

PRESSURE BROADENING MEASUREMENTS OF $J = 6 \Rightarrow 7$ ROTATIONAL LINE OF THE t-BUTYL CYANIDE MOLECULE*

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Self-broadened width of $J = 6 \Rightarrow 7$ rotational line in the ground state of t-butyl cyanide molecule has been measured at room temperature. The measurements of the linewidth as a function of the gas pressure were carried out with home-made spectrometer at the frequency $\nu_0 = 38\,498.308$ MHz. The mean value of the pressure-broadening coefficient $c = 76.9 \pm 0.6$ MHz Torr⁻¹ was obtained.

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1. Introduction

The previous investigations of the rotational spectra in the microwave [1-3] and millimeter-wave band [4, 5] of the t-butyl cyanide molecule yield interesting information on the vibration-rotational interactions. There is no information available on the intermolecular interactions. It is the aim of the present study to fill this gap through the measurement of the pressure-broadening coefficient of $J = 6 \Rightarrow 7$ rotational line in the ground state.

2. Experimental

The measurements of the linewidth as a function of the gas pressure were carried out with home-made Stark modulated spectrometer. The microwave part of this spectrometer is shown in Fig. 1. The rest of the system was described ear-

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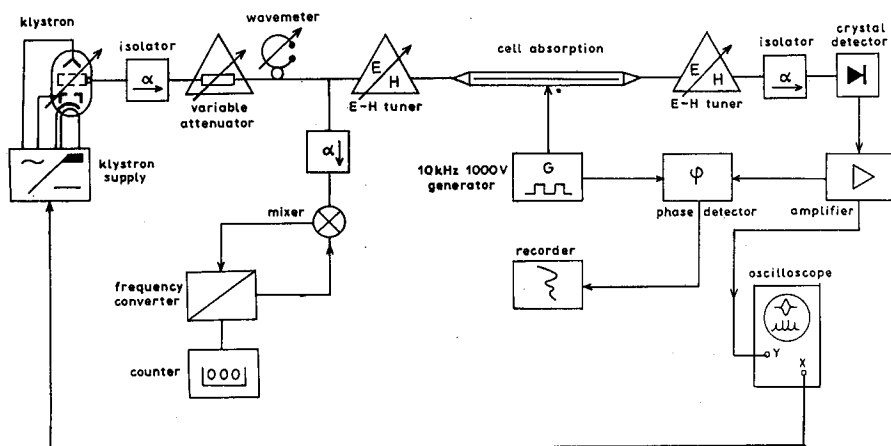


Fig. 1. Schematic diagram of the Q band spectrometer used for linewidth measurements.

lier [6]. All gas pressures were measured utilizing a thermocouple gauge which had been calibrated against the McLeod gauge. The gas pressure was monitored with the accuracy of ± 1 mTorr in the range from 4 to 25 mTorr. The $J = 6 \Rightarrow 7$ rotational transition was registered with the source frequency sweep at the frequency $\nu_0 = 38498.308$ MHz determined with ± 15 kHz accuracy. The measurements were carried out at a temperature of 293 K.

3. Measurements

The pressure broadening coefficient c was measured for the rotational transition labelled with the quantum numbers $(v, J, K) = (0, 6, 0) \rightarrow (0, 7, 0)$, which has central position and the highest amplitude in the spectrum (Fig. 2). Half-width was determined at half of its amplitude as function of the gas pressure.

The obtained c value was corrected according to the known mathematical procedures for the following phenomena: the collision of molecules with the cavity walls, the effects due to the length of the resonator, electric field modulation and the Doppler effect. The broadening resulting from molecular collisions with the cavity walls was calculated following the procedure by Luijendijk [7] and the corrections is

$$\Delta\nu_w = \Delta\nu - \Delta\nu_{\text{mol}} = 3.8 \text{ kHz},$$

where $\Delta\nu$ is Lorentzian linewidth HWHH, $\Delta\nu_{\text{mol}}$ — the half-width due to intermolecular collisions.

The change of the linewidth $\Delta\nu_L$ caused by the length of the absorber (L) is linearly dependent on the measured linewidth $\Delta\nu$ (Fig. 3). The length of the resonator, $L = 2.18$ m was adopted as the length of absorbant path. In the calculations of the $\Delta\nu_L$ corrections [8], the absorption coefficient of the $J = 6 \Rightarrow 7$

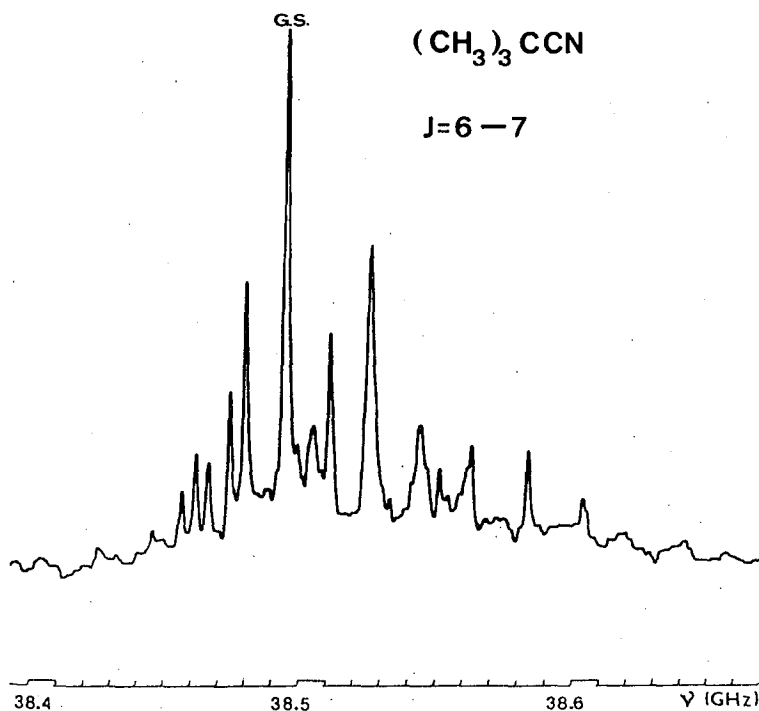


Fig. 2. The absorption line of the rotational transition $J = 6 \Rightarrow 7$ at the microwave band. (This spectrum has been recorded with HP8460A spectrometer in the Institute of Physical Chemistry of Justus Liebig University in Giessen, Germany).

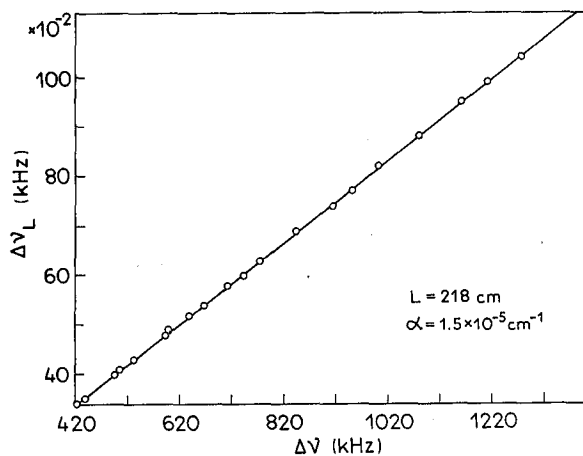


Fig. 3. The change of the linewidth $\Delta\nu_L$ of the rotational transition $J = 6 \Rightarrow 7$ of the $(\text{CH}_3)_3\text{CCN}$ molecule as a result of the length $L = 218 \text{ cm}$ of the absorption path.

rotational line of $(\text{CH}_3)_3\text{CCN}$ molecule had been calculated from the Gordy formula [9] with the rotational constants published elsewhere [3, 4]. The value of $\Delta\nu_L$ correction for the absorption line of 500 kHz width is around 0.4 kHz. The process of the electric field modulation results in additional contributions to the linewidth, $\Delta\nu_{\text{SM}}$ as described in [10–12]. Its magnitude at the constant frequency modulation $f = 10$ kHz depends on the measured linewidth $\Delta\nu$:

$$\Delta\nu_{\text{SM}} = \frac{1}{2}\Delta\nu \left(1 - \sqrt{1 - \frac{f^2}{\Delta\nu^2}} \right).$$

The span and the character of this dependence is shown in Fig. 4.

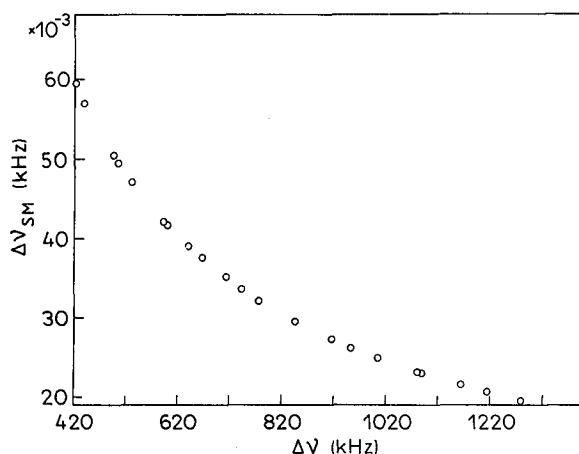


Fig. 4. The effect of the electric field modulation; change of the linewidth plotted as a function of the measured linewidth.

Translational motion of the molecules described by the Maxwell velocity distribution produces changes in the frequencies of the absorbed radiation and entails a change in both the lineshape and the linewidth [13, 14]. The range of the linewidth variation of the $J = 6 \Rightarrow 7$ rotational transition resulting from the Doppler broadening was determined by the method described by Parsons [13] and is shown in Fig. 5 as a function of the measured linewidth. Finally, the linewidth $\Delta\nu$ of the rotational transition $J = 6 \Rightarrow 7$, $\nu = 0$ of $(\text{CH}_3)_3\text{CCN}$ molecule, was corrected according to the above mentioned argumentation and plotted as a function of the gas pressure p (Fig. 6). The slope of the line drawn to the best linear least squares fit yields c , the pressure self-broadening coefficient:

$$c = 76.9 \pm 0.6 \text{ MHz Torr}^{-1}.$$

The correlation coefficient of the regression is 0.998. Furthermore, the effective cross-section for the collisions, $\sigma = 3700.0 \text{ \AA}^2$, and the collision parameter, $b = 34.3 \text{ \AA}$, were calculated from the c value.

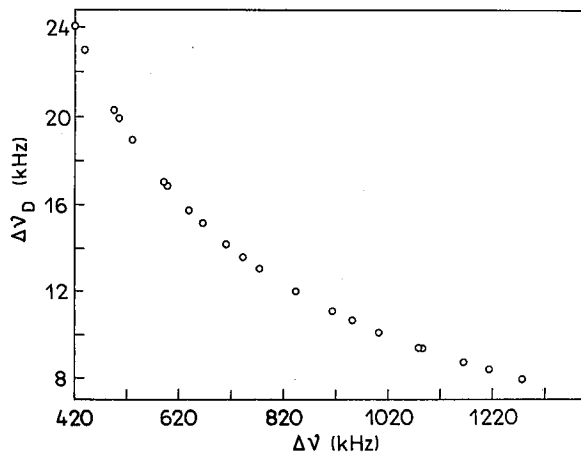


Fig. 5. Doppler-broadening effect on the $J = 6 \Rightarrow 7$, $\nu = 0$ transition of the $(\text{CH}_3)_3\text{CCN}$ molecule versus the measured linewidth.

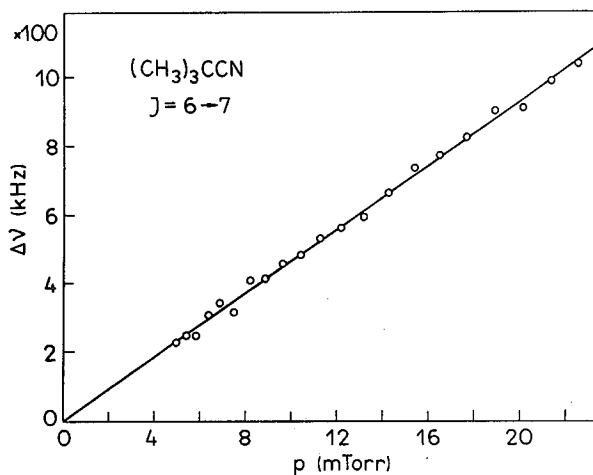


Fig. 6. The linewidth $\Delta\nu$ of the $J = 6 \Rightarrow 7$ rotational transition of the $(\text{CH}_3)_3\text{CCN}$ as a function of the gas pressure.

4. Discussion

To our knowledge, there is no information on measurements of self-broadened rotational lines of the t-butyl cyanide molecule. The obtained experimental value can be compared only with a theoretical one. The calculations of c^t had been made according to the Murphy-Boggs theory [15, 16] with the assumption of the following types of interactions: dipol-dipol, dipol-quadrupole, quadrupole-dipol and quadrupole-quadrupole. The theoretical value of line width parameter is: $c^t = 56.2 \text{ MHz Torr}^{-1}$, what is almost 26% lower than the observed value. Similar discrepancy of about 17% between experimental and theoretical c values were found for CH_3CN molecule [17].

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References

- [1] T. Sparstad, E. Amble, *J. Chem. Phys.* **27**, 317L (1957).
- [2] W. Zeil, J.F. Pfrommer, *Z. Electrochem.* **61**, 938 (1957).
- [3] L.J. Nugent, P.E. Mann, D.R. Lide, *J. Chem. Phys.* **36**, 965 (1962).
- [4] Z. Kisiel, *Chem. Phys. Lett.* **118**, 334 (1985).
- [5] Z. Kisiel, *J. Mol. Spectrosc.* **135**, 223 (1989).
- [6] J. Galica, J. Stankowski, S. Gierszal, W. Prussak, *Fiz. Diel. Radiosp.* **11**, 115 (1979).
- [7] S.C.M. Luijendijk, *J. Phys. B* **8**, 2995 (1975).
- [8] E. Rinehart, R.L. Legan, C.C. Lin, *Rev. Sci. Instr.* **36**, 511 (1965).
- [9] W. Gordy, R. Cook, *Microwave Molecular Spectra*, J. Wiley, New York 1970.
- [10] R. Karplus, *Phys. Rev.* **73**, 1027 (1948).
- [11] S. Geschwind, *Ann. N. Y. Acad. Sci.* **55**, 751 (1952).
- [12] M.W.P. Strandberg, H.R. Johnson, J.R. Eschbach, *Rev. Sci. Instr.* **25**, 776 (1954).
- [13] R.W. Parsons, J.A. Roberts, *J. Mol. Spectrosc.* **18**, 412 (1965).
- [14] C.M. Luijendijk, *J. Phys. B* **10**, 1735 (1977).
- [15] J.S. Murphy, J.E. Boggs, *J. Chem. Phys.* **47**, 691 (1967).
- [16] J.S. Murphy, J.E. Boggs, *J. Chem. Phys.* **47**, 4152 (1967).
- [17] G. Buffa, D. Giulietti, M. Lucchesi, M. Martinelli, O. Tarrini, M. Zucconi, *Nuovo Cimento D*, **10**, 511 (1988).