Vol. **101** (2002) *ACTA PHYSICA POLONICA A* No. 6

Pressure Broadening of $J = 1 \leftarrow 0$ Rotational Line of Fluoroform Caused by Spherical Perturbers

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(Received November 2, 2001; revised version February 25, 2002)

The foreign-gas broadening parameter was measured for CHF_3 molecule interacting with spherical (SF_6, CF_4, CH_4, CCl_4) perturbers and the pressure shift parameter of rotational transition $J = 1 \leftarrow 0$ in the CHF_3 molecule was obtained. For the systems of trifluoromethane molecule and four spherical molecules as perturbers the collision cross-sections were determined. Experimental line width parameters are interpreted using Anderson–Tsao–Curnutte as well as Murphy–Boggs theories. Accounting for the dispersive and inductive interactions the cross-section was determined. The theoretical values are in qualitative agreement with the experimental results, but the absolute values of the measured cross-section were larger than these calculated.

PACS numbers: 33.20.Bx, 33.20.Sn

1. Introduction

The studies of the collision broadening of microwave spectral lines at low pressures provide information about the nature of intermolecular forces which are responsible for rotational relaxation processes occurring in polar gases and in mixtures containing at least one polar gas. They are useful in interpretation of atmospheric and astrophysical data. The width $\Delta\nu$ of a microwave spectral line is closely related to the type of the intermolecular interaction responsible for the line

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broadening. In a single component polar gas, $\Delta\nu$ defines a cross-section σ, and the effective range of interaction b for the radiation interruption process,

$$\Delta\nu = (1/2\pi)Nv\sigma = (1/2)Nvb^2, \tag{1}$$

where N is the density of molecules and v — mean velocity. For gas mixtures the total line width is a sum of contributions from the different collisional partners. Studies of collisions between polar and nonpolar molecules can give an information about higher order interactions. The self-broadening of some rotational transitions of CHF_3 molecule have been reported earlier [1–3]. The pressure-broadened line width of the $J = 1 \leftarrow 0$ rotational transition of fluoroform molecule for foreign dipole and nonpolar gas broadening have been measured [4–6].

The aim of the present study is to provide a quantitative information on the molecular collision cross-sections for CHF_3 interacting with SF_6, CF_4, CH_4, and CCl_4 molecules.

When a dipolar absorption line is perturbed by noble gas or spherical molecules the molecular forces responsible for the broadening would be the induction forces (dipole-induced dipole, quadrupole-induced dipole, dipole-induced quadrupole), the dispersion and exchange forces.

The theory of pressure broadening in microwave region was given by Anderson–Tsao–Curnutte (ATC) [7, 8], Murphy–Boggs (MB) [9] and for the dispersion and exchange interactions developed by Krishnaji [10]. We use them for the interpretation of experimental results in which the line width measurements are to determine the collision cross-sections of CHF_3 interacting with nonpolar molecules.

2. Theory

The collision-cross section σ is defined with the integral

$$\sigma = \int_0^\infty 2\pi b S(b)\mathrm{d}b, \tag{2}$$

where b is impact parameter and $S(b)$ is the weight factor indicating the differential probability of collision induced transitions. The collisional cross-section σ is related to the foreign-gas broadening parameter C_w by the following relation:

$$\sigma = 0.447 C_\mathrm{w}\sqrt{MT}, \tag{3}$$

where M — reduced mass of colliding molecules, T — absolute temperature.

The function $S(b)$ depends upon the interaction Hamiltonian of both the absorber and the perturber.

The expression of $S(b)$ for the dispersion (DSP) and induction (IND) interactions, can be written

$$S(b) = S_\mathrm{DSP} + S_\mathrm{IND}, \tag{4}$$

where

$$S(b)_{\mathrm{DSP}} = \frac{A_{\mathrm{DSP}}}{b^{10}} F(k), \tag{5}$$

$$S(b)_{\mathrm{IND}} = \frac{A_{\mathrm{IND}}}{b^{10}} F(k), \tag{6}$$

$$A_{\mathrm{DSP}} = \frac{21\pi^3}{10240\hbar^2 kNT} \left[\frac{I_1 I_2}{I_1 + I_2} (\alpha_1^{\|} - \alpha_1^{\perp}) \alpha_2 \right]^2 M, \tag{7}$$

$$A_{\mathrm{IND}} = \frac{21\pi^3}{540\hbar^2 kNT} (\alpha_2 \mu_1^2)^2, \tag{8}$$

$$F(k) = \sum_{J_1'} Q(J_i J_i') g(k) + \sum_{J_f'} Q(J_f J_f') g(k) + B, \tag{9}$$

$$B = (-1)^{J_i + J_f} 2[(2J_i + 1)(2J_f + 1) Q(J_i J_i) Q(J_f J_f)]^{1/2} W(J_i J_f J_i J_f, 12), \tag{10}$$

and μ_1 — dipole moment of absorber, I_1, I_2 — ionization energies of the colliding molecules, J_i, J_f — initial and final states of absorber, $\alpha_1^{\|}$, $\alpha_1^{\perp}$ — components of the polarizability along and perpendicular to the molecular axis of the absorber, α_2 — mean polarizability of the perturber, T — absolute temperature, $Q(J_i J_i')$, $Q(J_f J_f')$ — quadrupole transition probabilities, $W(J_i J_f J_i J_f, 12)$ — Racah coefficient, N — Avogadro's constant, $g(k) = g([b/\nu]|\omega|)$ — function tabulated by Tsao-Curnutte [8], v — relative velocity, ω — change in the rotational energy of absorber.

3. Experimental

The measurements of microwave absorption were carried out with a custom made Stark spectrometer (Fig. 1) detailed previously [6, 11], with a few modifications which improve the spectroscopic properties. The microwave power supplied by a synthesizer Anritsu 68367C (SMG) is passed through the calibrated attenuator (MA) and coupled to a conventional H-band waveguide: two-meter long Stark absorption cell (SC), filled with the absorbing gas. Tapered transition sections connect the cell at both ends to the K-band waveguide. The cell is sealed from the atmosphere by mica windows placed at the K-band waveguide flanges. After the cell, the microwave power passes through the broad band isolator (α) model (KY2021) and is detected with Schottky barrier diode (D). The Stark septum is connected to a conventional 10 kHz square wave Stark generator (SG). The amplitude of the square pulse signal is continuously variable from 200 V to 2000 V. The vacuum installation connected to a SP-800 vacuum system (VS) provides an ultimate vacuum in the Stark absorption cell of 8×10^{-6} Torr. The sample pressure of the carbonyl sulphide (OCS) is measured with an absolute pressure

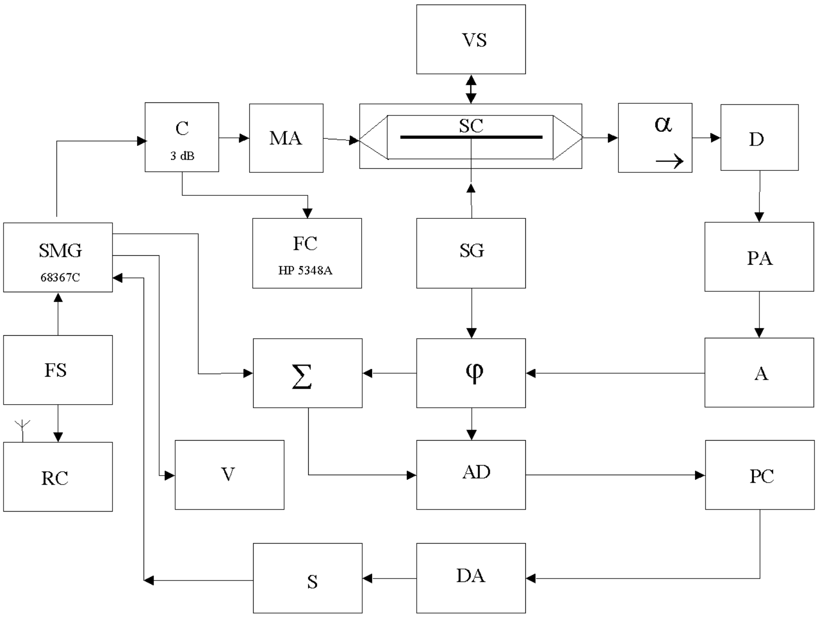

Fig. 1. Microwave scanning spectrometer: SMG — synthesized microwave generator, C — coupler 3 dB, MA — microwave attenuator, VS — vacuum system, SC — Stark cell, SG — Stark generator, α — isolator, D — detector DK 2, PA — preamplifier, A — amplifier, φ — lock-in detector, AD — analog-digital converter, DA — digital-analog converter, PC — personal computer, V — voltmeter, FS — frequency standard, RC — receiver and comparator, S — start circuit, $\sum$ — adder, FC — frequency counter.

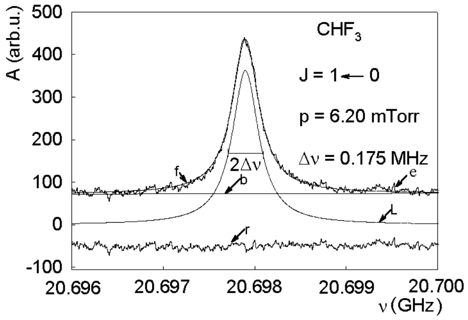

Fig. 2. The rotational transition $J = 1 \leftarrow 0$ of CHF_3 molecule obtained in gas pressure of 6.20 mTorr: b — background, e — experimental line, L — the Lorentzian line, f — fitted line, r — residuals between fitted and experimental lines, $\Delta\nu$ — half width at half height of amplitude of the line.

gauge MKS Baratron 220C with a resolution of 10^{-5} Torr and 1% accuracy. The pressure gauge MKS Baratron was calibrated using an oil absolute meter with the gas expansion method by applying a volume divider. During the recording of the absorption line the gas pressure is maintained constant to within 0.1 mTorr. The temperature of the cell during measurements is stabilized and measured to an accuracy better than ± 0.05 K. The output of the detector (D) is connected to the phase sensitive detector (φ) via UNIPAN 233.5 type preamplifier (PA) and amplifier (A); the total gain is 8×10^5 at a nonlinearity coefficient less than 1.2%. The absorption signal (Fig. 2) obtained at the output of the phase sensitive detector and frequency markers are added ($\sum$) and digitized with a 12 bit A/D converter (AD) and via standard IEEE 488 bus interface to an Intel 486 PC computer (PC).

4. Results

The line width of the transition of the fluoroform molecule in the pressure p_1 of the perturber is determined from the formula

$$\Delta\nu = C_{\mathrm{w}} p_0 + C_{\mathrm{w}}(x) p_1 + \sum \Delta\nu_{\mathrm{corr}}, \tag{11}$$

where C_{w} is pressure self-broadening coefficient, $C_{\mathrm{w}}(x)$ is pressure broadening coefficient of the gas mixture, $\Delta\nu_{\mathrm{corr}}$ are the corrections to the measured line width, p_0, p_1 are the partial pressures of CHF_3, and perturbers, respectively. After the value of $C_{\mathrm{w}} p_0 + \sum \Delta\nu_{\mathrm{corr}}$ is determined the line width is measured, using the pure CHF_3 at the initial pressure p_0. Gradually, the perturbing gas is added and the line width $\Delta\nu$ measured, hence, the difference $\Delta\nu - (C_{\mathrm{w}} p_0 + \sum \Delta\nu_{\mathrm{corr}})$, resulting from collisions with the perturber, can be calculated. The pressure broadening coefficient measured for pure CHF_3 is $C_{\mathrm{w}} = (34.49 + 0.24)$ MHz/Tr.

This value is more accurate than those reported elsewhere obtained at 293 K: $C_{\mathrm{w}} = 35.7$ [12], 35.4 ± 0.4 [13], 35.32 [14] MHz/Torr.

Adjusted for the temperature dependence of C_{w} ($\beta = -0.82 + 0.03$ [3]) these values and our results measured at 301 K agree within the experimental error.

The centre frequency ν and the line width $\Delta\nu$ of the digitized absorption signal were found using the Lorentzian line shape fit method. A quadratic polynomial base line correction was assumed. The centre frequency of transition $J = 1 \leftarrow 0$ CHF_3 molecule $\nu = (20697700 \pm 5)$ kHz was measured at 5 mTorr and corrected for the residual shift. The experimentally measured pressure shift parameter $C_{\mathrm{s}} = (2.23 \pm 0.08)$ MHz/Torr is in excellent agreement with the numbers (2.28 ± 0.16) MHz/Torr reported in literature [3].

For the molecules perturbed by foreign gas the collision cross-section σ given as [15]: $\sigma(x) = (2\pi kT/\nu) C_{\mathrm{w}}(x)$, where $C_{\mathrm{w}}(x)$ is the experimentally obtained foreign gas broadening parameter and $x = SF_6,\ CF_4,\ CH_4,\ CCl_4$.

The collisional cross-sections σ for CHF_3 molecule was measured and calculated for the DSP, IND and DSP+IND forces. All these forces have considerable effect on the line width.

We assume that the function $F(k)$ is independent of the energy levels structure of the collision partner and its value is denoted F_0 [15].

When we take into account IND + DSP interactions, then

$$\sigma = \frac{5}{4}\pi B^{1/5}\left[\left(\frac{I_1 I_2}{I_1 + I_2}\gamma\alpha_1\alpha_2\right)^2 M + 1600\mu_1^4\alpha_2^2 M\right]^{1/5} = \frac{5}{4}\pi B^{1/5} X, \tag{12}$$

where

$$B = \frac{21\pi^3}{5120\hbar^2 kNT}F_0, \tag{13}$$

$$X = M^{1/5}\left[\left(\frac{I_1 I_2}{I_1 + I_2}\gamma\alpha_1\alpha_2\right)^2 + 1600\mu_1^4\alpha_2^2\right]^{1/5} \tag{14}$$

and

$$\gamma = \frac{\alpha_1^{\|} - \alpha_1^{\perp}}{\alpha_1}. \tag{15}$$

The experimentally obtained cross-section vary linearly with X (Fig. 3). Such linear dependence is also predicted by Eq. (12), suggesting that the sum of dispersion and induction forces plays the leading role during the observed collisions.

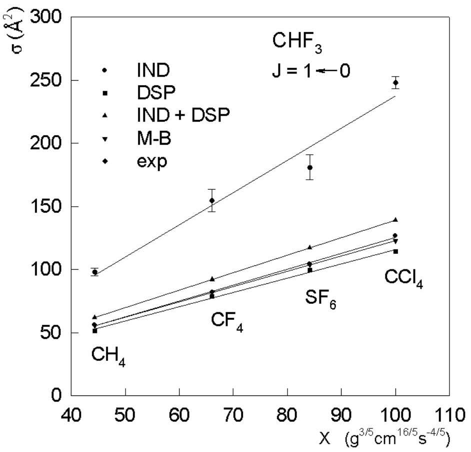

Fig. 3. Experimentally (exp) and theoretically (IND, DSP, IND + DSP, M-B) obtained collision cross-section of CHF_3 molecule as a function of X (see Eq. (14)) for various perturbers.

The theoretically and experimentally obtained cross-sections for CH_4, CF_4, SF_6, CCl_4 (Tables I and II) are plotted as a function of X (Fig. 3). We have also calculated the line broadening coefficient using Murphy–Boggs theory [9]. The values are smaller than those obtained using ATC theory (Table I). The experimental results of line width ($\Delta\nu$) and line shift ($\Delta\phi$) are plotted versus pressure of gas in Fig. 4a and b.

Figure 5 shows the collisional diameters obtained theoretically b_{calc}, experimentally b_{exp} and the kinetic diameters b_{kin} as a function of X.

TABLE I

Pressure broadening coefficients C_{w} [MHz/Tr], collision cross-sections σ [Å^2], collision diameters b [Å] determined for the $J = 1 \leftarrow 0$ transition of CHF_3 molecule in the mixtures with nonpolar molecules (calculated with data given in Table II).

	Interactions	C_{w} [MHz/Tr] σ [Å^2] b^* [Å]	CH_4	CF_4	SF_6	CCl_4
Anderson	IND	C_{w}	2.01	1.69	1.96	2.37
		σ	56.08	81.80	104.43	126.87
		b	4.23	5.10	5.76	6.36
	DSP	C_{w}	1.84	1.63	1.87	2.13
		σ	51.45	78.66	99.46	114.24
		b	4.04	5.01	5.63	6.03
	IND+DSP	C_{w}	2.22	1.91	2.20	2.6
		σ	61.99	92.20	117.16	139.09
		b	4.44	5.42	6.10	6.66
Murphy–Boggs	IND+DSP	C_{w}	1.98	1.69	1.95	2.29
		σ	55.28	81.85	103.78	122.68
		b	4.19	5.10	5.75	6.25
Experiment		C_{w}	3.5 ± 0.1	3.2 ± 0.2	3.4 ± 0.2	4.6 ± 0.1
		σ	98 ± 3	155 ± 9	181 ± 10	248 ± 5
		b	5.58 ± 0.08	7.0 ± 0.2	7.6 ± 0.2	8.85 ± 0.08

*calculated from formula p. 516 [16]

TABLE II

Polarizability and ionization energy of molecules and molecular constants used in theoretical calculations (cf. Table I).

	CHF_3	CH_4	CF_4	SF_6	CCl_4
Average polarizability [cm^3] $\alpha_1, \alpha_2 \times 10^{24}$	2.079[b]	2.593[a]	3.860[c]	6.48[d]	10.5[a]
Difference of polarizability $(\alpha_1^{\parallel} - \alpha_1^{\perp}) \times 10^{24}$ cm^3	0.8647[b]				
Ionization energy I_1, I_2 [eV]	12.77[b]	12.61[a]	16.20[e]	15.32[a]	11.47[a]
b_{kin} [Å]		3.132[f]	3.55[f]	3.96[f]	4.163[f]
Force constants of L–J potential E/k [K]	210[g]	148[h]	152[c]	200.9[d]	327[h]
b_{e} [Å]	2.803[g]	3.818[h]	4.7[c]	5.51[d]	5.88[h]

[a] [17]; [b] [18]; [c] [19]; [d] [20]; [e] [21]; [f] calculated from formula (17) [14]; [g] [22]; [h] [23]

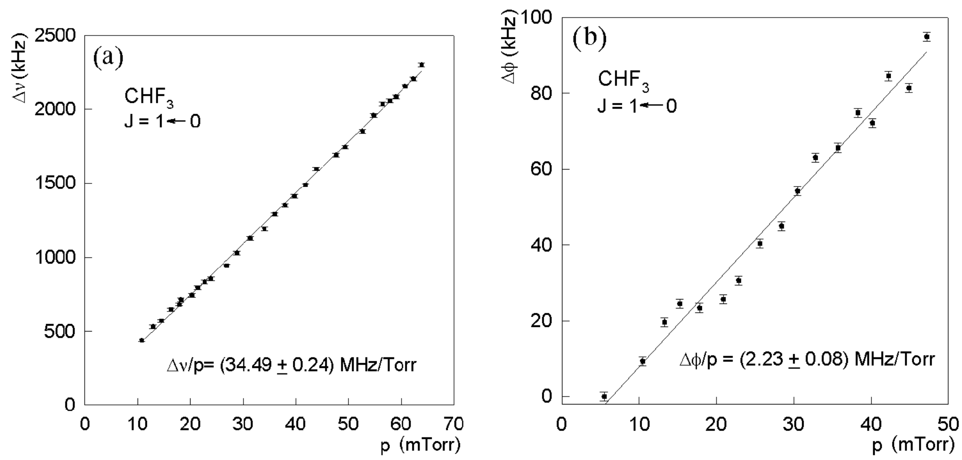

Fig. 4. (a) Line width $\Delta\nu$ versus pressure p for $J = 1 \leftarrow 0$ rotational transition of CHF$_3$ molecule; (b) the line shift $\Delta\phi$ versus pressure p for CHF$_3$ molecule.

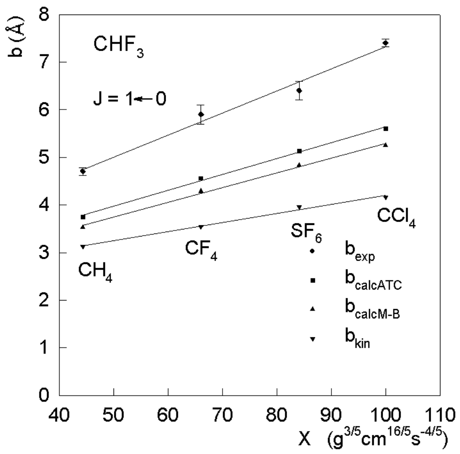

Fig. 5. The collision diameters obtained theoretically b_{calc}, experimentally b_{exp} and the kinetic diameters b_{kin}, as a function of X (see Eq. (14)).

The theoretical values are in qualitative agreement with the experimental results but the magnitudes of the measured cross-sections are about 40% larger than the calculated ones.

5. Conclusion

The collision cross-section depends linearly on the magnitude of X which defines the dispersion and dipole-induced dipole interactions with the exception of the other induction. The results obtained experimentally indicate however that the dependence of σ on the parameter X is linear (Fig. 3).

Hence it may be concluded that the arbitrarily adopted parameter X may be used to account for the experimental results.

References

[1] C.O. Britt, J.E. Boggs, *J. Chem. Phys.* **45,** 3877L (1966).

[2] S. Murphy, J.E. Boggs, *J. Chem. Phys.* **47,** 4152 (1967).

[3] W.A. Wensink, C. Noorman, H.A. Dijkerman, *J. Phys. B, At. Mol. Phys.* **12,** 1687 (1979).

[4] B.T. Berendts, A. Dymanus, *J. Chem. Phys.* **48,** 1361 (1968).

[5] D.S. Olson, C.O. Britt, V. Prakash, J. Boggs, *J. Phys. B, At. Mol. Phys.* **6,** 206 (1973).

[6] S. Gierszal, J. Galica, E. Miś-Kuźmińska, *J. Chem. Phys.* **108,** 8976 (1998).

[7] P.W. Anderson, *Phys. Rev.* **76,** 647 (1949).

[8] C.J. Tsao, B. Curnutte, *J. Quantum Spectrosc. Radiat. Transfer* **2,** 42 (1962).

[9] J.S. Murphy, J.E. Boggs, *J. Chem. Phys.* **47,** 691 (1967).

[10] Krishnaji, S.L. Srivastava, *J. Chem. Phys.* **41,** 2266 (1964).

[11] S. Gierszal, J. Galica, E. Miś-Kuźmińska, *Acta Phys. Pol. A* **79,** 451 (1991).

[12] J. Galica, S. Gierszal, E. Miś-Kuźmińska, *Phys. Scr.* **53,** 648 (1996).

[13] S. Gierszal, J. Galica, E. Miś-Kuźmińska, *J. Chem. Phys.* **108,** 8976 (1998).

[14] S. Gierszal, J. Galica, E. Miś-Kuźmińska, *Phys. Scr.* **61,** 581 (2000).

[15] H. Odashima, M. Kajita, Y. Matsuo, T. Minowa, *J. Chem. Phys.* **90,** 4875 (1989).

[16] G. Birnbaum, *Advance Chemical Physics*, Vol. XII, *Intermolecular Forces*, Wiley, New York 1967.

[17] *Handbook of Chemistry and Physics*, D.R. Lide, 78th ed., CRC Press, New York 1997–1998.

[18] Program MINDO/3 POLAR PRECISE.

[19] A. Rosenberg, G. Birnbaum, *J. Chem. Phys.* **48,** 1396 (1968).

[20] A. Rosenberg, G. Birnbaum, *J. Chem. Phys.* **52,** 682 (1970).

[21] Y.J. Kime, D.C. Driscoll, P.A. Dowben, *J. Chem. Soc. Faraday Trans. 2* **83,** 403 (1987).

[22] S.M. Breitling, A.D. Jones, R.B. Boyd, *J. Chem. Phys.* **54,** 3959 (1971).

[23] J.O. Hirschfelder, C.F. Curtis, R.B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York 1967.