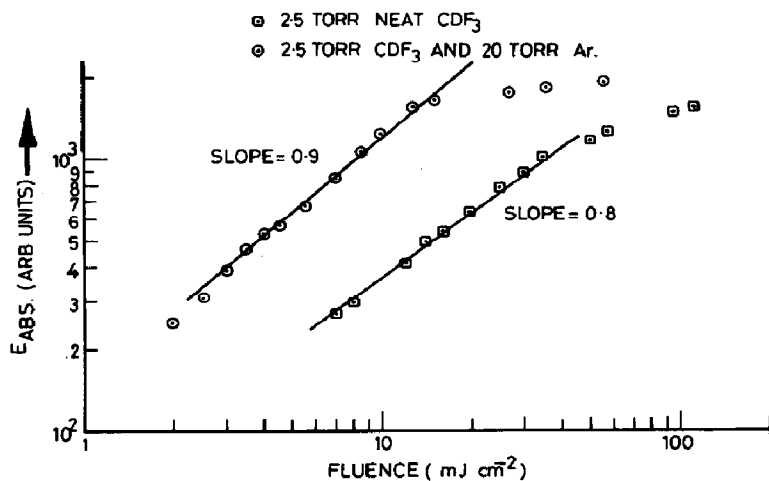


Fig. 6. Plot of energy absorbed vs. fluence for 10 R(10) excitation.

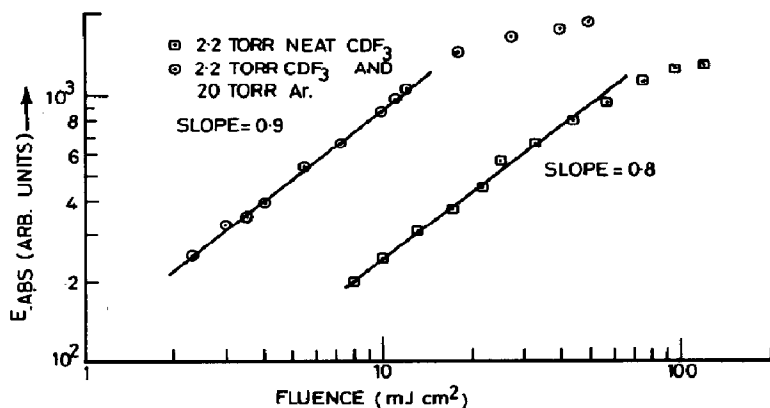


Fig. 7. Plot of energy absorbed vs. fluence for 10 R(26) excitation.

at higher fluences arises because of saturation of the microphone signal. Therefore, the q for neat CDF_3 and the CDF_3 -Ar mixture, 0.2 ± 0.02 and 0.1 ± 0.02 respectively, describe the variation in $\sigma(\Phi)$ with fluence in the working range $0 < \Phi < 0.2 \text{ J cm}^{-2}$, which is in good agreement with the literature value [10]. The lower value of q with increasing system pressure indicates that enhancing the number of collisions removes the bottleneck for MPE.

5. Conclusions

Pulsed OA spectroscopy is a very simple and powerful technique, since one has to monitor only the height of the first acoustically generated peak. This probe is best used when the vibrational relaxation time of the system is significantly faster than the acoustic response of the system.

With this technique, we have investigated various aspects of MPE and MPD in CDF_3 and CDF_3 -Ar. The absence of a red shift in the MPE and MPD spectra can be understood on the basis of the very small anharmonicity of the pumped mode. The fluence-dependent cross-section and the effect of collisions on it can be explained with a power-dependent model. The identification of such fluence and pressure regions should provide information valuable for the optimization of MPE and MPD processes.

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