

TEMPERATURE DEPENDENCE
OF PRESSURE BROADENED LINEWIDTH
OF $J = 1 \leftarrow 0$ ROTATIONAL TRANSITION
OF $\text{CH}_3\text{C}^{14}\text{N}$ MOLECULE
MIXED WITH OCS AND H_2 MOLECULE

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(Received August 2, 1994; revised version September 23, 1994)

The temperature dependence of the pressure-broadening parameters of the $J = 1 \leftarrow 0$ rotational transition of OCS and H_2 in the ground vibrational state of $\text{CH}_3\text{C}^{14}\text{N}$ molecule is measured in the temperature range between 248 and 293 K. The line shape of the absorption is recorded with a Stark modulated microwave spectrometer. Using least squares fits of the data to the Voigt line function, several contributions to the linewidth have been deduced. The experimental results are compared with the calculated results using Murphy and Boggs collision broadening theory. The pressure-broadening parameters $C_w(x)$ of the gas mixture $\text{CH}_3\text{CN}+\text{OCS}$ and $\text{CH}_3\text{CN}+\text{H}_2$ are 14.05 ± 0.30 MHz/Tr, 9.15 ± 0.12 MHz/Tr, respectively and the temperature dependence parameters α are -0.90 ± 0.07 and -0.77 ± 0.08 .

PACS numbers: 33.20.Bx, 33.70.Jg

1. Introduction

The collision broadening of microwave spectral lines at low pressures provides information about the nature of intermolecular forces in pure gases and their mixtures [1-4]. The relationship between the experimentally observed linewidths and the intermolecular forces is quite complicated and has been reviewed by various researchers, namely Anderson [5], Murphy and Boggs [1-3], Birnbaum [4], Tsao and Curnutte [6]. In this paper we use the relations of the Murphy-Boggs theory.

Since the last few decades the acetonitrile molecule has attracted attention of both astrophysicists [7] and spectroscopists. The CH_3CN molecule is very abundant in interstellar space and its rotational spectrum has been detected in several

interstellar molecular clouds [8] even in the excited state. It constitutes a very good probe for monitoring the kinetic temperature and density of interstellar clouds [9]. From the spectroscopic point of view, methyl cyanide is a symmetric top, light molecule with a large dipole moment and its spectra in microwave, millimeter, submillimeter and IR region [10–12] give the possibility for testing structural [13] and dynamical [14–17] theories.

Actually, the dynamics of methyl cyanide, which is in the center of our interest, has often been investigated. In 1968 Roberts et al. [18] measured the linewidth of the rotational transition $J = 1 \leftarrow 0, K = 0, \Delta F = 2 \leftarrow 1$ of $\text{CH}_3\text{C}^{14}\text{N}$ and they obtained linewidth parameter $C_w = 94.2$ MHz/Tr. Later, the value of this parameter was published by Swindle and Roberts [19] who obtained $C_w = (42.6 \pm 4.0)$ MHz/Tr, by Buffa et al. [20] $C_w = (50 \pm 5)$ MHz/Tr in 1986, $C_w = (71.8 \pm 1.1)$ MHz/Tr in 1988 [17] and by Haekel and Mader $C_w = (72.72 \pm 0.4)$ MHz/Tr [21]. Rather large differences in magnitudes of linewidth parameter partly result from systematic errors [14] and complications resulting from the occurrence of the hyperfine structure of this rotational transition. The linewidth parameters (C_w) for a number of the lines of $\text{CH}_3\text{C}^{14}\text{N}$ were measured by different authors and with different techniques [19, 21, 22, 23]. The lines of the rotational transitions with $J = 4$ and $K = 2, 3$ broadened by foreign gases in low temperature have been investigated [16, 24].

In this paper we report on foreign gas broadening experiments performed in the 248–293 K temperature range on the $J = 1 \leftarrow 0$ rotational transition of $\text{CH}_3\text{C}^{14}\text{N}$ at 18 GHz. The buffer gases are OCS and H_2 on account of their relevance for planetary atmosphere studies.

2. Theory

We calculated the width of the measured lines from the Murphy and Boggs theory [1–3] using the relation

$$\Delta\nu = (1/4\pi)(1/\tau_i + 1/\tau_f), \quad (1)$$

where τ_i and τ_f are, respectively, the average lifetimes of the initial and final energy levels of the radiating molecule. Denoting by J_1 the rotational state of absorbing molecule and by J_2 energy level of the perturber, the lifetime of state J_1 can be obtained from

$$1/\tau_{J_1} = \sum_{J_2} P_B(J_2)\Phi(J_1, J_2), \quad (2)$$

where $\Phi(J_1, J_2) = 2\pi N \int dbb \int dvvF(v) \{1 - \exp[-\Gamma_{J_1, J_2}(b, v)]\}$ is the number of transitions per unit time out of the J_1 energy level caused by collisions with molecules in the J_2 level, $P_B(J_2)$ — the Boltzmann factor for molecule 2, N — the number of molecules per unit volume, b — the impact parameter, v — the relative velocity, $F(v)$ — the Maxwell–Boltzmann velocity distribution function, $\Gamma_{J_1, J_2}(b, v)$ — the function of the energy of interaction $V(t)$.

For general case where the interaction energy is a combination of many of forces, $V(t)$ may be written

$$V(t) = \sum_Y V^Y(t), \quad (3)$$

where $Y = DD, DQ, QD, QQ, DSP$ and consequently

$$\Gamma_{J_1, J_2} = \sum_Y \Gamma_{J_1, J_2}^Y \quad (4)$$

The symbols $V^Y(t)$ denote the energy of interaction: V^{DD} — dipole-dipole, V^{DQ} — dipole-quadrupole, V^{QD} — quadrupole-dipole, V^{QQ} — quadrupole-quadrupole and V^{DSP} — dispersion interaction.

The functions Γ and their scale factors are cited in the Murphy-Boggs paper [1].

3. Experimental

The home made microwave spectrometer we used was described previously [25]. Since that time we have modified a few details of this instrument to improve the accuracies of the frequency calibration and the pressure of the studied gas. A block diagram of the Stark modulated spectrometer is shown in Fig. 1. The microwave power from the klystron K-746 is swept at a very slow rate over

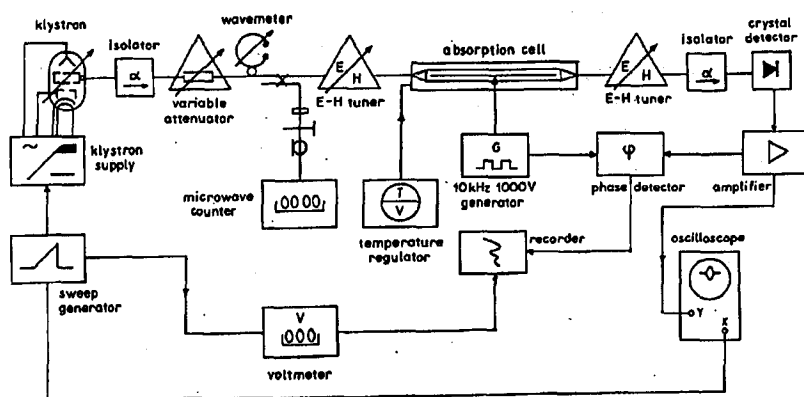


Fig. 1. Block diagram of the microwave K-band spectrometer.

a 15 MHz frequency range containing the absorption line $J = 1 \leftarrow 0$ of methyl cyanide molecule. The power passes through 2 m long H-band waveguide, Stark absorption cell filled with the mixture of the gases. The modulating 10 kHz square wave Stark voltage of 1 kV amplitude is applied to the electrode in the guide. The square wave rise and fall times are smaller than $0.3 \mu\text{s}$. The reflections in the cell are minimized with the help of two EH tuners. Vacuum installation provides a base pressure in the cell of 8×10^{-6} Tr. The gas pressure is measured with an absolute pressure gauge MKS Baratron type 220C with resolution of 10^{-5} Tr and 1% accuracy. During the recording of the absorption line the pressure of the gas is maintained stable within 0.1 mTr. The H-band waveguide is connected at both ends to the K-band waveguide by means of tapered transition sections 14 cm long. The cell is sealed from the atmosphere by mica windows placed at the K-bands of these transition sections. Two tubes of oval cross-section, used as cooling tubes, are

placed along the cell, soldered to the two broad sides of the cell. The thermocouple is positioned in the middle of the length of the cell. The H-band waveguide is placed in a circular brass tube of 6.5 cm diameter. The volume between the waveguide and the brass tube is pumped out by rotary pump to 10^{-3} Tr. Such system of thermal isolation is used in the temperature range from 248 K to 293 K. The temperature of the nitrogen gas coolant is measured with a platinum resistance at the outlet of the tube connected to 15 liter dewar filled with liquid nitrogen. The voltage drop on this resistance controls the UNIPAN temperature controller model 650H. A resistive heater is placed inside the liquid nitrogen dewar and via 650H controller regulates the stream of the coolant. This system ensures temperature stability better than 0.05°C during measurements.

The microwave part contains two isolators used to prevent microwave power reflections from the absorption cell and crystal detector. The fraction of microwave power that is coupled to the waveguide-coaxial transition is used for precise frequency measurements with Hewlett Packard microwave frequency counter model HP 5348A. Reproducibility of the frequency measurement of a line is better than ± 15 kHz. The microwave power level, absorbed by the gas, is monitored with type D 705 diode at the microwave diode mount. The linearity coefficient determined for the output voltage at the detector as function of the input power amounts to 9%. Output of the detector is connected to the phase sensitive detector via 233.5 type preamplifier; total gain is 0.8×10^6 at the nonlinearity coefficient smaller than 1.2%. Final recording of the absorption signal obtained at the output of the phase sensitive detector is made using a Servogor type analog pen recorder.

4. Measurements

The analog plot of the absorption curve is point by point traced with a computer controlled plotter and DIGIT program. The digitized absorption represented by 520 points, of $J = 1 \leftarrow 0$ transition of CH_3CN molecule shows the resolved hyperfine structure with $F = 0, 1, 2$ (Fig. 2). The lineshape function of the hyperfine components is approximated with Voigt's function, their envelope fitted to the experimental points. The best fit value of the linewidth parameter of each component is regarded as the measured linewidth.

The background signal of the quadratic form is subtracted and the theoretical, Voigt's curves, are fitted to the gas absorption plot, as shown in Fig. 2. The correlation coefficient is $r^2 = 0.997$. The measured widths of the hyperfine components $F = 0, 1, 2$ are obtained 0.481, 0.260, 0.457 MHz, respectively at the pressure value $p = 5.7$ mTr. These values constitute the collisional broadening contribution to the linewidth.

The same procedure is repeated for each absorption spectrum obtained at the given pressure and temperature.

The gas pressure, adjusted to 3 to 30 mTr was measured to the accuracy 10^{-4} Tr with MKS Baratron capacitance vacuumeter.

Each value of the linewidth obtained in this procedure, was subsequently corrected for the Stark-modulation broadening ($\Delta\nu_{\text{corr}}$) [25] (Fig. 3), and for the length of the absorption cell [26]. The first correction is connected with the action of switching a microwave transition on and off resonance by applying a Stark field

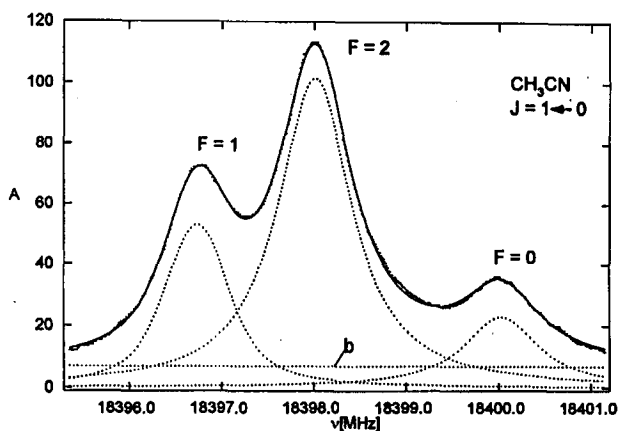


Fig. 2. Digitalized absorption curve of the $J = 1 \leftarrow 0$ rotational transition of CH_3CN molecule with the theoretical curve fit composed of three hyperfine components $F = 0, 1, 2$; A — signal amplitude, b — background.

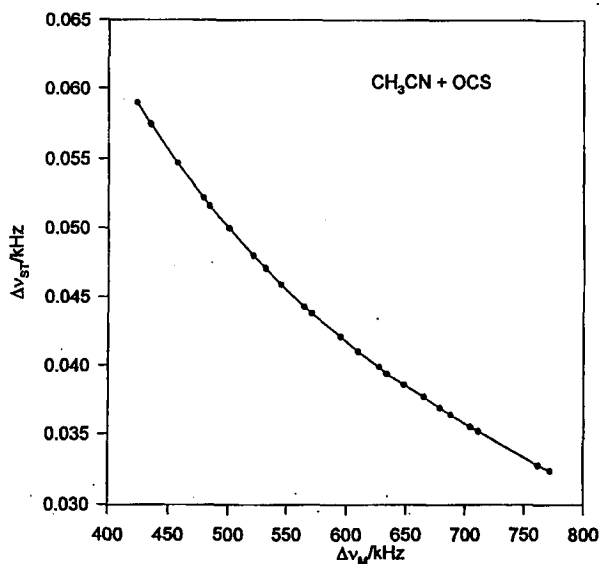


Fig. 3. Stark modulation effect on the linewidth.

which causes broadening due to the finite response of the molecular system. The length correction arises from the fact that the increase in the absorption path length leads to the reduction of the power incident upon the molecules at the end of the resonator when at the line center, which appears as a broadening. With a crude approximation for a short path length l , this correction is proportional to the linewidth and for our cell ($l = 218 \text{ cm}$) the slope constant is 5.45×10^{-3} .

The study of the linewidth as a function of pressure at several constant temperatures, was performed for the rotational transition $J = 1 \leftarrow 0$, $F = 2 \leftarrow 1$ of CH_3CN molecule in the mixture of OCS and H_2 gas perturbers. The linewidth of the transition of acetonitrile molecule in the presence of the perturber was determined from the formula

$$\Delta\nu = C_w p_1 + C_w(x) p_2 + \sum \Delta\nu_{\text{corr}} \dots, \quad (5)$$

where C_w — pressure self-broadening coefficient, $C_w(x)$ — pressure broadening coefficient of the gas mixture, $\Delta\nu_{\text{corr}}$ — the corrections to the measured linewidth, p_1 and p_2 — partial pressures of CH_3CN and OCS or H_2 , respectively.

The value of $C_w p_1 + \sum \Delta\nu_{\text{corr}}$ was determined from the linewidth measurement made on the pure CH_3CN at the initial pressure p_1 . Gradually, the perturbing OCS or H_2 gas was added and the linewidth $\Delta\nu$ was measured, hence, the differences $\Delta\nu - (C_w p_1 + \sum \Delta\nu_{\text{corr}})$ effected by collisions with the perturber gas, could be calculated. These values are plotted against the partial pressure of the perturbing gas $p - p_1$, where $p = p_1 + p_2$ and displayed in Fig. 4 for CH_3CN mixtures with OCS and H_2 measured at 293 K.

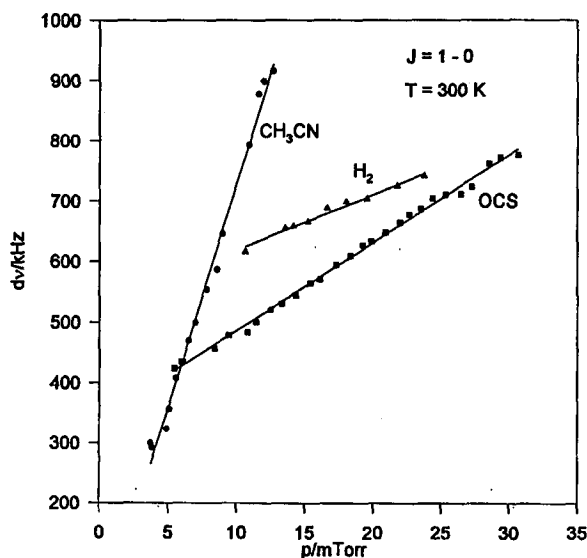


Fig. 4. Linewidth $\Delta\nu$ of $J = 1 \leftarrow 0$ rotational transition of CH_3CN molecule as a function of gas pressure p of CH_3CN , OCS and H_2 mixture, respectively.

The pressure broadening coefficients could subsequently be obtained as the least squares linear fit; they amount to 14.05 ± 0.30 MHz/Tr and 9.15 ± 0.12 for acetonitrile + OCS mixture and acetonitrile + H_2 mixture, respectively. The pressure broadening coefficient measured for the pure acetonitrile is $C_w = 73.90 \pm 40$ MHz/Tr.

Subsequently, the measurements of the pressure broadening coefficient of the pure CH_3CN at different temperatures made it possible to calculate the tempera-

ture coefficient of the pressure broadening α . The latter has been concluded from the Anderson and Murphy-Boggs theory [1-5]:

$$C_w(T) = C_w(293 \text{ K})(T/293 \text{ K})^\alpha, \quad (6)$$

in which $C_w(293 \text{ K})$ denotes the line broadening coefficient at the temperature 293 K.

The coefficient α' for the gas mixtures was calculated on the basis of the equation describing the half width of the absorption [27], measured under well defined conditions of partial pressures and the temperature

$$\Delta\nu = C_w(293)p_1(T/293)^\alpha + C_w(x, 293)p_2(T/293)^{\alpha'} + \sum \Delta\nu_{\text{corr}}. \quad (7)$$

C_w and α are available from the measurement of self-broadening, while $C_w(x)$ is measured from the linewidth pressure broadening coefficient, in the presence of buffer gas at the temperature set to 293 K ($x = \text{CH}_3\text{CN} + \text{OCS}$, $\text{CH}_3\text{CN} + \text{H}_2$).

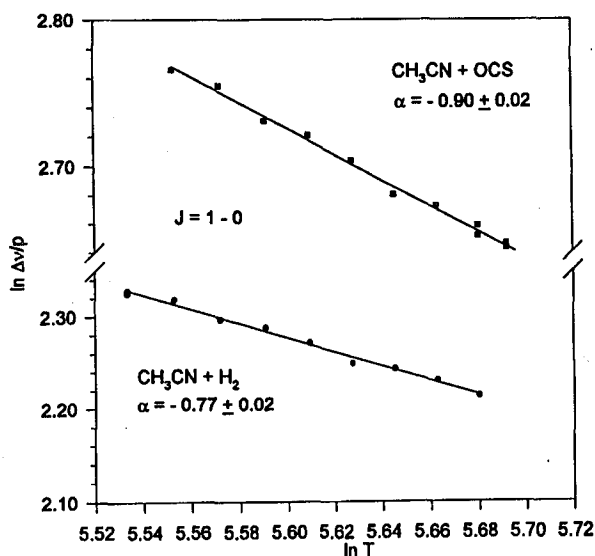


Fig. 5. Dependence of $\ln \Delta\nu/p$ on $\ln T$ measured at $J = 1 \leftarrow 0$ rotational transition of CH_3CN molecule in the mixture with OCS (■) and H_2 (·).

Figures 5 show two \ln - \ln plots of $C_w(\text{CH}_3\text{CN} + \text{OCS})$ and $C_w(\text{CH}_3\text{CN} + \text{H}_2)$, as a function of temperature. The temperature coefficient of the pressure broadening α is equal to the slope of the curve obtained as the least squares fit to the experimental points. The experiment yields $\alpha(\text{CH}_3\text{CN} + \text{OCS}) = -0.90 \pm 0.07$ and $\alpha(\text{CH}_3\text{CN} + \text{H}_2) = -0.77 \pm 0.08$. Using the collision parameter, valid within the rigid spheres approximation

$$b^2 = C_w(x)/(2N_0/\pi mkT)^{1/2}, \quad (8)$$

where N_0 — Avogadro's constant, m — the reduced mass of the molecules, k — Boltzmann constant, T — temperature, x — the perturber + CH_3CN , and the

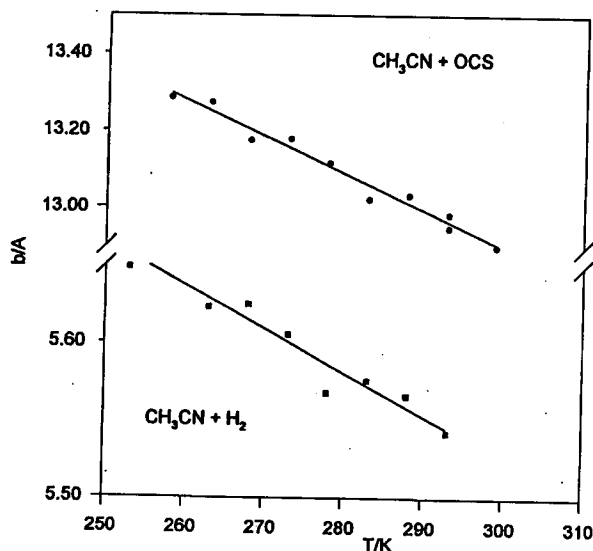


Fig. 6. The changes of the collision parameter b vs. temperature in $\text{CH}_3\text{CN} + \text{OCS}$ (·) and $\text{CH}_3\text{CN} + \text{H}_2$ (■) mixture.

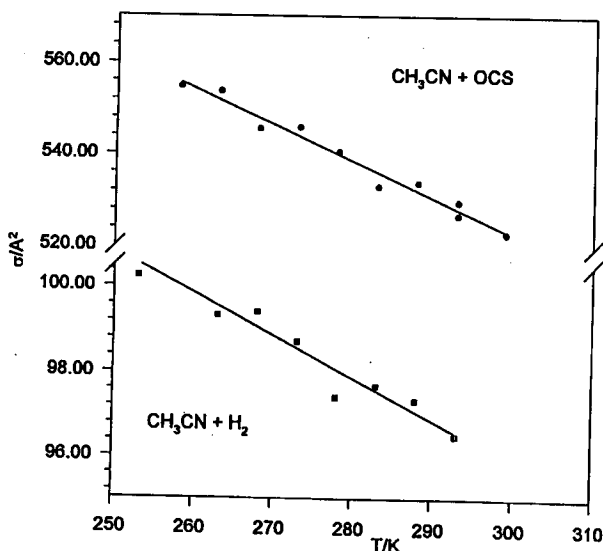


Fig. 7. Dependence of the collision cross-section on temperature of $\text{CH}_3\text{CN} + \text{OCS}$ (·) and $\text{CH}_3\text{CN} + \text{H}_2$ (■) mixture.

cross-section defined as $\sigma = \pi b^2$, the dependences of the collision parameters of $\text{CH}_3\text{CN} + \text{OCS}$ and $\text{CH}_3\text{CN} + \text{H}_2$ mixtures on temperature are shown in Fig. 6. Partial cross-section for the collisions as a function of temperature is displayed in

Fig. 7. The form of these curves reflects the nature of the interactions occurring in the collision process [28].

5. Calculations and the conclusions

The calculations of the pressure broadening coefficient were made using the equation (Eq. (2)), which can be recast in the form

$$C_w = \Delta\nu/p = 4.87 \times 10^9 [\mu_1 \mu_2 / AT] I(J_1, J_2) \text{ [Hz/Tr]} \quad \text{for } \mu_2 \neq 0, \quad (9)$$

$$C_w = 3.217 \times 10^8 [(\mu_1 Q_2)^{2/3} / Am^{1/6} T^{5/6}] I(J_1, J_2) \quad \text{for } \mu_2 = 0, \quad (10)$$

where

$$A = \sum_{J_2=0}^{\infty} \sum_{K_2=0}^{J_2} S(I, K_2) (2J_2 + 1) \exp\{-[MJ_2(J_2 + 1) + NK_2^2]/T\},$$

$$I(J_1, J_2) = f[P_B(J_2), \Phi'(J_1, J_2)],$$

Φ' is calculated with 14-point Gauss-Laguerre approximation $\Phi(J_1, J_2)$, P_B — Boltzmann's population function, $S(I, K_2)$ — coefficient of statistical weight of the nuclear spin, I — spin of the nuclei sited beyond the symmetry axis, m — reduced mass, μ_1, μ_2 — dipole moments of absorber and perturber, respectively, Q_2 — quadrupole moment of the perturber, M, N — coefficients containing the rotational constants. The molecular constants, entering the formulae (Eqs. (9), (10)) are collected in Table I. The pressure broadening coefficient C_w is calculated with the assumption that the intermolecular interaction is entirely of dipole-dipole (DD) character or the dipole-dipole interactions are modified by others, mixed dipole-quadrupole, quadrupole-dipole (QD), quadrupole-quadrupole (QQ) and the dispersive interaction. The values C_w are calculated at the rotational transition $(J, K, F) = (1, 0, 2) \leftarrow (0, 0, 1)$, of pure CH_3CN gas, as well as of the gas in the mixtures with OCS and H_2 . The results are displayed in Table II.

TABLE I
Molecular constants used in theoretical calculations of pressure broadening coefficients.

Molecule	CH_3CN	OCS	H_2
Rotational constant B [MHz]	9198.99 ^a	6081.48 ^b	1.824×10^6 ^c
Dipole moment μ [D]	3.913 ^d	0.712 ^b	0
Quadrupole moment Q [DA]	1.8 ^d	5.58 ^c	3.37 ^c
Difference of polarizabilities ($\alpha_{\parallel} - \alpha_{\perp}$) [10^{-24} cm^3]	3.35 ^d	6.04 ^b	0.22 ^c
Average polarizability [10^{-24} cm^3]	4.56 ^d	5.53 ^b	0.79 ^c
Ionization energy [eV]	12.2 ^d	11.24 ^c	15.6 ^c

^a in reference [10], ^b in reference [29], ^c in reference [3], ^d in reference [24].

TABLE II
Comparison of self- and foreign gas pressure-broadened parameters $C_w(T)$ and α available for ground state rotational line $(J, K, F) = (1, 0, 2) \leftarrow (0, 0, 1)$ of $\text{CH}_3\text{C}^{14}\text{N}$ molecule.

Perturber	Parameter ^a	Experimental	M-B theory		Reference
			DD	DD+DQ+QD +QQ+DSP	
CH ₃ CN	C_w	94.2	91.67 ^b		[18]
	C_w	42.6(40)	91.67 ^b		[19]
	C_w	50(5)			[20]
	C_w	71.8(11)			[17]
	C_w	72.72(41)		76.4 ^c	[21]
	C_w	73.90(40)	73.92	74.74	this work
	α	-0.87(9)	-0.829	-0.829	this work
OCS	C_w	14.05(30)	13.95	16.39	this work
	α	-0.90(8)	-0.83	-0.89	this work
H ₂	C_w	9.15(12)	-	11.14 ^d	this work
	α	-0.77(5)	-	-0.74 ^d	this work

^a Pressure broadening coefficient C_w in MHz/Tr.

^b The theoretical methods refer to Anderson theory.

^c Modified Murphy-Boggs theory.

^d Without DD interaction.

Theoretical values of the temperature coefficients of the pressure broadening are obtained with Eq. (6) for the self-broadening mechanism, and Eq. (7) for the mixed systems.

Comparison of the experimental results, as shown in Figs. 4 and 5 with the theoretical values of Table II, points to the predominant role of the DD interaction in the self-broadening of the rotational line of CH₃CN molecule. The value of C_w coefficient calculated under the assumption of only the dipole-dipole interaction differs by less than 0.01% from the experiment and after including the mixed interactions (DD+DQ+QD+QQ+DSP) the calculated C_w changes by 1.1%. The value of α coefficient, calculated within DD model, does not change after accounting for the mixed type interactions. The calculated C_w values of CH₃CN+OCS mixed molecular system indicates the dominant role of DD interactions as well as the significance of the interactions of the mixed type, their contribution enlarges the value of C_w by 14.9%. Similar effect of the mixed terms interaction can be seen in the calculation of α , where the increase by 6.7% improves the accord between the theoretical C_w and the experiment. Such effect of the mixed type interactions on the values of C_w and α' coefficients is observed because the DD interaction is much weaker in this case than in the case of self-broadening. The reason for this

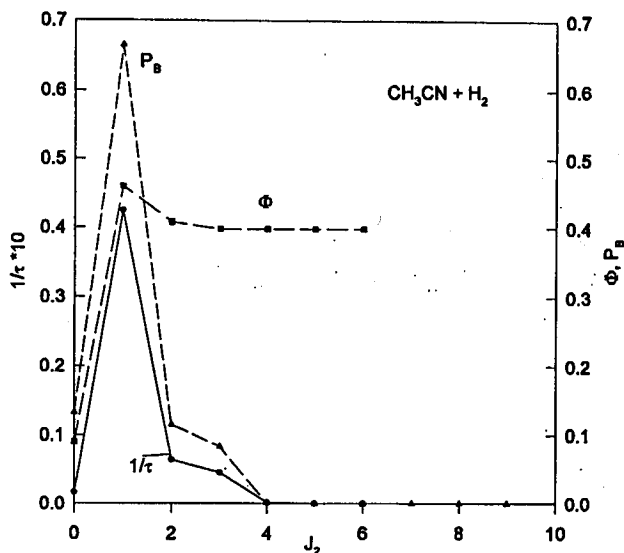


Fig. 8. Theoretical dependence of $1/\tau$, Φ and P_B on the quantum number J_2 of $\text{CH}_3\text{CN} + \text{H}_2$ mixture at 295 K.

is the small value of the OCS dipole moment (Table I). In the collisions occurring between the molecules of acetonitrile and hydrogen the DD interaction is absent as there is no dipole moment of the perturbing molecule. In this collision process, the DQ interaction plays a major role whereas the other interactions, namely QQ + DSP, cause an enlargement of C_w merely by 0.25% and α coefficient by 0.13%. The theoretical values of C_w and α , of the $\text{CH}_3\text{CN} + \text{H}_2$ mixture, are calculated with Eq. (10). The form of the most important functions Φ , P_B contributing to this formula are plotted in Fig. 8. The maximum of $1/\tau$ function is determined by the shape of the Boltzmann distribution function of hydrogen molecule, as well as by the function Φ which describes the number of transitions per unit time out of the J_1 energy level caused by collisions with molecules in the J_2 level.

For the mixture of gases $\text{CH}_3\text{CN} + \text{OCS}$ the function $1/\tau$ and the others: P_B and Φ , are shown in Fig. 9.

With the assumption of the mixed-type interactions between CH_3CN and OCS the highest transition probability within the rotational states, per unit time at temperature 250 K, is expected at $J_2 = 1$ state of OCS molecule. Increase in the temperature causes insignificant growth of the function value in all the range of J_2 quantum numbers. Maximum of the Boltzmann distribution function of the rotational states of the perturber, occurs at $J_2 = 20$ for 250 K and increasing of the temperature of the mixture results in an appreciable decrease and shift of this maximum towards higher J_2 . Therefore, $1/\tau$ values decrease which in turn, reduces C_w , the pressure broadening coefficient response to the increase in temperature. This conclusion, also valid for the acetonitrile + hydrogen mixture, is corroborated with the experimental data collected in Figs. 5-8 and Table II.

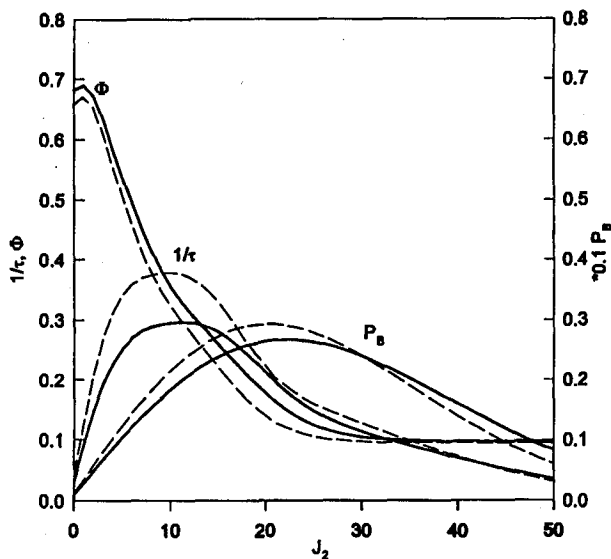


Fig. 9. Theoretical dependence of $1/\tau$, Φ and P_B functions on the quantum number J_2 of the perturber of $\text{CH}_3\text{CN} + \text{OCS}$ mixture at two temperatures: 250 K (dashed line) and 300 K (solid line).

Acknowledgment

We gratefully acknowledge the financial support provided by the Institute of Molecular Physics of the Polish Academy of Sciences.

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