Scientific Paper

Multiphoton Processes in Gas Mixture: Determination of Rotational Relaxation Parameters†

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Abstract

We present a new experimental approach to the study of average macroscopic (bulk) (R→R/T) rotational relaxation parameters of highly vibrationally excited molecules in gas mixtures, where collisions enhance absorption processes. Bulk parameters were derived from measured enhanced cross section, which contains information on photon and collision physics, by means of calibrated multiphoton photoacoustic spectroscopy. All measurements were carried out at room temperature, for the 10P(16) TEA CO_2 laser line with fluence range of (1-7)·10^3 Jm^{-2} and for buffer gas pressures ranging from 1–140 mbar. Particular attention was paid to evaluate the effects of collision partner and buffer pressure dependence on relaxation parameters. Significant buffer pressure effects were observed for all investigated gas mixtures. Two buffer pressure regimes can be distinguished: low and high. It is shown that the data obtained from the proposed method is in good accordance with data obtained from the "slope" and "point" method presented in earlier papers.

Key words: rotational relaxation, multiphoton, photoacoustic spectroscopy.

Introduction

Infrared multiphoton (MP) processes have been the subject of many experimental and theoretical works since the first observation of chemical reactions induced by infrared lasers.[1-4] The most important parameters which describe the MP processes are the average number of absorbed photons per one molecule and the cross section. These parameters are in most cases obtained in experiments at different laser fluences and pressures.[5–7] The most significant characteristics in understanding the physical and chemical kinetics of MP processes are relaxation mechanisms. Various experimental methods and theoretical models were developed to study vibrational–vibrational (V–V),[8] vibrationa–translational (V–T),[9–10] vibrational–to–translational/rotational (V→T/R),[11] and rotational–to–rotational/translational (R→R/T)[12–14] transitions. There are significant changes of rotational relaxation parameters of absorbing molecules with increasing gas pressure or with addition of an absorbing or nonabsorbing gas. A common opinion is that rotational energy transfer (RET) is the dominant process in gas mixtures, resulting in an increase in number of molecules which are excited effectively by IR laser radiation. Most of experimental investigations related to R–R energy transfer elucidate the specific energy transfer pathways.[15,16] Investigations of average (bulk) macroscopic R→R/T energy transfer mostly utilize two spectroscopic method: transmission (TR)[12] and photoacoustic (PA)[13,14] spectroscopy. PA experimental studies are restricted to the measurement of quantities averaged over the rotational states, such as the average rotational energy of molecules. Two different approaches to evaluate bulk rotational relaxation parameters were presented till now: the "slope" method[13] and the "point" method.[14]

Determinations of bulk rotational parameters with TR and PA technique are based on the measurements of saturation intensity. In most MP experiments the enhanced absorption cross section is usually measured. In this paper we present a new approach to determine bulk rotational relaxation parameters (R→ R/T) from measured enhanced absorption cross sections. The proposed method was tested by a calibrated photoacoustic spectrometer[20] in gas mixtures consisting of absorbing SF_6 and a nonabsorbing gas.

Method for determination of rotational relaxation parameters

Experimental studies of bulk rotational relaxation were largely interpreted in the framework of the relaxation equation. The photoacoustic (PA) method determines quantities averaged (bulk) over the rotational states, hence data determined by PA method obeys the relaxation equation

$$t_R = \frac{\langle\langle E_{\text{rot}}\rangle\rangle_\infty - \langle\langle E_{\text{rot}}\rangle\rangle_t}{\mathrm{d}\langle\langle E_{\text{rot}}\rangle\rangle_t / \mathrm{d}t}, \qquad (1)$$

where t_R is the bulk rotational relaxation time, $\langle\langle E_{rot}\rangle\rangle_\infty$ is the average rotational energy of the molecule at equilibrium, and $\langle\langle E_{\text{rot}}\rangle\rangle_t$ is the bulk average rotational energy at time t. The bulk cross sections, σ_R, are commonly defined as

$$\sigma_R = \frac{1}{N\langle v\rangle t_R}, \qquad (2)$$

where N is the density of absorbing molecules, and $\langle v\rangle$ their mean relative velocity. These bulk rotational relaxational parameters, t_R, and σ_R, can be extracted from experimental measurements.

For the PA method two different approaches are reported: (*i*) the “slope method”,[13] based on measurements of saturation intensity dependence on buffer gas pressure, and (*ii*) the “point method”,[14] founded on measurements of saturation intensity, at selected buffer gas pressures.

It would be quite interesting to determine the t_R and σ_R in MP processes from common measurements of enhanced absorption cross section values, σ^e, without additional measurements. In order to achieve this, a “calibration” procedure should be established, i.e. a relation between the measured quantity, σ^e, and the saturation intensity I_S. In this way, rotational relaxation parameters can be determined directly from σ^e data.

Saturation intensity

Saturation intensity, I_S, is the quantity which is defined as the photon irradiant for which the small signal absorption coefficient is reduced the down to half of its small signal value. I_S is given by[17]

$$I_S = \frac{1}{\sigma_a\, t_{\text{eff}}}, \qquad (3)$$

where σ_a is the absorption cross section for the specific laser line and t_{eff} is the effective lifetime. Numerical computation for an illuminated gas mixture absorber and absorbing gas[18,19] shows that rotational relaxation energy transfer is the dominant process. Hence, the effective lifetime, t_{eff}, only determines the bulk rotational relaxation time t_R, i.e. $t_{\text{eff}} = t_R$. This time is an average over all initial and final states. Under this condition, where the other relaxation processes can be neglected, t_R can be estimated from I_S

$$t_R = \frac{1}{\sigma_a\, I_S}. \qquad (4)$$

The saturation intensity, $I_S^{(AB)}$, in gas mixtures, containing the absorbing (A) and nonabsorbing (B) particles (buffer gas), can be expressed through the Equation[19]

$$I_S^{(AB)} = I_S^{(A)} + \frac{1}{\sigma_a t_R^{(AB)}} = \frac{1}{\sigma_a t_R^{(A)}} + \frac{1}{\sigma_a t_R^{(AB)}}, \qquad (5)$$

where $I_S^{(A)}$ denotes the saturation intensity for pure gas absorber. According to Equation (5), two rotational relaxation times can be distinguished: (*i*) $t_R^{(A)}$, the bulk rotational relaxation time of the absorbing molecule caused in collision with another absorbing molecule (self collision), and (*ii*) $t_R^{(AB)}$ the bulk rotational relaxation time of absorbing particle A under collision with nonabsorbing B species.

Different experimental methods are used to measure I_S. Here we shall mention only the transmission (TR) and the photoacoustic (PA) method. The saturation intensity in gas mixture for optically thick absorber can be deduced from transmission (TR) measurements[19]

$$I_{S,TR} = \frac{4}{h\nu d^2 t_i} \frac{E_i - E_T}{\ln\left(\frac{E_T}{E_i}\right) + \alpha p^{(A)} L} \qquad (6)$$

where $h\nu$ is the laser photon energy, d is the diameter of the laser beam, t_i is laser pulse duration, E_i is the laser excitation energy, E_T is the laser excitation energy transmitted through the cell of length L, α is the absorption coefficient of absorber gas at pressure $p^{(A)}$. Equation (6) can be adapted for PA measurements by following redefinitions. The photoacoustic method measures the absorbed energy, E_{abs}, directly by the first peak from microphone signal (photoacoustic signal), P_a (Figure 2), only in the volume in front of the microphone, i.e. along the length l_m of the PA detector

$$E_{\text{abs}} = E_i - E_T = S \cdot P_a\ . \qquad (7)$$

In Equation (7), the quantity $S = S(p, T, \gamma)$ is the sensitivity of the used photoacoustic system (gas–cell–detector). Sensitivity depends on pressure, p, temperature, T, and nature, γ, of the gas constituents. Therefore, for quantitative determination of relaxation parameters in gas mixtures, the calibration of the PA detector is necessary. In our case for the specified gas mixture, and at room temperature, sensitivity behavior can be described by $S = S(p)$. The detailed calibration procedure was reported in a previous study.[20]

According to Equation (7), Equation (6) can be adopted for PA parameters[13]

$$I_{\mathrm{S,PA}} = \frac{4}{h\nu d^2 \pi t_i} \frac{SP_{\mathrm{a}}}{\ln\left(1-\frac{\mathrm{SP_a}}{E_i}\right)+\alpha p^{(A)} l_{\mathrm{m}}} \quad . \tag{8}$$

Equation (8) can be applied to determine the saturation intensity in a pure gas absorber, $I_{\mathrm{S,PA}}^{(\mathrm{A})}$, as well in a gas mixture, $I_{\mathrm{S,PA}}^{(\mathrm{AB})}$, by the PA method.

"Calibration" procedure

From Equations (2), (4) and (5), the bulk rotational cross sections for a pure gas absorber, $\sigma_{\mathrm{R}}^{(\mathrm{A})}$ and for absorbing particle A under collision with nonabsorbing B species, $\sigma_{\mathrm{R}}^{(\mathrm{AB})}$are related to the saturation intensities, $I_{\mathrm{S}}^{(\mathrm{A})}$ and $I_{\mathrm{S}}^{(\mathrm{AB})}$

$$\sigma_{\mathrm{R}}^{(\mathrm{A})} = \frac{\sigma_{\mathrm{a}} I_{\mathrm{S}}^{(\mathrm{A})}}{N\langle v_{\mathrm{AA}}\rangle}$$

$$\sigma_{\mathrm{R}}^{(\mathrm{AB})} = \frac{\sigma_{\mathrm{a}}\left(I_{\mathrm{S}}^{(\mathrm{AB})} - I_{\mathrm{S}}^{(\mathrm{A})}\right)}{N\,\langle v_{\mathrm{AB}}\rangle} \quad . \tag{9}$$

Thereby, if it is possible to find a relationship between saturation intensity, I_{S}, and measured enhanced cross section, σ^{e}, the rotational relaxation parameters can be evaluated without separately measured I_{S}.

The quantity σ^{e} contains information on photon and collision physics and can be obtained from the transmission (TR) method[21]

$$\sigma_{\mathrm{TR}}^{\mathrm{e}} = -\frac{1}{NL}\ln\left(\frac{E_{\mathrm{T}}}{E_i}\right) \quad . \tag{10}$$

The enhanced cross sections can also be determined from PA measurements[22]

$$\sigma_{\mathrm{PA}}^{\mathrm{e}} = -\frac{1}{Nl_{\mathrm{m}}}\ln\left(1-\frac{SP_{\mathrm{a}}}{E_i}\right) \quad , \tag{11}$$

The Equation (11) is a presentation of the Beer–Lambert absorption law appropriate for quantitative PA method. From Equations (11) and (8) the "calibration" procedure can be established. It follows that the relation between measured data $\sigma_{\mathrm{PA}}^{\mathrm{e}}$ and $I_{\mathrm{S,PA}}$ can be expressed

$$I_{\mathrm{S,PA}}\left(\sigma_{\mathrm{PA}}^{\mathrm{e}}\right) = \frac{\phi}{h\nu t_i} \frac{1-\exp\left(-\sigma_{\mathrm{PA}}^{\mathrm{e}} N l_{\mathrm{m}}\right)}{l_{\mathrm{m}}\left(\alpha\, p^{(\mathrm{A})} - \sigma_{\mathrm{PA}}^{\mathrm{e}} N\right)} \quad , \tag{13}$$

as where $\phi = 4E_i/\pi d^2$ is the laser fluence. Consequently, knowing $\sigma_{\mathrm{PA}}^{\mathrm{e}}$ the saturation intensities in the pure gas absorber and in gas mixtures can be calculated. Equation (13) can be applied to a gas mixture, as well as to a pure gas absorber. After the "calibration", i.e. establishing the relation between $\sigma_{\mathrm{PA}}^{\mathrm{e}}$ and $I_{\mathrm{S,PA}}$, the parameter σ_{R} can be determined from Equation 9 (Figure 1).

The same consideration can be applied to other experimental methods which determine $\sigma_{\mathrm{TR}}^{\mathrm{e}}$. For instance, for transmission (TR) measurements, from Equations (6), and (10) it follows

$$I_{\mathrm{S,TRS}}\left(\sigma_{\mathrm{TR}}^{\mathrm{e}}\right) = \frac{\phi}{h\nu t_i} \frac{1-\exp\left(-\sigma_{\mathrm{TR}}^{\mathrm{e}} NL\right)}{L\left(\alpha\, p^{(\mathrm{A})} - \sigma_{\mathrm{TR}}^{\mathrm{e}} N\right)} \quad . \tag{14}$$

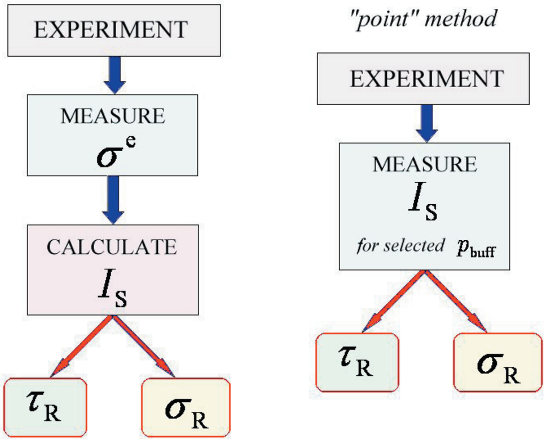

Figure 1. Schematic representation of the proposed method and the "point" method for evaluation of bulk rotational parameters.

Experimental

The multiphoton photoacoustic spectrometer has been described previously.[20] Briefly, the TEA CO_2 laser was operating at 947.75 cm^{-1} (45ns, FWHM) and in fluence range of $0.1 < \phi < 0.5$ Jcm^{-2}. The multiphoton parameters were measured by adding the buffer gas in the pressure range of 0–140 mbar to the PA cell containing SF_6 under constant pressure of p_{SF_6}=0.47 mbar and p_{SF_6}=0.13 mbar. All measurements were carried out at room temperature (T=300K) .

Results and discussion

Typical signals of PA detector (microphone) in gas mixture SF_6–Ar have the waveforms presented in Figure 2. The waveforms (p_{Ar} = const) are averaged over five signals to produce a single data point for analysis – the amplitude of the photoacoustic signal, P_{a}, (the height of the first peak).

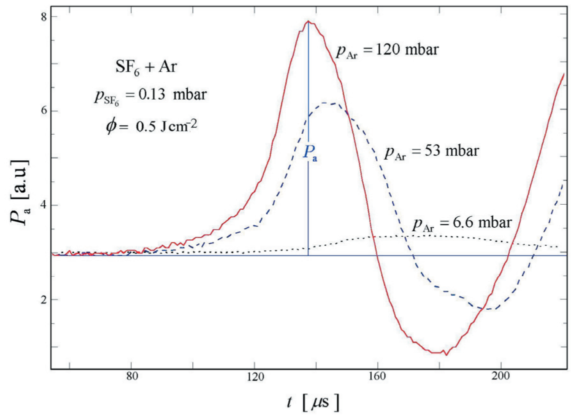

Figure 2. PA detector signals for different pressures of SF_6–Ar mixture in the cell. P_a is the first peak from the microphone signal (photoacoustic signal).

The Equation (11) was used to evaluate enhanced cross sections, σ^e_{PA}, from PA measurements. The obtained results are displayed in Figure 3 as a function of buffer gas pressure for SF_6–Ar gas mixture for different laser fluences and for p_{SF_6}=0.13 mbar.

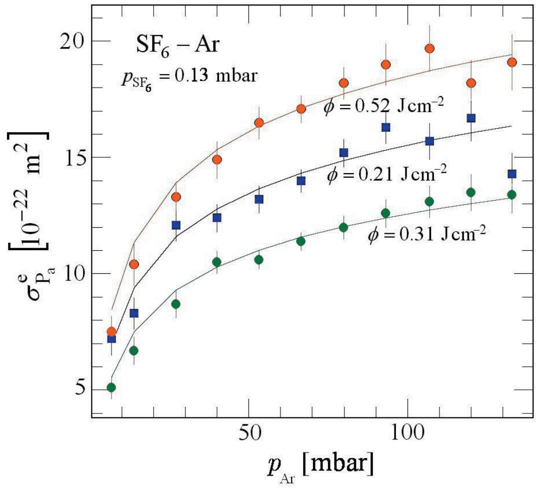

Figure 3. The enhanced absorption cross section versus argon gas pressure for different laser fluences.

The “calibration” relation between $\sigma^e_{P_a}$ and $I_{S,PA}(\sigma^e_{PA})$ (Equation 13) was used to determine saturation intensities for pure gas and gas mixtures. After that, according to Equation (9), bulk rotational relaxation cross sections, $\sigma^{(A)}_{P_a}$ and $\sigma^{(AB)}_R$ were calculated for different laser fluences in the investigated pressure range. The calculated values for $\sigma^{(AB)}_R$ in SF_6–Ar gas mixture are shown in Figure 4. The results show that in the investigated pressure and fluence range two pressure regions can be distinguished: (*i*) the low and (*ii*) the high-pressure range (Figure 4). Hence, two different sets of rotational relaxation parameters are determined: for low and high pressure ranges. The widths of pressure ranges depend on buffer gas type, i.e. on the mass ratio of the gas absorber (A) and buffer gas (B), $K = m_A/m_B$. For higher K, the low pressure range is narrow, and the high pressure range is broader. For gas mixture SF_6–CH_4 the low pressure range extends up to p_{CH_4}= 20 mbar. Opposite to this, for SF_6–Ar the low pressure range is two times bigger (p_{Ar} = 55 mbar). In SF_6–N_2 mixture the low pressure range extends up to p_{N_2}= 40 mbar.

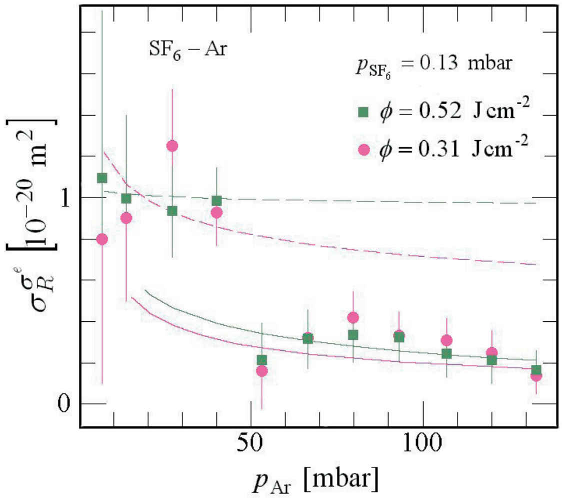

Figure 4. The pressure dependence of bulk rotational cross sections $\sigma^{(AB)}_R$ in SF_6–Ar gas mixture for different laser excitation fluences.

Two pressure ranges for relaxation parameters appear as a consequence of diverse influence of collisional effects in these regions. Laser fluence also has an influence on the rotational relaxation processes. For the low fluence range the hole filling proceses[23] have the dominant role in rotational relaxation. They increase the number of molecules interacting with laser radiation. With increasing laser fluence, a greater fraction of rotational states interacts with the laser field. Consequently, the rotational hole filling processes at these fluences do not enhance absorption. Such conditions are met in the experiment described here.

In the low pressure range, collisions effect has the highest influence on molecular absorption efficiency. This influence is followed by rapid growth of the enhanced cross sections, $\sigma^e_{P_a}$, (Figure 3), i.e. more absorbing molecules inside the irradiated volume are directly coupled with the laser radiation field. Such behavior is due to R–R relaxation, which includes all rovibrational transitions and eliminates the rotational hole filling effect.[23]

The high pressure range is characterized by the saturation effect of $\sigma^e_{P_a}$ (Figure 3). The collisions achieve their maximum regarding to their influence on MP processes. Hence, all absorbing molecules in the irradiated volume are directly coupled with radiation field due to laser fluence and collision inside gas mixture.

It is interesting to compare the results of this calculation for $\sigma_R^{(AB)} = \sigma_R^{\sigma^e}$ with those obtained previously from the "slope"[13], σ_R^S and "point"[14] $\left\langle \sigma_R^P \right\rangle$ methods that were produced in the same experimental conditions. In order to perform that, the average values $\left\langle \sigma_R^{(AB)} \right\rangle$ were determined (Figure 5). Typical results for SF_6–Ar p_{SF_6} = 0.47 mbar and p_{SF_6} = 0.13 mbar and SF_6–N_2 (p_{SF_6} = 0.47 mbar) gas mixtures are presented in Tables 1- 3. The estimated uncertainty of last figures is shown in parentheses.

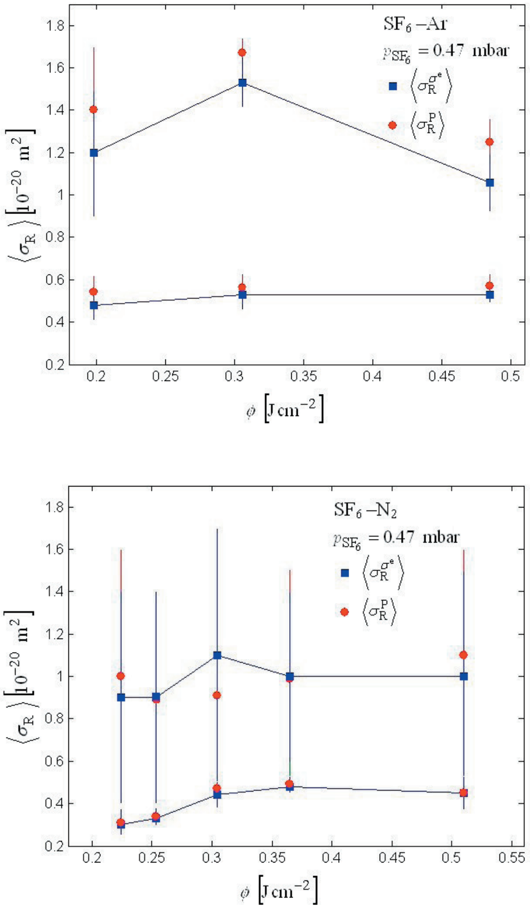

Figure 5. Average bulk rotational relaxation cross sections, $\left\langle \sigma_R^{\sigma^e} \right\rangle$, in SF_6–Ar and SF_6–N_2 gas mixtures as a function of laser fluence. Average values obtained from the "point" methods $\left\langle \sigma_R^P \right\rangle$ for different gas mixtures are also presented.

In order to determine the efficiency of RET in gas mixtures we compare the bulk rotational cross section, $\sigma_R^{\sigma^e}$ with the enhanced absorption cross section, $\sigma_R^{(AB)}$, for the same experimental conditions. The results show that for both pressure regions $\sigma_R^{\sigma^e} > \sigma_{P_a}^e$.

Table 1. Bulk rotational cross sections in SF_6–Ar gas mixtures (p_{SF_6} = 0.47 mbar).

ϕ ϕ [Jcm⁻²]	$\left\langle \sigma_R^{\sigma^e} \right\rangle$ [10⁻²⁰ m²]	$\left\langle \sigma_R^P \right\rangle$ [10⁻²⁰ m²]	σ_R^S [10⁻²⁰ m²]
P_{SF_6} = 0.47 mbar			
low pressure range: $0 \le p_{Ar} \le 55$ mbar			
0.198(7)	1.2(3)	1.3(3)	1.0(8)
0.306(8)	1.53(11)	1.56(12)	1.6(6)
0.4856(8)	1.06(14)	1.09(13)	0.9(9)
high pressure range: $55 \le p_{Ar} \le 140$ mbar			
0.198(7)	0.48(7)	0.50(7)	0.48(27)
0.306(8)	0.53(7)	0.56(7)	0.5(4)
0.4856(8)	0.53(4)	0.55(4)	0.53(25)

The ratio $\sigma_R^{\sigma^e} / \sigma_{P_a}^e$ is shown in Figure 6. This is in accordance with the prediction of the four–state kinetic method for laser pulse transmission trought SF_6 gas mixure.[18] In this method the absorber molecules are divided into four groups. The molecules which can directly interact with laser radiation in (*i*) ground and (*ii*) vibrationaly excited states, and the rest of molecules in (*iii*) ground and in (*iv*) excited states. The main conclusion of detailed numerical calculation (steady–state rate equations) is that the dominant relaxation processes are the average rotational relaxation transitions.

Table 2. Bulk rotational cross sections in SF_6–Ar gas mixtures (p_{SF_6} = 0.13 mbar).

ϕ [Jcm⁻²]	$\left\langle \sigma_R^{\sigma^e} \right\rangle$ [10⁻²² m²]	$\left\langle \sigma_R^P \right\rangle$ [10⁻²² m²]	σ_R^S [10⁻²² m²]
P_{SF_6} = 0.13 mbar			
low pressure range: $0 \le p_{Ar} \le 50$ mbar			
0.210(21)	8.5(11)	8.9(11)	8.5(12)
0.310(4)	10.1(16)	10.1(17)	10.2(18)
0.516(11)	9.40(13)	9.42(16)	9.5(17)
high pressure range: $50 \le p_{Ar} \le 140$ mbar			
0.210(21)	3.5(3)	3.5(3)	3.2(9)
0.310(4)	2.4(10)	3.0(4)	2.6(4)
0.516(11)	3.37(20)	3.39(22)	3.1(9)

Table 3. Rotational cross sections in SF_6–N_2 gas mixtures (p_{SF_6}= 0.13 mbar).

ϕ $\lfloor Jcm^{-2} \rfloor$	$\langle \sigma_R^{\sigma^e} \rangle$ $[10^{-20}\ m^2]$	$\langle \sigma_R^P \rangle$ $[10^{-20}\ m^2]$	σ_R^S $[10^{-20}\ m^2]$
$P_{SF_6} = 0.47$ mbar			
low pressure range; $0 < p_{N2} < 40$ mbar			
0.510(3)	1.0(5)	1.1(5)	0.59(21)
0.365(10)	1.0(4)	1.0(5)	0.57(21)
0.304(4)	1.1(6)	0.91(17)	0.51(17)
0.253(7)	0.9(5)	0.9(5)	0.43(15)
0.224(6)	0.9(5)	1.0(6)	0.39(14)
high pressure range: $40 < p_{N2} < 140$ mbar			
0.510(3)	0.45(8)	0.45(8)	0.50(15)
0.365(10)	0.48(4)	0.49(4)	0.50(15)
0.304(4)	0.44(9)	0.47(15)	0.47(15)
0.253(7)	0.33(3)	0.34(3)	0.33(15)
0.224(6)	0.30(6)	0.31(6)	0.34(12)

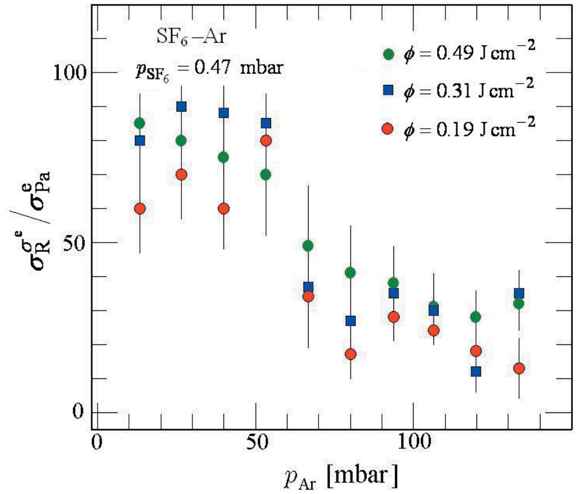

Figure 6. The ratio of bulk rotational cross-section $\sigma_R^{\sigma^e}$ and enhanced absorption cross–section, $\sigma_R^{(AB)}$, as a function of buffer gas pressure for different laser fluences.

Conclusions

In this work we have presented a new approach to determine bulk rotational relaxation cross sections, σ_R. It is shown that significant information for σ_R can be determined from measured values of enhanced cross sections, σ^e, by using a relationship between σ^e and saturation intensity values, I_S. The method was tested in gas mixture SF_6–Ar for two different absorber gas pressures, p_{SF_6} = (0.47 mbar and 0.13 mbar) and in SF_6–N_2 (0.47 mbar). Enhanced cross sections involved in MP processes were measured by calibrated pulsed PAS technique. It was shown that the obtained results for σ_R are in good accordance with the data obtained from the "slope" and the "point" method. This method offers the number advantages. First of all, it gives the possibility to determine bulk data from the usual measured σ^evalue in MP excitation processes. This method also avoids the need for additional measurements of saturation intensities in gas mixtures as in case of "point" and "slope" methods. The proposed method was tested in relatively large pressure range of buffer gas (0 - 140 mbar), and hence it is not restricted to any pressure range. The same "calibration" enables to determine bulk rotational in both pressure ranges. In this work the "calibration" for TR determination of σ_R was also established. The accuracy of this method is limited by the accuracy of σ^edata.

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Povzetek

Predstavljamo nov eksperimentalni pristop k raziskavam povprečnih makroskopskih (R→R/T) rotacijskih relaksacijskih parametrov visoko vibracijsko vzbujenih molekul v plinski zmesi, kjer trki ojačajo absorpcijske procese. Z več fotonsko umerjeno optoakustično spektroskopijo smo želene parametre izračunali iz izmerjenega ojačanega absorpcijskega preseka, ki vsebuje podatke o fotonih in fiziki trkov. Vse meritve smo opravili pri sobni temperaturi z uporabo 10P(16) emisijske črte laserja TEA CO_2 s površinsko gostoto energije v območju 1 - 7 × 10^3 Jm^{-2} in za tlake od 1 do 140 milibarov. Posebno pozornost smo posvetili oceni vplivov kolizijskih parametrov in tlaka na relaksacijske parametre. V vseh zmeseh smo ugotovili pomemben vpliv tlaka na osnovi katerega lahko razlikujemo visoko in nizkotlačno območje meritev. Podatki dobljeni s predlagano in enostavnejšo metodo se dobro ujemajo s podatki, ki jih dajeta že poznani točkovna metoda in metoda naklona.