Calculation of the Highly Excited SF_6 Vibrational State Distributions and Dissociation Yields in Different Gas Mixtures

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Influence of the buffer gas on the multiphoton absorption and dissociation in different mixtures was investigated. Simple method based on the empirical and theoretical vibrational energy distribution is applied for high fluence regime. Collisional effects of buffer gas (Ar) are introduced to enhance the absorption and relaxation of irradiated molecules (SF_6 and C_2H_4). Functional dependences of mean number of absorbed photons per molecule ($\langle n \rangle_{\text{total}}$) on the molecular excitation level are presented, enabling us to confirm or predict the level of excitation, number of molecules directly involved in the absorption process and dissociated during the laser pulse.

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1. Introduction

In recent times the atmospheric pollution has become an issue of a great concern. It has been recognized that even trace concentrations of some atmospheric species can have a substantial impact in diverse areas. In the past, numerous techniques have been developed and successfully applied to the trace gas monitoring. One of them is infrared photoacoustics spectroscopy (PAS), which is used not only for precise detection and measurements of minimal trace gas concentrations in the atmosphere but for their intensive investigation on atmospheric and subatmospheric pressures trying to reach the through understanding of complex physical and chemical processes and interactions involved [1–5].

Our aim in this paper is to show how a simple method, so-called vibrational state distribution (VSD) method, can be applied for a quantitative prediction

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of vibrational energy distribution and dissociation [6–9] under the high fluence (multiphoton absorption (MPA)) and low pressure regime. The importance of this knowledge lying in the fact that some of the theoretical models (like generalized coupled two-level (GCTL) model [1]), which are very important in the molecular behavior analysis, could give misinterpreted results because they do not recognize dissociation and vibrational energy distribution as important parameters. We will present our results for two molecular infrared (IR) laser light absorbers with completely different behavior under the same experimental conditions, SF_6 and C_2H_4, mixed with argon (Ar) as a buffer gas.

2. Experimental setup and theoretical model

In this investigation, TEA CO_2 laser was used (45 ns FWHM, 2 μs long tail), tuned on 10P(16) (for SF_6) or 10P(14) line (for C_2H_4), with total output fluence of 0.3–1.0 J/cm^2 for SF_6 and C_2H_4 excitation. The "top hat" laser beam spatial profile approximation was used. Nonresonant long photoacoustic cell was utilized with a built-in Knowles capacitive microphone. All results are obtained at the room temperature (300 K). Argon pressure was changed in the range 10–133 mbar and absorber pressure was kept constant at 0.46 mbar.

In order to obtain vibrational state distribution, one has to solve rate equations [1]:

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

where N_n is the population of the n-th level, I is the laser beam intensity, σ is the cross-section for given transition and ρ is the state density. We can approximate Eq. (1) with the simpler one in which we neglect all terms multiplied by the state density ratio. This leads to equation

$$\dot{N}_n + a N_n = b N_{n-1}, \quad a = \sigma_{n,n+1} I \quad \text{and} \quad b = \sigma_{n,n-1} I. \qquad (2)$$

Solution of Eq. (2) is represented by Poisson's distribution

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

where τ_{p} is the laser pulse duration, σ is the absorption cross-section (enhanced absorption cross-section σ^{e} [5]), n is the level of excitation, $h\nu$ is the photon energy, and $\langle n \rangle = \sigma I \tau_{\mathrm{p}}/h\nu = \langle n \rangle_v$ [8] is the mean number of absorbed photons per molecule stored in vibrational modes. In our investigation partial pressure of absorbing molecules is very low (0.46 mbar) in comparison to buffer-gas pressure range and we use atomic buffer, so vibrational to vibrational $(V-V)$ intermolecular energy transfer can be neglected. This means that we can put $\langle n \rangle_{\mathrm{total}} = \langle n \rangle_{\mathrm{v}}$ into Eq. (3), knowing that there are no other contributions to that value. Also, using Eq. (3) and obtained experimental results [5] it is easy to calculate the dissociation yield.

As we know from GCTL model [1, 5], only molecules in optimal ro-vibrational state absorb. That is why initial ensemble divides in two: *vibrationally hot* and *vibrationally cold ensemble*. During irradiation, portion of the molecules remains at lower discrete levels, so we have to superpose two distributions (of hot and cold ensemble) to get the complete picture.

3. Results and discussion

As we mentioned earlier, in some cases theoretical models (specially GCTL model) could give a $\langle n \rangle_{\text{total}} = f(p_{\text{buff}})$ functional dependence, even if the dissociation is present in a significant number of irradiated molecules. This fact could lead to the misinterpreting of the results. To avoid this kind of mistake we use VSD method to quantitatively analyze vibrational state distribution and dissociation yield (D_{y}) of the irradiated molecules.
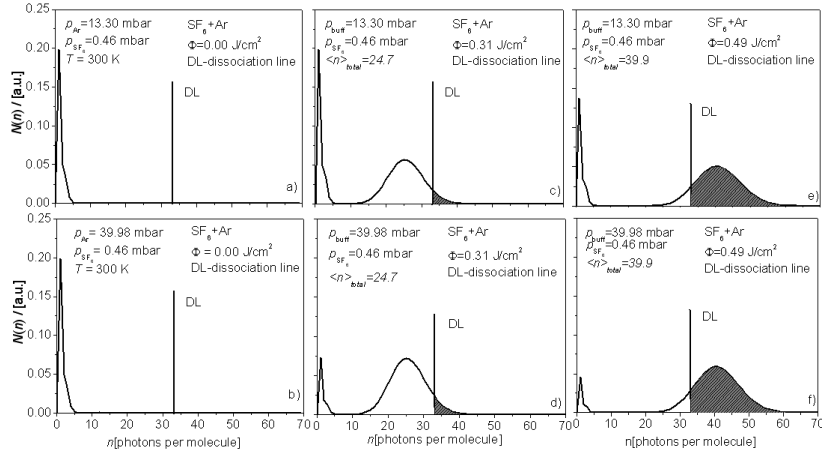

Fig. 1. The vibrational energy distribution $N(n)$ versus the level of molecular excitation n for SF$_6$+Ar mixtures, at constant $p_{\text{SF}_6} = 0.46$ mbar, and different laser fluences and Ar pressures, at $T = 300$ K: (a) before laser irradiation, $p_{\text{Ar}} = 13.30$ mbar; (b) before laser irradiation, $p_{\text{Ar}} = 39.98$ mbar; and ((c)–(f)) immediately after the laser pulse: (c) $p_{\text{Ar}} = 13.30$ mbar, $\Phi = 0.31$ J/cm^2; (d) $p_{\text{Ar}} = 39.98$ mbar, $\Phi = 0.31$ J/cm^2; (e) $p_{\text{Ar}} = 13.30$ mbar, $\Phi = 0.49$ J/cm^2; (f) $p_{\text{Ar}} = 39.98$ mbar, $\Phi = 0.49$ J/cm^2. DL denotes the dissociation limit.

In Fig. 1, SF$_6$ vibrational energy distribution $N(n)$ is presented, obtained for SF$_6$+Ar mixture by Eq. (3) for two different fluences (0.31 J/cm^2 and 0.49 J/cm^2) and two buffer pressures ($p_{\text{Ar}} = 13.3$ mbar and 39.98 mbar) measured at 300 K. We will assume that the fraction of molecules in the absorbing (usually ground) vibrational level is $f_{\text{i}} = 0.30$ for SF$_6$ at 300 K [1, 5], and other 70% of molecules are on the higher vibrational levels having the maximum at $\langle n \rangle_{\text{v}} = 1$. We assume that, during the laser pulse, all molecules in ground state, and the
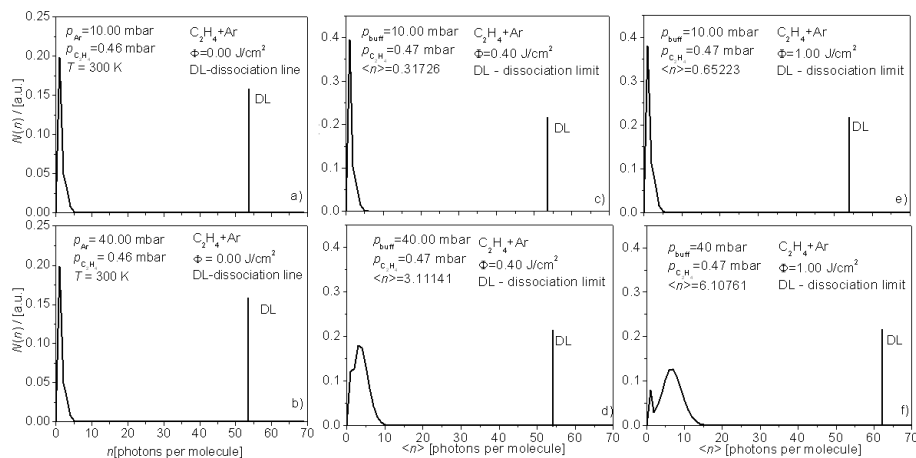
Fig. 2.   The vibrational energy distribution $N(n)$ versus the level of molecular excitation n for C_2H_4+Ar mixtures, at constant $p_{C_2H_4} = 0.46$ mbar, and different laser fluences and Ar pressures, at $T = 300$ K: (a) before laser irradiation, $p_{Ar} = 10.0$ mbar; (b) before laser irradiation, $p_{Ar} = 40.00$ mbar; and ((c)–(f)) immediately after the laser pulse: (c) $p_{Ar} = 10.0$ mbar, $\Phi = 0.40$ J/cm^2; (d) p_{Ar} $\Phi = 40.00$ mbar, $\Phi = 0.40$ J/cm^2; (e) $p_{Ar} = 10.0$ mbar, $\Phi = 1.00$ J/cm^2; (f) $p_{Ar} = 40.00$ mbar, $\Phi = 1.00$ J/cm^2. DL denotes the dissociation limit.

part of molecules at higher vibrational levels, take part in the absorption process. The distributions depicted in Fig. 1 are obtained by putting the maximum value of $\langle n \rangle_{total} = \langle n \rangle_v$ in Eq. (3). The effect of adding the buffer gas, in this case, is promoting molecules from cold to hot ensemble, thus giving rise to the amount of absorbing molecules (seen as increase in the distribution peak positioned at maximum $\langle n \rangle_{total} = \langle n \rangle_v$ value), while the peak of the cold ensemble distribution at $\langle n \rangle_v = 1$ decreases. Also depicted is the portion of molecules that exceeded dissociation limit DL. This portion defines the dissociation yield, and it is represented by the shaded area under the curve. Simple calculations give $D_y = 6.34\%$ for lower and 7.99% for higher pressure at $\Phi = 0.31$ J/cm^2 and $D_y = 72.88\%$ for lower and 85.11% for higher pressure at $\Phi = 0.49$ J/cm^2. As it can be seen, D_y value is significant at fluence of 0.49 J/cm^2. In such a case, CTL model must be reconsidered generally and/or breakes down. For lower fluences (0.31 J/cm^2 in our case presented in Fig. 1) small amount of molecules exceed the dissociation limit, so their contribution to the total amount of the absorbed energy is very small, and GCTL model can be applied.

In Fig. 2, C_2H_4 vibrational energy distribution $N(n)$ is presented, obtained for C_2H_4+Ar mixture by Eq. (3) for two different fluences (0.40 J/cm^2 and 1.00 J/cm^2) and two buffer pressures ($p_{Ar} = 10.0$ mbar and 40.00 mbar) measured at 300 K. We will assume that the most C_2H_4 molecules at 300 K are in the ground vibrational state. All the absorption assumptions mentioned for SF$_6$

are taken here for C$_2$H$_4$ also, including $\langle n \rangle_\text{total} = \langle n \rangle_\text{v}$ in Eq. (3). The effect of adding the buffer gas is the same as it is presented in Fig. 1, but with one obvious difference: for both fluences ethylene does not reach the dissociation limit. In such a case, GCTL model can be applied even in a different functional form comparing to the other absorber (SF$_6$ in our case).

4. Conclusions

The results presented in this paper show the applicability of the VSD method for a quantitative prediction of vibrational energy distribution and dissociation in different gas mixtures (SF$_6$+Ar and C$_2$H$_4$+Ar), under the high fluence and low pressure regime. It is clear from these results that SF$_6$ reaches dissociation limit much faster than C$_2$H$_4$ for nearly the same fluences and gas mixture pressures, which means that the theoretical models like GCTL can be applied for both molecular absorbers only in the case of low fluences (< 0.4 J/cm^2), where the dissociation is very low or not present. It is also clear, from the vibrational state distributions in both cases, that the absorber collisions with buffer gas play a significant role in the absorption dynamics [10, 11], allowing the molecules to reach the proper ro-vibrational state and then directly interact with the laser radiation field, bringing much more energy into the irradiated gas sample. This process is much more efficient in the case of SF$_6$ and this is the reason why the excitation levels of this molecule are much higher than in the case of ethylene. These obvious differences in SF$_6$ and C$_2$H$_4$ behavior under the same or nearly the same experimental conditions could help one to understand much better their contribution to the energy transfer processes and absorbing efficiency in the atmosphere.

Acknowledgments

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