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Buffer-gas influence on multiphoton absorption and dissociation in different gas mixtures

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Abstract

Buffer-gas influence on the multiphoton absorption and dissociation in different mixtures was investigated using the simple method based on the empirical and theoretical vibrational energy distribution, generalized coupled two-level model and photoacoustic cell especially designed for low pressures studies. Energy transfer efficiency was analyzed by means of pulsed photoacoustic spectroscopy technique. Collisional effects of buffer-gas (Ar) pressure are introduced to enhance the absorption and relaxation characteristics of irradiated absorbing molecules (SF_6). Functional behavior of mean number of absorbed photons per molecule $\langle n \rangle_{total}$ and a dependence on buffer-gas pressure (p_{buff}) which enables us to confirm or predict some physical and chemical processes are presented. Limitation of proposed model was analyzed depending on both gas pressure and laser fluence. Results are compared with other previously obtained by the same experimental technique but for different absorber and different molecular buffer-gas.

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Keywords: Buffer-gas; Energy transfer; Photoacoustic spectroscopy; Laser

1. Introduction

Detailed knowledge of collisional relaxation processes such as vibrational or rotational relaxation of polyatomic molecules in gas mixtures is essential for accurate prediction of molecular behavior during and after the intensive multiphoton absorption (MPA). This kind of knowledge can be used for a variety of applications including infrared (IR) spectroscopy, atomic and molecular physics, chemistry and environmental studies. Many experimental techniques can be used for this type of investigation, but pulsed photoacoustic spectroscopy was found to be the most sensitive and suitable for obtaining quantitative results with good quality [1–5]. It possesses all advantages of common techniques such as good spatial, temporal and spectral resolution [6–9].

Different methods can be adopted for the analysis of the effects that result from collisional transfer of energy between molecules. Our goal in this paper is to show simple empirical method for prediction of vibrational energy distribution and dissociation, which are collisionally induced or enhanced. Also, our aim is to show how the theory of generalized coupled two-level (GCTL) model [1,5] can (or cannot) be used to calculate precise absorption efficiency data for an irradiated molecules.

2. Experimental

IR pulsed photoacoustic experimental set-up used here has been previously described in detail [5,10–14]. In brief, TEA CO_2 laser was used, tuned on 10P(16) line, with total output fluence in the range of 0.2–0.5 J/cm^2 for excitation and 0.6–1.4 J/cm^2 for dissociation regime. Laser beam

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had "top hat" spatial profile, in pulsed regime with 45 ns FWHM and 2 μs tail. Nonresonant 18.5 cm long photoacoustic cell, specially designed for the low pressure MPA monitoring, was utilized with built-in Knowless capacitive microphone. Ambient temperature was approximately 300 K. Buffer-gas (Ar) pressure was changed in the range 1–133 mbar for excitation, 1–100 mbar for dissociation regime and absorber pressure was kept constant at 0.46 mbar. Total mixture pressure inside the cell was measured with CCM capacitive pressure gauge.

In our analysis, GCTL model was used to fit experimental results obtained for $\langle n\rangle_{\text{total}}$ and calculate its functional dependence $\langle n\rangle_{\text{total}} = f(p_{\text{buff}})$, where p_{buff} is the pressure of buffer-gas (Ar). The basic equation of GCTL model for SF_6–buffer-gas mixture investigation in most suitable form

$$\langle n\rangle_{\text{total}}(p_{\text{buff}}, \Phi) = \{[1 - \exp(-a \cdot p_{\text{buff}})] \cdot b\}^{1/3} \cdot (\sigma_0 \Phi)^{2/3}, \tag{1}$$

where a and b are fitting parameters corresponding to the number of collisions in the given gas mixture and fraction of molecules directly involved in the laser field–molecule interaction, respectively. It is well known that, especially working with gas mixtures in collisional regime and with long tail pulses, $\langle n\rangle_{\text{total}}$ does not have to be equal to the number of photons stored in the vibrational modes of irradiated molecules ($\langle n\rangle_{\text{v}}$) [5]. As shown in previous study [5], $\langle n\rangle_{\text{total}}$ can be written as a sum of two main parts: $\langle n\rangle_{V-T}$, originating from V–T relaxation and $\langle n\rangle_{\text{v}}$ which consists of laser fluence ($\langle n\rangle_{\Phi}$) and R–R relaxation influence ($\langle n\rangle_{\text{rot}}$) on MPA. These partial values can be calculated using obtained rotational relaxation times and fitting parameters from Eq. (1) (procedure explained earlier [5,13]). Also, if one knows functional behavior of $\langle n\rangle_{\text{total}}$ at higher pressure, it could serve as a prediction for strong dissociation and/or (V–V) energy transfer processes. Simplifying our case, knowing that part of energy stored in the pulse tail is less than 10% of total energy of the laser pulse, we will further assume that $\langle n\rangle_{\text{total}} = \langle n\rangle_{\text{v}}$. If that is the case, one can use GCTL model combined with other spectroscopy methods to analyze MPA processes calculating partial values of $\langle n\rangle_{\text{total}}$.

In order to obtain vibrational state distribution, one has to solve rate equations, which describe the rate of population and depopulation of an arbitrary level, through the state density of the neighboring levels [1]:

$$\dot{N}_n = \sigma_{n,n-1} I \left(N_{n-1} - \frac{\rho_{n-1}}{\rho_n} N_n \right) - \sigma_{n,n-1} I \left(N_n - \frac{\rho_n}{\rho_{n+1}} N_{n+1} \right) \tag{2}$$

where N_n represents the population of the nth level, I is the laser beam intensity, σ is the cross section for given transition and ρ is the state density. Considering the fact, that in quasicontinuum upper levels have significantly higher state density, we can approximate Eq. (2) with the simpler one in which we neglect all terms multiplied by the state density ratio, which can be analytically solved. Solution of Eq. (2) is represented by Poisson's distribution:

$$N_n = \frac{\left(\frac{\sigma I \tau_{\text{p}}}{h\nu}\right)^n}{n!} \exp\left(-\frac{\sigma I \tau_{\text{p}}}{h\nu}\right) \rightarrow N(n) = \frac{\langle n\rangle^n}{n!} \exp(-\langle n\rangle), \tag{3}$$

where I is the laser pulse intensity, τ_{p} is the laser pulse duration, σ is the absorption cross section, n is the level of excitation and at the same time number of laser field photons, $\langle n\rangle = \langle n\rangle_{\text{total}}$ is the mean number of absorbed photons per molecule and $h\nu$ is the energy of a photon. As we know from GCTL model, not all the molecules in the ensemble absorb during irradiation, but only those in optimal ro-vibrational state (ground state in our case). For low pressures, although a great majority of molecules is excited from ground level to quasicontinuum, some of them remain at first discrete level, so we have to superpose their distribution to that of highly excited molecules. Using this equation and obtained experimental results for $\langle n\rangle_{\text{total}}$ [5], it is easy to calculate dissociation yield for different laser fluences and pressures of buffer-gas.

3. Results and discussion

Experimental results for SF_6–Ar mixtures, obtained using well known procedure [1,4] and Eq. (1), are presented in Figs. 1 and 2. In Fig. 1, $\langle n\rangle_{\text{total}}$ functional dependence on buffer-gas pressure (p_{Ar}) is presented for different laser fluences Φ. For $p_{\text{buff}} < 50$ mbar (lower pressure region) strong influence of collisional processes leads to quick rise of $\langle n\rangle_{\text{total}}$ values with the pressure increment; for $p_{\text{buff}} >$ 50 mbar (higher pressure region) $\langle n\rangle_{\text{total}}$ values tend to be constant or slowly rising up to 130 mbar. Such a behavior as a consequence of collisional influence is known from the literature [1–5,15,16]. Detailed investigation shows

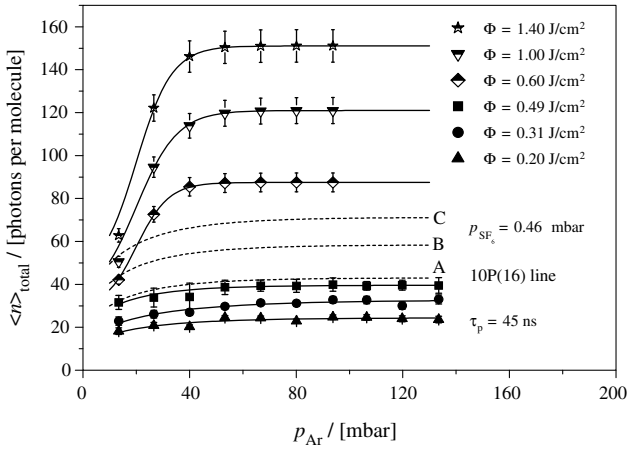

Fig. 1. Functional dependence of $\langle n\rangle_{\text{total}}$ on buffer-gas pressure (p_{Ar}) for different laser fluences Φ. The results for $\langle n\rangle_{\text{total}} = f(p_{\text{Ar}})$ obtained in a new experiment ($\Phi = 0.60$ J/cm^2, $\Phi = 1.00$ J/cm^2 and $\Phi = 1.40$ J/cm^2) are compared with older ones ($\Phi = 0.20$ J/cm^2, $\Phi = 0.31$ J/cm^2 and $\Phi = 0.49$ J/cm^2) [5]. Curves A, B and C represent the theoretical prediction of $\langle n\rangle_{\text{total}} = f(p_{\text{Ar}})$ behavior based on GCTL model $\Phi = 0.60$ J/cm^2, $\Phi = 1.00$ J/cm^2 and $\Phi = 1.40$ J/cm^2, respectively.