Temperature Dependence of N_2-Relaxation of Rotational Lines of Propionitrile

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The temperature dependence of the rotational relaxation of propionitrile, $CH_3CH_2C^{15}N$, has been investigated by means of microwave transient emission signals. From analysis of the pressure dependence of the coherence decay rates for the rotational lines $(J, K_-, K_+) = (2, 0, 2)-(3, 0, 3)$, $(2, 1, 2)-(3, 1, 3)$, and $(2, 2, 1)-(3, 2, 2)$ pressure broadening parameters have been derived for mixtures with nitrogen in the 210–300 K range and for the pure gas at ambient temperatures.

Introduction

The Voyager mission has revealed that the atmosphere of Saturn's moon Titan consists mainly of nitrogen with traces of nitriles, which are key molecules in prebiotic chemistry [1]. Great interest has now arisen in the chemistry of such a reducing atmosphere [2], and it has been shown that electric discharges or UV light with molecular hydrogen escape yields the synthesis of organic nitriles [3]: HCN, HC_3N, C_2N_2 and C_4N_2 were observed by Voyager 1 [1, 4], whereas CH_3CN, and CH_3CH_2CN are predicted at a significant level [5].

Once a molecular species is detected, the main goal is to deduce its vertical density distribution from the measured line profile, a retrieval process which requires previous laboratory measurements of the involved pressure broadenings at the low temperatures prevailing in such an atmosphere (≈ 100 K).

The temperature dependence of the relaxation induced by N_2 on millimeter lines of HCN [6], CH_3CN [7] and HC_3N [8] has already been measured whereas, to our knowledge, no relaxation study has been published in the case of CH_3CH_2CN.

Propionitrile, CH_3CH_2CN, is a slightly asymmetric top molecule with a strong electric dipole moment (≈ 4.1 D), and its rotational spectrum has been extensively studied (for a review see [9]). The most interesting transitions for radio astronomical purposes are of μ_a-type and belong to the vibrational ground state; for these lines the splittings related to the internal rotation of the CH_3 methyl group are negligible [10].

The propionitrile relaxation induced by nitrogen has been investigated in the 210–300 Kelvin temperature range at frequencies of about 26 GHz. The measurements were performed on the ^{15}N isotopomer [11] in order to avoid the quadrupolar structure of the rotational lines related to the ^{14}N nucleus. As already observed [6] or calculated [12] on other nitriles, the relaxation is insensitive to such an isotopic substitution.

Experimental and Analysis

The experiments were carried out with a bridge-type microwave Fourier transform spectrometer operating in the K-band [13]. The gas is polarised by a strong and nearly resonant electromagnetic pulse (duration ≈ 150 ns) and then emits a transient signal (optical precession) which is nothing but the Fourier transform of the spectrum in a small range ($\approx \pm 3$ MHz) around the line under investigation. The cell was cooled by means of a cold methanol flow and the temperature, measured with platinum resistors, was kept stable within 1 K in the 210–300 K temperature range. Gas pressures were measured with two absolute capacitance gauges (MKS Baratron 310 B) calibrated to better than 1%. On account of the small gas pres-

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sures that we have used (<15 mTorr), the observed values were corrected for the thermal transpiration phenomenon [14] which is responsible for a pressure gradient associated with the temperature gradient existing between the gauge and the gas cell. The propionitrile sample used was ^{15}N enriched to 51%.

In addition to the signal damping due to the Doppler effect which can be calculated exactly, the signal decay depends on molecular collisions and is simply described by an exponential damping law. The time constant (T_2) for this decay is related to coherence relaxation, that is to the usual collisional line broadening. As a matter of fact non-exponential signal decay behaviour due to collisions may be observed on account of the dependence of the relaxation rate on the speed of the absorbing molecules. This feature is particularly pronounced for a large ratio of the masses of perturbing and active gas molecules [15]. Although this effect has been observed previouly [16, 17], it could be neglected in the case of the present study since the molecular mass of the buffer gas (N_2) is half the active gas one. Thus an exponential damping law was used for data analysis (after correcting for Doppler dephasing) and the corresponding rate constant ($1/T_2$) was deduced by least squares fitting of the time domain signal. The linear pressure dependence of the corresponding halfwidth of the line ($1/2\pi T_2$) was then determined from a linear regression analysis yielding the pressure broadening parameter

$$C_w = \mathrm{d}(1/2\pi T_2)/\mathrm{d}p$$

for each temperature under investigation.

The investigated R-branch ($J=2-3$) μ_a-type lines were chosen according to the frequency range of our spectrometer. Only three of the five possible transitions were studied however: the transition $(J, K_-, K_+) = (2, 1, 1)-(3, 1, 2)$ occurs at a resonance frequency (26761.4 MHz) outside the range of our spectrometer, and the transition $(J, K_-, K_+) = (2, 2, 0)-(3, 2, 1)$ at 26110.3 MHz was perturbed by a satellite line only 300 kHz apart which made a reliable analysis impossible. For the investigated lines $(J, K_-, K_+) =$ (2, 0, 2)–(3, 0, 3), (2, 1, 2)–(3, 1, 3), and (2, 2, 1)–(3, 2, 2), some weak lines due to vibrational excited states or other isotopomers were also observed in the vicinity (≥ 1 MHz) of the line of interest: they were taken into account, assuming that the observed signal results from a simple addition of all contributing lines, each of them having the same relaxation parameter.

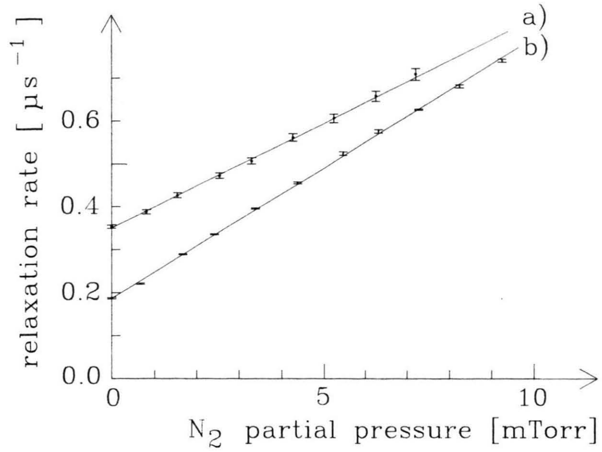

Fig. 1. Experimental results for the N_2 partial pressure dependence of the coherence decay rate $1/T_2$ for the $(J, K_-, K_+) = (2, 0, 2)-(3, 0, 3)$ rotational transition of $CH_3CH_2C^{15}N$, together with the fitted straight lines. The error bars give one standard deviation for $1/T_2$, resulting from fit analysis of the transient emission signals. a) $T=281$ K, active gas partial pressure: 0.62 mTorr; b) $T=212$ K, active gas partial pressure: 0.37 mTorr. From the slope of the lines we obtain the broadening parameters a) $C_w = 7.80(9)$ MHz/Torr, b) $C_w = 9.67(7)$ MHz/Torr.

An example for the linear pressure dependence of the relaxation rate $1/T_2$ is given in Fig. 1, which depicts $1/T_2$ vs. the N_2 partial pressure for two different temperatures together with the corresponding fit lines resulting from the linear regression analysis. The zero pressure intercept of the lines is primarily due to wall and self-collisions and was not further considered whereas the slope is proportional to the temperature-dependent pressure broadening parameter.

Results and Discussion

Most of the experiments were carried out on mixtures of propionitrile with N_2 at different temperatures in the 210–300 K temperature range. At each temperature, the partial pressure of the active gas was kept constant ($\approx 0.2-1.0$ mTorr) and the partial pressure of N_2 was varied between 0.2–15 mTorr. In addition to the investigations with N_2 as buffer gas, self-broadening was also studied at ambient temperatures (298 ± 2 K) in the 0.2–3.5 mTorr range; all room temperature results are summarized in Table 1.

The temperature dependence of N_2-broadening was analysed assuming that the broadening parameter C_w changes with temperature according to [18]

$$C_w(T)/C_w(T_0) = (T/T_0)^{-n},$$

where T_0 is a reference temperature chosen to be $T_0 = 296$ K.

The exponent n may be obtained from linear least squares analysis of a double logarithmic plot of C_w vs. temperature, which is depicted for the investigated transitions in Figure 2. The results are summarized in Table 2, which also gives a comparison with N_2-relaxation studies of other nitriles.

No attempt has been made here to compare the experimental results with theoretical predictions from collisional scattering calculations which were not available for an asymmetric top molecule having more than one dipole moment component along the principal axes. However, on account of the large dipole moment components of propionitrile ($\mu_a \approx 3.9$ D, $\mu_b \approx 1.2$ D [9]) and of the large quadrupole moment of the nitrogen molecule ($Q \approx -1.4$ D · Å [19]), collisions are mainly governed by the $1/r^4$-dependence of the dipole-quadrupole interaction potential which results in large effective collision diameters (≈ 9 Å from our experimental results). Thus an approximate perturbative treatment of molecular collisions can be used [18], which predicts a theoretical temperature exponent $n = 5/6$ in case of dipole-quadrupole interaction, in good agreement with the observed values.

Table 1. Experimental results for the self- and N_2-broadening parameters C_w of rotational transitions of $CH_3CH_2C^{15}N$ at ambient temperatures (298 ± 2 K). The errors quoted in parantheses are in the last digit given and equal to the standard deviation.

Transition	Buffer gas C_w [MHz/Torr]	
$J, K_-, K_+ - J', K'_-, K'_+$	self	N_2
2, 0, 2 − 3, 0, 3	77.3 (3)	7.28 (6)
2, 1, 2 − 3, 1, 3	88.0 (5)	7.40 (3)
2, 2, 1 − 3, 2, 2	87.5 (6)	7.70 (10)

On comparing the experimental results for N_2-relaxation parameters of different nitriles in Table 2 we note that similar values are obtained in the centimeter and millimeter wavelength range. This feature can be explained roughly from the approximate treatment of the collisions [18], taking into account the nearly exclusive role of dipole-quadrupole interaction and the similar magnitude of the dipole moments for these molecules.

The large values for the self-broadening parameters C_w of propionitrile (see Table 1) are primarily due to the strong dipole-dipole interaction. The magnitude of C_w has also been found to be relatively large for rotational transitions of acetonitrile, CH_3CN (see [7] and references cited therein), but somewhat smaller than the reported ones here. This may be explained qualitatively by the presence of additional relaxation channels due to the additional μ_b-component of the dipole moment or propionitrile.

No information about the J-dependence of rotational relaxation data could be obtained from our

Table 2. Experimental results for N_2-broadening parameters C_w at the reference temperature 296 K and for the temperature dependence exponent n of rotational transitions of different nitriles. The errors quoted in parantheses are in the last digit given and equal to the standard deviation.

Active gas	Transition	Frequency [MHz]	C_w (296 K) [MHz/Torr]	n	Experimental technique *	Ref.
$CH_3CH_2C^{15}N$	$J, K_-, K_+ - J', K'_-, K'_+$					this work
	2, 0, 2−3, 0, 3	26 055.8	7.38 (6)	0.81 (3)	transient emission,	
	2, 1, 2−3, 1, 3	25 395.7	7.47 (5)	0.90 (4)	power switching	
	2, 2, 1−3, 2, 2	26 083.7	7.74 (11)	0.88 (6)		
CH_3CN	$J, K - J', K'$					[7]
	4, 2−5, 2	91 980.0	7.80 (21)	0.68 (8)	delayed nutation,	
	4, 3−5, 3	91 971.4	7.50 (8)	0.72 (4)	stark switching	
$HC^{15}N$	$J - J'$					[6]
	0−1	86 055.0	7.05 (7)	0.80 (3)	id.	
HC_3N	$J - J'$					[8]
	10−11	100 076.4	7.62 (13)	0.74 (5)	delayed nutation, frequency switching	

* Transient emission (optical precession) is related to coherence relaxation (T_2), and delayed nutation is related to population relaxation (T_1). For the considered rotational transitions, T_1 and T_2 are expected to be similar [20].

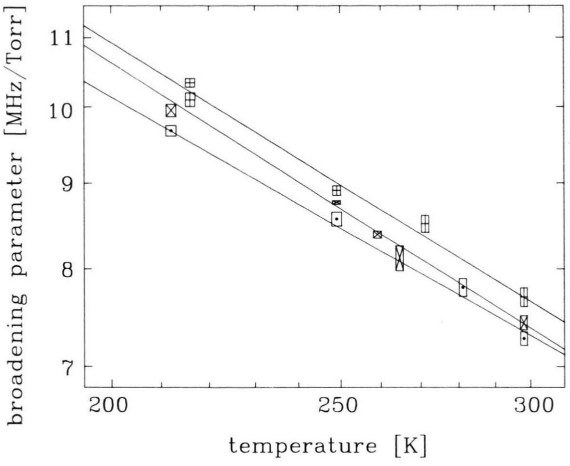

Fig. 2. Experimental results for the temperature dependence of N_2-broadening parameters for rotational lines of $CH_3CH_2C^{15}N$. The figure shows the log-log plot for the broadening parameter C_w vs. the temperature T, together with the fitted straight lines according to the T^{-n} dependence of C_w. The uncertainties given are one standard deviation for C_w and 1 K for temperatures. Transitions $(J, K_-, K_+)-(J', K'_-, K'_+)$: (●): (2, 0, 2)–(3, 0, 3), (×): (2, 1, 2)–(3, 1, 3), (+): (2, 2, 1)–(3, 2, 2).

experiments. Although some dependence of the C_w-values on the quantum number K_- may be indicated by our results (see Tables 1, 2 and Fig. 2), it is not very well pronounced. The observed slight increase with K_- is also in contrast to the behaviour for symmetric top molecules which exhibit a decrease of C_w with K as was predicted theoretically and observed experimentally in case of CH_3CN (see Table 2 and [7]). We thus conclude that further transitions in other frequency ranges must be studied in order to obtain for propionitrile more information about the pressure and temperature dependence of N_2-relaxation rates and in order to analyse its variation with the quantum states.

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