

THE BROADENING AND SHIFTING OF THE $J = 0 \rightarrow 1$ LINE OF CH_3Cl by THE FOREIGN GASES CH_3Br , OCS AND CO_2

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Received 21 November 1974

The results of a series of measurements on the broadening and shifting of the $J = 0 \rightarrow 1$ absorption line of CH_3Cl by foreign gases are reported.

Many measurements have been made of the self and foreign-gas broadening of microwave spectral lines in gases, but rather few measurements have been made of pressure-induced line shifts. Matsuura et al. [1], using an ammonia maser, observed small shifts of the inversion frequency of NH_3 with increasing pressure; more recent measurements on NH_3 have been made by Story et al. [2, 3] and by Hewitt et al. [4] using a frequency-modulated microwave spectrometer. The self-shift was found to be towards higher frequencies with increasing pressure, while, for all the cases studied, the contribution of the foreign gas was found to be towards lower frequencies.

Luijendijk [5], using a Stark-cell microwave spectrometer, has recently measured collision-induced widths and shifts in the rotational spectra of pure OCS , CH_3Cl and H_3CCCH at various temperatures. He found that the direction of the pressure induced shift depended on the quantum numbers of the transitions under study. The purpose of the present letter is to report a series of measurements, made at room temperature, of the broadening and shifting of the $J = 0 \rightarrow 1$ line of CH_3Cl at 26570.77 MHz by the foreign gases CH_3Br , OCS and CO_2 .

Measurements were made using the Stark-cell spectrometer constructed by Luijendijk. Binary mixtures were prepared from "Matheson" gases, and for each mixture the width and shift parameters C_w and C_s

were determined from measurements at a series of pressures in the range 20 to 120 mtorr; the fraction x of CH_3Cl in each mixture was determined at the time of preparation from partial pressure measurements. Fig. 1 shows the relation (obtained from experimental results) between the line shift parameter C_s and the fraction x . To within the experimental error, C_s depends linearly on x according to $C_s = C_{ss}x + C_{sf}(1-x)$, and so C_{ss} and C_{sf} were interpreted as the self and foreign-gas shift parameters, respectively. Similar quantities, C_{ws} and C_{wf} , were interpreted as the self and foreign-gas broadening parameters, respectively. Experimental results for C_{ws} and C_{wf} -values are shown in fig. 2.

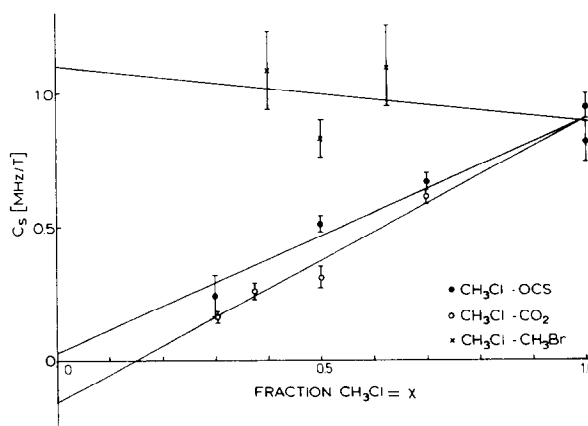


Fig. 1. The lineshift parameter C_s as a function of the fraction x of CH_3Cl in a mixture with some foreign gases.

* This work was performed during the stay at the State University of Utrecht in 1974.

Table 1
Line width parameter, C_{ws} or C_{wf} , and line shift parameter, C_{ss} or C_{sf} , in MHz/torr for the pressure-determined shape of the $J = 0 \rightarrow 1$ absorption line of CH_3Cl at 300°K .

Perturber	CH_3Cl	CH_3Br	OCS	CO_2
Width	21.6 ± 0.3	19.1 ± 1.4	10.0 ± 0.3	8.0 ± 0.3
Shift	0.9 ± 0.07	1.1 ± 0.16	0.02 ± 0.08	-0.16 ± 0.06

The results of the measurements are given in table 1. During the course of measurements with any one mixture, the cell temperature remained constant to within approximately $\pm 0.5^\circ\text{C}$; however, room temperature, and hence the cell temperature, varied from day to day. The values of C_w and C_s listed in tables 1 are appropriate to 300°K and were found from the measured values by assuming that $C_w \sim T^{-0.83}$ and $C_s \sim T^{-1.75}$; these variations of width and shift-parameters with temperature T had been found by Lujendijk for self-broadening and selfshifting of CH_3Cl .

For this spectral line, it appears from the limited evidence available that the collision-induced shift due to long-range dipole-dipole interactions is towards higher frequencies, while that due to the shorter range dipole-quadrupole forces involved in the $\text{CH}_3\text{Cl}-\text{CO}_2$ interaction is towards lower frequencies. However, attempts to interpret microwave line-shifts quantitatively in terms of a collision theory have not yet been successful.

The authors are indebted to Dr. S.C.M. Lujendijk for helpful discussions and also for making available the computer programmes necessary for analysing the experimental data.

This work is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.)" and was made possible by financial support

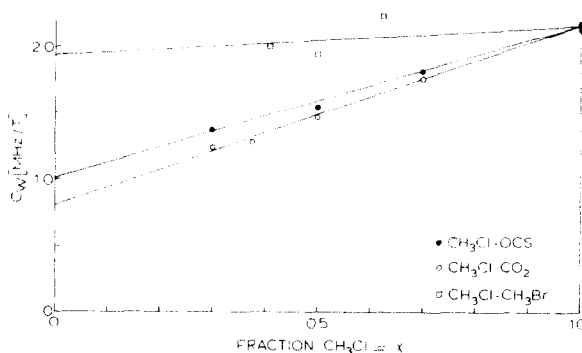


Fig. 2. The linewidth parameter C_w as a function of the fraction x of CH_3Cl in a mixture with some foreign gases.

from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Z.W.O.).

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