Limitations of the Generalized Coupled Two-Level Model during the Multiphoton Absorption in Different Gas Mixtures

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Generalized coupled two-level model is applied in different gas mixtures
and investigated for high fluence regime. Functional dependences of mean
number of absorbed photons per molecule $\langle n \rangle_{\text{total}}$ on buffer-gas pressure
(p_{buff}) are presented, used to confirm or predict some possible physical and
chemical processes, like enhanced absorption and/or dissociation. Limitations of proposed models are analyzed depending on both gas pressure and
laser fluence. Results are compared with other previously obtained by the
same experimental technique, but for different absorbing molecule.

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1. Introduction

Detailed knowledge of collisional relaxation processes such as vibrational or
rotational relaxation of polyatomic molecules in different gas mixtures is essential
for accurate prediction of molecular behavior during and after the intensive multiphoton absorption processes. This kind of knowledge can be used for a variety of
applications including infrared 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 of good quality
[1–4]. Emphasis has been put on the investigation of SF_6, which plays a significant
role in the global warming and atmospheric particle transportation processes, as
a good infrared absorber and the vibrational energy transfer partner.

The main physical quantity in this investigation, $\langle n \rangle_{\text{total}}$ [1, 4], represents the
total amount of energy absorbed into the sample during the laser pulse. Knowing

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this quantity and its dependence on the laser fluence and buffer-gas pressure, it is possible, using generalized coupled two-level (GCTL) model, to predict a variety of processes, which can occur under the given conditions.

Here we present the results of our collisional effect analysis for two molecular absorbers, SF_6 and C_2H_4, in the buffer gas (Ar) surrounding. We choose the gas mixtures consisting of SF_6 or C_2H_4 molecules as an infrared (IR) laser light absorbers on the very low pressure (0.46 mbar), and argon atoms as a buffer-gas species in the higher, 10–133 mbar, pressure range for a demonstrating sample in our experiment.

2. Experimental setup and theoretical model

IR pulsed photoacoustic experimental setup used here has been previously described in detail [4–7]. In brief, TEA CO_2 laser was used, tuned on 10P(16) (for SF_6) and/or 10P(14) line (for C_2H_4), with total output fluence lying in the range of 0.2–0.5 J/cm² for SF_6 and C_2H_4 excitation, and 0.6–1.4 J/cm² for SF_6 dissociation regime. We used "top hat" laser beam spatial profile approximation which gives satisfactory results. Laser beam temporal characteristics are 45 ns FWHM with 2 μs tail. Nonresonant 18.5 cm long photoacoustic cell was utilized with a built-in Knowles capacitive microphone. Ambient temperature was approximately 300 K. Buffer-gas (argon) pressure was changed in the range 10–133 mbar and absorber pressure (SF_6, C_2H_4) was kept constant at 0.46 mbar. Total mixture pressure inside the cell was measured by CCM capacitive pressure gauge.

In our analysis, GCTL model was used to fit experimental results for $\langle n \rangle_{\text{total}}$, obtained through analysis of the photoacoustic signal, and calculate its functional dependence $\langle n \rangle_{\text{total}} = f(p_{\text{buff}})$, where p_{buff} is the buffer-gas (Ar) pressure. The basic equation of GCTL model for SF_6–buffer gas mixture investigation has the form of [4]:

$$\langle n \rangle_{\text{total}}(p_{\text{buff}}, \Phi) = \langle f \rangle^{\frac{1}{3}} (\sigma_0 \Phi)^{\frac{2}{3}}$$

$$= \left\{ f_i \left[1 - \exp\left(\frac{-f_r}{1 - f_r} \cdot \frac{\tau_p}{\tau} \right) \right] \right\}^{\frac{1}{3}} (\sigma_0 \Phi)^{\frac{2}{3}}, \tag{1}$$

where f_i is the fraction of molecules in the absorbing (usually ground) vibrational level ($f_i = 0.3$ for SF_6 at 300 K), and f_r is the fraction of f_i molecules in the initial distribution that interacts directly with the radiation field, τ_p is the laser pulse duration, τ is the equilibration time of the absorber level and reservoir level, usually taken as rotational relaxation time, and σ_0 is the small-signal absorption cross-section for SF_6 [2]. Equation (1) was used for fitting procedure in the most suitable form

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

where a and b are fitting parameters corresponding to the number of collisions in given gas mixture and the fraction of molecules directly involved in the laser field–molecule interaction, respectively. Equation (2) gives us a dependence of $\langle n \rangle_{\text{total}}$

on the buffer-gas pressure for constant laser fluence Φ. Knowing the $\langle n \rangle_{\text{total}} = f(p_{\text{buff}})$ functional characteristics, one can draw qualitative conclusions about the influence of collisions on the absorbing process.

3. Results and discussion

Experimental results for $SF_6 + Ar$ and $C_2H_4 + Ar$ mixtures, obtained using well-known procedure [1, 3], are presented in Figs. 1 and 2. In Fig. 1a, $\langle n \rangle_{\text{total}}$ functional dependence on buffer-gas pressure (p_{Ar}) for $SF_6 + Ar$ is presented for
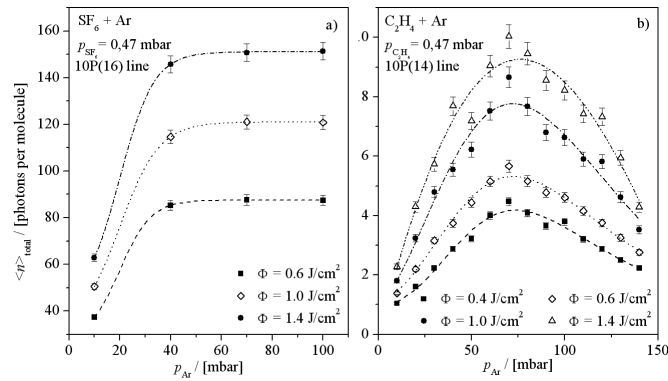

Fig. 1. Total mean number of absorbed photons per molecule $\langle n \rangle_{\text{total}}$ versus Ar buffer pressure p_{Ar} in (a) $SF_6 + Ar$ and (b) $C_2H_4 + Ar$ mixtures are depicted for different laser fluences and $\tau_p = \text{FWHM} = 45$ ns.
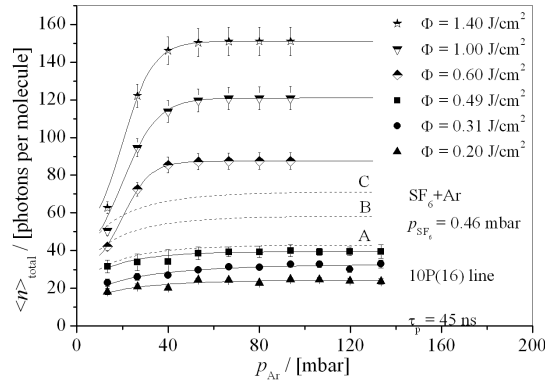

Fig. 2. Functional dependence of $\langle n \rangle_{\text{total}}$ on buffer-gas pressure (p_{Ar}) in $SF_6 + Ar$ mixtures for different higher laser fluences Φ and $\tau_p = \text{FWHM} = 45$ ns. The results for $\langle n \rangle_{\text{total}} = f(p_{Ar})$ obtained in our experiment ($\Phi = 0.60$ J/cm^2, $\Phi = 1.00$ J/cm^2 and $\Phi = 1.40$ J/cm^2) are fitted with arbitrary functions, and compared with curves A, B and C representing the theoretical prediction of $\langle n \rangle_{\text{total}} = f(p_{Ar})$ possible behavior based on the GCTL model for the same fluences, respectively. Previous results [5] for $\Phi = 0.20$ J/cm^2, $\Phi = 0.31$ J/cm^2, and $\Phi = 0.49$ J/cm^2 are depicted, too.

high values of different laser fluences Φ (> 0.60 J/cm^2). 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 adding the buffer-gas into the mixture; for $p_{\text{buff}} > 50$ mbar (higher pressure region) $\langle n \rangle_{\text{total}}$ values tend to be constant or slowly rising with the addition of the buffer-gas up to 100 mbar. Such a behavior of the $\langle n \rangle_{\text{total}}$ values as a consequence of the collisional influence is known from the literature [1–4, 7–9]. Detailed investigation shows strong influence of rotational relaxation (R–R) processes for lower, and $V-T$ relaxation processes for higher pressure region. The $\langle n \rangle_{\text{total}} = f(p_{\text{Ar}})$ lines presented in Fig. 1a are obtained with arbitrary fitting function, because GCTL model (Eq. (1) and Eq. (2)) cannot be applied in this case of high fluence values. In Fig. 1b, $\langle n \rangle_{\text{total}}$ functional dependence on buffer-gas pressure (p_{Ar}) for C$_2$H$_4$+Ar mixture is presented for different laser fluences Φ. Increment of the buffer-gas (Ar) pressure increases the absorption until its maximum at about $p_{\text{Ar}} = 75$ mbar. This means that collisionally induced rotational relaxation is dominant (as in SF$_6$ case), to overcome so-called rotational hole-filling effect [10]. Adding the buffer-gas for $p_{\text{Ar}} > 75$ mbar is followed by the rising influence of the collisionaly induced deactivating processes, mainly $V-T$ relaxation, quenching the multiphoton absorption and decreasing the excitation level of the absorbing molecules. This is completely different process comparing to the rotational relaxation influence mentioned before, for $p_{\text{Ar}} < 75$ mbar. One can see that functional dependence for $\langle n \rangle_{\text{total}}$ in the case of C$_2$H$_4$ completely differs from the SF$_6$ case. The C$_2$H$_4$+Ar mixture shows steep decrease in $\langle n \rangle_{\text{total}}$ value with increment of the pressure above 75 mbar, since $V-T$ relaxation predominates all other processes quenching the absorption in this pressure region. The $\langle n \rangle_{\text{total}} = f(p_{\text{Ar}})$ lines presented for C$_2$H$_4$+Ar mixtures in Fig. 1b are obtained with arbitrary fitting function, within the frame of the GCTL model, but not the same as in the SF$_6$ case.

Figure 2 depicts the functional dependence $\langle n \rangle_{\text{total}} = f(p_{\text{Ar}})$ for SF$_6$+Ar mixtures, but for different laser fluences. For lower fluence region (< 0.60 J/cm^2) $\langle n \rangle_{\text{total}} = f(p_{\text{Ar}})$ experimental points could be easily fitted with GCTL model fitting function, Eq. (2). These experimental points and GCTL functions are obtained earlier [4], and presented here as an example of good matching between GCTL prediction and experimental results. For higher fluences (> 0.60 J/cm^2) the obtained $\langle n \rangle_{\text{total}}$ experimental points could not be fitted with GCTL and Eq. (2), and functional dependence $\langle n \rangle_{\text{total}} = f(p_{\text{Ar}})$ lines presented in Fig. 2 for these points originate from arbitrary functions. The possible reason for that is a strong dissociation of SF$_6$ molecules induced by laser fluence and collisional processes, producing significant number of dissociated molecules, which absorb also during the laser pulse. Based on these facts, it is obvious that for this fluence region (> 0.60 J/cm^2) GCTL model brakes down. Just to see the difference, the theoretical prediction for this fluence region > 0.60 J/cm^2 based on GCTL model is also presented in Fig. 2 (0.60 J/cm^2 curve A, 1.00 J/cm^2 curve B and 1.40 J/cm^2

curve C) in order to show the possible behavior of $\langle n \rangle_{\text{total}}$ if dissociation is not present. In that case, only strong intermolecular $V-V$ relaxation could give such high values of $\langle n \rangle_{\text{total}}$. But in the case of low absorber pressure and Ar as a buffer gas, $V-V$ transfer is not possible.

There is a question remaining: where is the limit of GCTL application? It is clear from Fig. 1 that the same functional dependence for different molecular absorbers cannot be applied. Also, it is clear from Fig. 2 that amount of energy absorbed into the system ($\langle n \rangle_{\text{total}}$) during the laser pulse for higher fluences exceeds the dissociation limit (DL) for given absorber (SF$_6$ $\langle n \rangle_{\text{DL}} = 33$ photons absorbed). Increasing the fluence and adding the buffer gas into the gas mixture, nonlinear excitation and collisional effects become very powerful, increasing the number of dissociated molecules and allowing them to absorb.

On the other hand, at higher pressures the collisions quench the dissociation (Fig. 2) thus maintaining a high concentration of absorbing molecules (SF$_6$ and its dissociation products: SF$_5$ or SF$_4$). That allows them to absorb the radiation field photons during the laser pulse. Final result for higher fluences (> 0.60 J/cm^2) is a significant increase in the $\langle n \rangle_{\text{total}}$ values for whole buffer pressure region. In such a case, when absorbed energy exceeds dissociation limit, or namely for fluences higher than 0.50 J/cm^2 for SF$_6$, GCTL model cannot be applied.

4. Conclusions

We have demonstrated here the simple method used to confirm or predict some physical and chemical processes which can occur during the multiphoton absorption and dissociation processes in investigated gas mixture applying GCTL model. For our experimental conditions and SF$_6$ as an absorber, it was shown that GCTL model can be used to explain and predict influence of some collision-ally induced processes, such as rotational, $V-T$ or $V-V$ relaxation [4], but only for limited (lower) fluence range. For laser fluences $\Phi_{\text{b}} < 0.5$ J/cm^2 functional behavior of $\langle n \rangle_{\text{total}} = f(p_{\text{buff}})$ follows GCTL model curve. For fluences higher than Φ_{b}, GCTL model breaks down due to high concentration of SF$_6$ dissociation products which educes much higher absorption during the laser pulse. In the case of ethylene, the same functional dependence within the GCTL model, as in the case of SF$_6$ for the same experimental conditions, cannot be applied, especially for p_{Ar} higher than 75 mbar. There is a great interest to go further with this kind of investigation, because knowing the molecular absorption capability and its re-laxation characteristics in buffer surroundings (especially molecular) on sub- and atmospheric pressures, one can understand and predict behavior of some green-house gases (such as SF$_6$ and SF$_6$-like molecules) under the different conditions [6–8, 11, 12].

Acknowledgments

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