

Measurements of molecular absorption line broadening and shift induced by collisions with selectively excited buffer gas molecules. 2. Estimated change in line shift

Yu.N. Ponomarev, A.D. Bykov, and V.N. Savel'ev

*Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk*

Received January 27, 2005

The influence of vibrational excitation of SF₆ molecules on the shift of CH₄ absorption lines in the CH₄–SF₆ binary system has been estimated. It is shown that if 10–30% of buffer gas molecules are excited, the change in the line shift can achieve 12%, which is detectable with the spectrometer resolution of 10^{–3} cm^{–1}.

Introduction

High-resolution spectroscopy allows a detailed investigation into the dependence of the line profile and its characteristics, namely, buffer gas pressure induced broadening and shifting coefficients. The set of data on the spectral line profile and its parameters provides for the possibility of determining the constants of intermolecular interaction potential, electrooptical characteristics (for example, polarizability¹) of the absorbing molecule in excited vibrational states.

Now almost all experiments dealing with the investigation into the influence of collisions on the broadening and shift of spectral lines are conducted for the case when a buffer gas molecules are in the ground vibrational state. In Ref. 2, it was proposed to conduct an experiment to study the broadening and shift of ro-vibrational absorption lines by collisions with selectively excited buffer gas molecules and the design of the corresponding laser-based photoacoustic spectrometer has been proposed as well. The spectrometer includes a powerful CO₂ laser for selective excitation of buffer gas molecules, such as SF₆ and C₂H₄, and a tunable diode laser, operating in the range of 1.6 to 1.65 μm with the linewidth of ~10^{–4} cm^{–1} in the single-mode regime. This spectral range includes several CH₄ absorption lines, for which the typical shift due to the buffer gas (for example, Ar) pressure of 400 Torr is ~5 · 10^{–3} cm^{–1} [Ref. 3]. Such a shift can be reliably detected at the spectrometer resolution ~10^{–3} cm^{–1}.

The experiment proposed in Ref. 2 assumes the detection of the difference in the shift of methane absorption lines due to collisions with only unexcited buffer gas molecules and with both unexcited and excited (~20% of the total number) buffer gas molecules.

This level of excitation for SF₆ and C₂H₄ molecules can be obtained at a moderate power of a CO₂ laser,⁴ and this can lead to the change in the line shift value. To determine the requirements to the

spectral resolution of a photoacoustic spectrometer and to develop the technique, it is necessary to estimate the shift of spectral lines of the absorbing molecule upon the appearance of a marked (~20%) fraction of excited buffer gas molecules in the binary gas mixture of the absorbing and buffer gases. The aim of this paper is just to obtain such estimates for the binary mixture of CH₄ (absorbing gas) and SF₆ (buffer gas) in order to analyze the capabilities of the experimental technique.

1. Main factors of the change in the line-shifting coefficient upon the vibrational excitation of buffer gas molecules

The spectral line shifts will be estimated within the framework of the Anderson–Tsao–Curnutte (ATC) semiclassical impact theory,⁵ in which collisions are believed binary, the collision time is short as compared to the time between collisions, and the trajectories of particles are straight-lines. The spectral line shift (δ) for the transition $i \rightarrow f$, where i and f are the quantum numbers of the initial and final states of the principal molecule, is described by the equation

$$\delta_{if} = \frac{n\nu}{2\pi c} \sum_{j_2} \rho_{j_2} \text{Im} \sigma_{j_2}, \quad (1)$$

where $\text{Im} \sigma_{j_2}$ is the imaginary part of the complex collisional cross section; n is the density of buffer gas molecules; ν is the velocity of molecules; c is the speed of light; ρ_{j_2} is the population of the j_2 level of the buffer gas;

$$\sigma_{j_2} = 2\pi \int_0^\infty b db S(b); \quad (2)$$

$$S(b) = iS_1(b) + S_2(b). \quad (3)$$

Here b is the impact parameter; $S_1(b)$, $S_2(b)$ are the well-known interruption functions of the Anderson theory. The quantum indices i and f of the active molecule include both vibrational and rotational quantum numbers. The interruption functions include matrix elements of the intermolecular potential calculated with the ro-vibrational wave functions and therefore depend on the vibrational quantum numbers.

For example, for the strongest dipole-dipole interaction, the interruption function $S_2(b)$ is determined in the form

$$S_2(b) = \frac{4}{9\hbar^2 v^2 b^4} \sum_{j_2} D^2(j_2 j_2') \times \left\{ \sum_{i'} D^2(i i') \varphi(k_{i i' j_2 j_2'}) + \sum_{f'} D^2(f f') \varphi^*(k_{f f' j_2 j_2'}) \right\}, \quad (4)$$

where $D(j j')$, $D(i i')$, $D(f f')$ are "generalized" line strengths, that is, line strengths divided by $2j + 1$ square of reduced matrix elements for dipole transitions in the buffer gas and the absorbing molecules, respectively. In the method of effective operators, the total wave function is represented in the form of the product $\psi_v \psi_r^{[v]}$ of the vibrational (ψ_v , v denotes the set of vibrational quantum numbers) and rotational ($\psi_r^{[v]}$, r is the set of rotational quantum numbers) wave functions. Therefore, the main parts of the generalized line strengths, corresponding to the dipole transitions in the buffer molecule in Eq. (4), can be factorized as:

$$D^2(j_2 j_2') = |\langle \psi_v | \mu_z | \psi_v \rangle|^2 |\langle \psi_r^{[v]} | K_{zz} | \psi_r^{[v]} \rangle|^2. \quad (5)$$

Here μ_z is the component of the dipole moment of the buffer molecule (it is assumed that the axis z of the molecular coordinate system is directed along the dipole moment vector); K_{zz} is the direction cosine. Each of these factors depends on the vibrational quantum numbers: the first one accounts for the change in the average dipole moment upon the vibrational excitation, and the second one accounts for the change in rotational wave functions due to the variation of effective moments of inertia. Usually, both these effects are assumed small, because they are determined by the first and second derivatives of the dipole moment with respect to normal coordinates in the first case and by the rotational-vibrational interaction in the second case. However, it should be noted that for some molecules, for example, H_2S , CO , and H_2O , the corrections due to the above intramolecular effects can be significant.

The complex resonance functions

$$\varphi(k) = f_i(k) + i f_f(k) \quad (6)$$

depend on the parameter

$$k_{i i' f f'} = \frac{2\pi c b}{v} (E_i - E_{i'} + E_{j_2} - E_{j_2'}), \quad (7)$$

which, in its turn, depends on the RV energy levels of a buffer molecule. As a consequence, the change of the rotational energy spectrum due to the vibrational excitation of buffer gas molecules can also cause the change in line half-widths and shifts.

Similar factors manifest themselves at other types of the interaction: quadrupole, octupole, etc.

If the mixture of gases is at room temperature, the fraction of vibrationally excited buffer gas molecules is small. In this case, the operation of averaging over states in Eq. (1) is performed only over the rotational levels of the lower vibrational state and $S(b)$ depends only on the characteristics of the buffer molecule in the ground vibrational state. When the gas mixture is exposed to laser radiation, which is absorbed by the buffer gas molecules, this leads to their excitation. As a consequence, the intermolecular interaction potential changes due to the changes in the multipole moments, in the distribution of buffer molecules over the rotational energy levels, and in the transition frequencies and probabilities in the buffer molecule in the excited vibrational state. The higher is the vibrational excitation energy of the buffer molecules, the larger is the change in the line shift.⁶⁻⁸

2. Estimated influence of vibrational excitation on the CH_4 line shift

Consider the shifts of methane lines in a non-polar buffer gas (for example, C_2H_4 , SF_6). We will take into account only the contributions of the isotropic part of the potential to the function $S_1(b)$ and the main octupole-quadrupole interaction to $S_2(b)$, because the first nonzero multipole moment of methane in the ground vibrational state is octupole.

In this case, the terms of the interruption function take the form⁹⁻¹¹:

$$S_1(b) = i\Delta_{1,i} - i\Delta_{1,f}, \quad (8)$$

$$S_1(b) = -\frac{3\pi}{8\hbar v b^5} \alpha_2 \left\{ \frac{3U_1 U_2}{2(U_1 + U_2)} [\alpha_1^{ii} - \alpha_1^{ff}] \right\}, \quad (9)$$

$$S_2(b) = {}^{32}S_2(b)_i - {}^{32}S_2(b)_f = \frac{1024}{875} \left(\frac{\Omega_1 \Theta_2}{\hbar v} \right)^2 \frac{1}{b^{10}} \times \left\{ \left(1 + \delta_{0K_i} \right)^{-1} \sum_{j_2' j_i' K_i'} \left(1 + \delta_{0K_i'} \right)^{-1} \times \left[C_{j_i' K_i' 32}^{j_i K_i' 2} + C_{j_i' K_i' 3-2}^{j_i K_i' 2} + C_{j_i' K_i' 3-2}^{j_i -K_i' 2} \right] \times C_{j_i' K_i' 20}^{j_i K_i' 2} \times f_4(k) - (i \rightarrow f) \right\}. \quad (10)$$

In Eqs. (9) and (10), $\alpha_1^{ii} = \langle v_i | \alpha_1 | v_i \rangle$ is the mean polarizability of the principal molecule in the vibrational state i ; α_2 is the mean polarizability of the buffer molecule in the ground or excited

vibrational state; U_1, U_2 are the ionization potentials of the molecules; Ω_1, Θ_2 are the octupole and quadrupole moments; $C_{jKmm}^{j'K'}$ are the Clebsh–Gordon coefficients, determining the line strengths of radiationless transitions in molecules; $f_4(k)$ are the resonance functions for the octupole-quadrupole interaction.

In the estimates, we take into account the following:

1. In the non-polar molecules considered, the rotational interaction is low and the rotational-vibrational constant is at least three orders of magnitude lower than the rotational constant; therefore, the change in the rotational spectrum upon the excitation of several vibrational quanta can be neglected.

2. The estimates also show that the difference in the line strengths $(C_{jKmm}^{j'K'})^2$ for the ground and the excited states can be neglected, because it is determined by the effects caused by deviations from the Born–Oppenheimer approximation. For the vibrational levels of the ground electronic state of the buffer molecule, whose energy is much lower than the dissociation threshold, these effects can be neglected.

3. As is shown by calculations,¹² the change in the quadrupole moment upon the excitation of several vibrational quanta is 7–10%. Thus, in the estimates, the shifts of methane lines with $v = 2$ upon the collisions with excited non-polar molecules can be neglected.

4. The direct calculation of the broadening and shift of methane lines (performed for other non-polar buffer molecules: N_2 and O_2) showed^{13,14} that the total contribution of all multipole and disperse interactions ($S_2(b)$) as compared to the contributions of the isotropic part of the potential ($S_1(b)$), given in the Table, does not exceed 13–16%. The Table summarizes the contributions of different multipole interactions to $S_2(b)$.

Based on the above-said, in the estimation of the change in the shift of methane spectral lines upon the buffer gas excitation, we can restrict our consideration to the contribution $S_1(b)$ and neglect the contribution $S_2(b)$.

Buffer gas	N ₂ , %	O ₂ , %
Total contribution of multipole interactions as compared to the contribution of the isotropic part of the potential ($S_1(b)$)	13.2	16.5
Including		
octupole-quadrupole	65.7	12.0
octupole-hexadecapole	28.18	73.3
disperse contributions	5.7	14.02
hexadecapole-quadrupole	0.24	0.05
hexadecapole-hexadecapole	0.18	0.63

Taking into account Eqs. (1)–(3) and (8)–(10), one can write the equation for the shift of the methane spectral line:

$$\delta_{if} = -\frac{9\pi n\alpha_2}{16\hbar c} \frac{U_1 U_2}{(U_1 + U_2)} (\alpha_i^{ii} - \alpha_i^{ff}) \int_0^\infty \frac{bdb}{b^5}. \quad (11)$$

If now we denote the part of the Eq. (11) independent of the vibrational characteristics of the buffer molecule as D :

$$D = -\frac{9\pi}{16\hbar c} \frac{U_1 U_2}{(U_1 + U_2)} (\alpha_i^{ii} - \alpha_i^{ff}) \int_0^\infty \frac{bdb}{b^5},$$

then the line shift can be written as

$$\delta_{if} = n\alpha_2 D. \quad (12)$$

If n^* is the concentration of excited buffer gas molecules, then the shift of a spectral line of the absorbing molecule can be presented as

$$\delta_{if}^* = (n - n^*)\alpha_2 D + n^*\alpha_2^* D. \quad (13)$$

Here α_2^* is the mean polarizability of the buffer molecule in the excited vibrational state. The relative change in the spectral line shift upon the vibrational excitation of some buffer gas molecules can be expressed as

$$\frac{\delta_{if}^* - \delta_{if}}{\delta_{if}} = \frac{n^* \alpha_2^* - \alpha_2}{n \alpha_2}. \quad (14)$$

Thus, the strongest effect can be expected to come from the change in the polarizability upon the vibrational excitation. The estimates obtained for the buffer gas molecules under consideration^{7,8} give the increase of several tens percent in the polarizability upon the vibrational excitation.

For example, if 30% of buffer gas molecules are vibrationally excited and $\alpha_2^* \approx 1.4\alpha_2$, then the relative change in the shift is $(\delta_{if}^* - \delta_{if})/\delta_{if} \approx 0.12$.

It is known from the experiment that the absolute values of the shifts of different lines in methane ro-vibrational bands can achieve $0.015 \text{ cm}^{-1} \cdot \text{atm}^{-1}$ [Refs. 14, 15]. Therefore, under given conditions, we can expect the following change in the absolute shift of a line: $(\delta_{if}^* - \delta_{if}) \sim 0.002 \text{ cm}^{-1}$. This shift is really detectable with the spectrometer developed for such studies.²

Figure 1 shows the record of the methane spectrum along with the record of the transmission spectrum of an interferometric wavelength meter. The distance between peaks in the interferometer spectrum is 0.05 cm^{-1} , the peak width (determined by the interferometer finesse ~ 20) amounts to 0.0025 cm^{-1} and determines the spectral resolution of the spectrometer in general, since the radiation line width, used to record the methane absorption spectrum (Sacher Laser technik TEC-100), is an order of magnitude smaller $\sim 10^{-4} \text{ cm}^{-1}$. The resolution attained is quite sufficient for recording small shift values $\sim 10^{-3} \text{ cm}^{-1}$, as was demonstrated in Ref. 3 when studying the CH_4 absorption line shift by helium and neon.

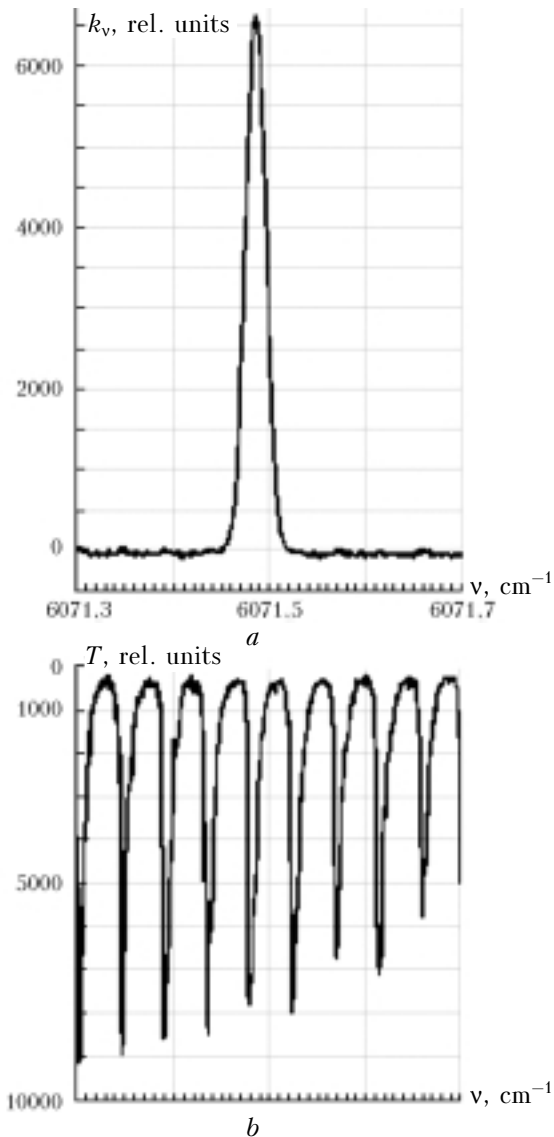


Fig. 1. Methane absorption spectrum at 8 Torr (*a*) and transmission spectrum of the interferometer-wavelength meter (*b*). The distance between neighboring peaks in the interferometer spectrum is 0.05 cm^{-1} .

Acknowledgments

The authors are grateful to I.S. Tyryshkin and N.P. Krivolutskii for the data illustrating the spectral resolution of the instruments used.

This work was supported by the Russian Foundation for Basic Research (Project No. 04-03-32627) and the Russian Academy of Sciences (Program "Optical Spectroscopy and Frequency Standards").

References

1. E.V. Browell, B.E. Grossman, A.D. Bykov, V.A. Kapitanov, V.V. Lazarev, Yu.N. Ponomarev, L.N. Sinita, E.A. Korotchenko, V.N. Stroinova, and B.A. Tikhomirov, *Atm. Opt.* **3**, No. 7, 617-630 (1990).
2. Yu.N. Ponomarev, V.A. Kapitanov, A.I. Karapuzikov, and I.V. Sherstov, *Atmos. Oceanic Opt.* **17**, No. 10, 763-766 (2004).
3. V. Zeninari, B. Parvitte, D. Courtois, V.A. Kapitanov, and Yu.N. Ponomarev, *Appl. Phys. B* **72**, 953-959 (2001).
4. V.F. Ponurovskii, *Opt. Spektrosk.* **37**, No. 2, 246-249 (1974).
5. C.J. Tsao and B. Curnutte, *J. Quant. Spectrosc. Radiat. Transfer* **2**, 41-91 (1962).
6. M.O. Bulanin, A.P. Burtsev, and G.Yu. Tret'yakov, *Khim. Fiz.* **7**, No. 12, 1615-1619 (1988).
7. K.M. Gough, *J. Chem. Phys.* **91**, No. 4, 2424-2432 (1989).
8. M.A. Spackman, *J. Chem. Phys.* **94**, No. 2, 1288-1294 (1991).
9. P. Varanasi, *J. Quant. Spectrosc. Radiat. Transfer* **14**, No. 10, 995-1008 (1974).
10. G.D.T. Tejwani, P. Varanasi, and K. Fox, *J. Quant. Spectrosc. Radiat. Transfer* **15**, No. 3, 205-281 (1975).
11. V.N. Saveliev and N.N. Lavrentieva, *Proc. SPIE* **2205**, 367-369 (1993).
12. V.N. Saveliev and N.N. Lavrentieva, *Atmos. Oceanic Opt.* **7**, No. 1, 15-19 (1994).
13. D.C. Cartwright and T.H. Dunning, *J. Phys. B* **7**, No. 13, 1776-1781 (1974).
14. V.M. Devi, C.P. Rinsland, M.A.H. Smith, and D.C. Benner, *Appl. Opt.* **27**, No. 11, 2296-2308 (1988).
15. K. Fox and D.E. Jennings, *J. Quant. Spectrosc. Radiat. Transfer* **42**, No. 3, 201-206 (1989).