Centrifugal Distortion Analysis and Study of T_2-Relaxation for *l*-Type Doublet Transitions of Nitrous Oxide ($^{15}N_2O$) by a Microwave Pulse Technique

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Z. Naturforsch. **48a,** 720–724 (1993); received March 31, 1993

We investigated *l*-type doublet transitions of $^{15}N_2O$ in the first excited state of the degenerate bending vibration ν_2 with $14 \leq J \leq 34$. From analysis of the *J*-dependence of the line center frequencies, the doubling constant $q^{(0)}$ was obtained together with the first and second order centrifugal distortion constants $q^{(1)}$ and $q^{(2)}$, respectively. For the lines in the *J*-band (4 to 8.2 GHz) and *K*-band (18 to 26.5 GHz) we have also investigated the pressure broadening due to self-collisions with use of the transient emission technique. The experimental results for the pressure broadening parameter Γ_p are compared with predictions from binary collision theory, based on the modified Murphy-Boggs perturbative treatment.

1. Introduction

In the microwave range *l*-type doublet transitions of linear molecules have mainly been investigated to determine the doubling constant for degenerate vibrational modes with a vibrational angular momentum $l\hbar$ along the symmetry axis. In some cases a centrifugal distortion analysis has been included. The determination of the doublet constants is useful to get more information about the intramolecular Coriolis interaction between vibration and rotation, which removes the $\pm l$-degeneracy of the rovibrational energy levels.

Pressure broadening parameters for *l*-type doublet transitions have been determined rarely [1–6] in the microwave region. The investigation of pressure broadening parameters of *l*-type doubling transitions is useful in addition to the investigation of the self-broadening of pure rotational lines because these studies provide additional information about rotational relaxation caused by differences of collision-induced energy transfer involved in the two types of transitions. These differences are mainly due to the two following reasons.

(i) According to the first order dipole-type selection rules collision-induced transitions with $\Delta J = 0$ are forbidden for pure rotational transitions and allowed in *l*-doublet transitions.

(ii) The collision partners (perturber) for emitting molecules in the investigated *l*-doublet states (absorber) are dominated by molecules in the ground state. This means that the states of absorber and perturber are different in most cases.

In the present paper we report the results from microwave studies of *l*-type doublet transitions of $^{15}N_2O$ in the frequency region of 4.8 to 33.8 GHz. For the transitions in the J- and in the K-band we determined pressure broadening parameters at ambient temperature. The low intensity of the signals made it impossible to determine significant data for the absorber speed dependence of the line-broadening as reported previously in [7–9, 19].

More information about the experiments are given in Section 2. In Sect. 3 the results of the centrifugal distortion analysis are presented and in Sect. 4 those of the pressure broadening studies. The conclusions of the paper are given in Section 5.

2. Experimental

The transient emission technique involves the detection of the transient emission signals of the molecular sample following an intense microwave pulse.

For the experiments microwave Fourier transform spectrometers in J- [10], X- [11], Ku- [12], K- [13], and V-band [14] were used.

1024 points were sampled at an interval of 10 ns, i.e. with a rate of 100 MHz. The results of consecutive

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experiments were accumulated in a 16-bit memory of a digital averager to achieve signal-to-noise improvements.

To avoid the hyperfine splittings due to the ^{14}N-nuclear quadrupole coupling we used nitrous oxide with both nitrogen atoms being ^{15}N. NH_4NO_3 (Medgenix Co. purity exceeding 99%) was dehydrated by heating to get N_2O. The sample was destilled twice under vacuum. The isotopic purity was better than 95%. For the pressure broadening studies the pressure was varied from about 1.5 to 90 mTorr. Pressure measurements were made with a MKS Baratron 310B capacitance manometer.

The transient emission signal was analysed by a least squares fit program according to the expression

$$S(t) = S_0 \, e^{-t^2/4q^2} \, e^{-t/T_2} \cos(2\pi \nu t + \Phi) \qquad (1)$$

with S_0, T_2, ν, and Φ as fitting parameters. S_0 is the value of the signal at the end of the microwave pulse, $1/T_2$ the decay rate due to collisions either with other molecules or with the wall of the sample cell, ν corresponds to the frequency of the oscillating signal and q is related to the Doppler halfwidth ($\Delta\nu_D = (\ln 2)^{1/2}/2\pi q$) of the line. All measurements were done at room temperature.

3. Centrifugal Distortion Analysis

We measured the lines which were included in our studies of the pressure broadening several times, each time at a different pressure. No significant pressure-induced lineshift was observed. So it was possible to use the mean value of the line-center frequency for the further analysis. The lines which were not used for the determination of the pressure dependence of $1/T_2$ were recorded only once at the lowest possible pressure. The experimental resonance frequencies for l-type doublet transitions may be approximated by the expression [15]

$$\nu_0 = q^{(0)} J(J+1) - q^{(1)} J^2(J+1)^2 + q^{(2)} J^3(J+1)^3 - + \dots, \qquad (2)$$

where $q^{(0)}$ is the l-type doubling constant for the considered vibrational mode. The $q^{(i)}$ ($i \geq 1$) are correction terms for effects from centrifugal distortion.

A calculation of Pliva [16] gave $q^{(0)} = 22.84$ MHz. This calculation was confirmed by his infrared measurements.

Table 1. l-type doublet transition frequencies for $^{15}N_2O$ in the vibrational state $v_2 = 1$. J is the rotational quantum number, ν_0(obs.) is the observed and ν_0(calc.) the calculated frequency. The calculation was made by use of (2) and the constants of Table 2.

J	ν_0(obs.) [MHz]	ν_0(calc.) [MHz]	ν_0(obs.)$-\nu_0$(calc.) [kHz]
14	4 788.4426	4 788.4422	0.44
15	5 472.2991	5 472.2987	0.34
16	6 202.6891	6 202.6889	0.22
17	6 876.6022	6 876.6017	0.54
18	7 797.0259	7 797.0255	0.42
19	8 662.9475	8 662.9479	−0.38
20	9 574.3570	9 574.3560	1.08
21	10 531.2350	10 531.2361	−0.68
22	11 533.5767	11 533.5739	2.79
23	12 581.3540	12 581.3545	−0.47
24	13 674.5611	13 674.5621	−0.99
25	14 813.1791	14 813.1805	−1.38
26	15 997.1929	15 997.1927	0.17
27	17 226.5798	17 226.5811	−1.39
28	18 501.3251	18 501.3275	−2.37
29	19 821.4116	19 821.4129	−1.35
30	21 186.8174	21 186.8178	−0.40
31	22 587.5225	22 587.5220	0.50
32	24 053.5031	24 053.5046	−1.57
33	25 554.7460	25 554.7443	1.69
34	27 101.2235	27 101.2189	4.58
35	28 692.9099	28 692.9056	4.21
36	30 329.7766	30 329.7813	−4.67
37	32 011.8212	32 011.8219	−0.71

Table 2. l-type doublet constants for the vibrational state $v_2 = 1$ of $^{15}N_2O$. The errors in the parentheses are in the last digit given and equal twice the standard deviation.

Molecule	Ref.	$q^{(0)}$ [MHz]	$q^{(1)}$ [Hz]	$q^{(2)} \cdot 10^5$ [Hz]
$^{15}N_2O$	this work	22.808140(8)	28.769(17)	16.13(86)
$^{15}N_2O$	[16]	22.84		

We used our observed frequencies to get the constants $q^{(i)}$ ($0 \leq i \leq 2$) from a least squares fit. Table 1 contains the observed and the calculated frequencies for the various rotational quantum numbers J. The predictions were made with the constants $q^{(0)}$, $q^{(1)}$, $q^{(2)}$ from Table 2. The agreement between experimental and theoretical values (see Table 1) is indicated by the resulting 1.9 kHz root mean squares deviation of the fit. The fitting of $q^{(3)}$ showed no further improvement.

4. Pressure Broadening

Recent theoretical treatments of the transient emission signal with consideration of absorber speed de-

Table 3. Halfwidth parameter Γ_p (in MHz/torr) due to self-broadening of l-type doublet lines of $^{15}N_2O$ in the vibrational state $v_2=1$ at room temperature. J: rotational quantum number; Γ_p(obs.): observed halfwidth parameter; Γ_p(calc.): calculated halfwidth parameter according to modified Murphy-Boggs theory [17]. The errors in the parentheses are in the last digit given and equal the standard deviation.

J	Γ_p(obs.)	Γ_p(calc.)
14	3.794(19)	4.511
15	3.667(18)	4.493
16	3.611(16)	4.476
17	3.561(22)	4.460
18	3.564(16)	4.443
28	3.33(12)	4.230
29	3.27(5)	4.202
30	3.30(4)	4.175
31	3.15(9)	4.147
32	3.15(6)	4.119
33	3.31(9)	4.091

pendent relaxation rates [9, 18] predict nonexponential decay behaviour. Such a speed dependence of the rotational relaxation for the $J=0\rightarrow 1$ transition of N_2O was described in [7] and [8]. For the investigated l-type doublet transitions no significant speed dependence of the rotational relaxation rates was observed.

The pressure dependence of $1/T_2$ (see (1)) was obtained by a linear least squares fit according to the expression

$$1/T_2=\alpha+\beta p\,. \tag{3}$$

The intercept α accounts mainly for wall collisions. The slope β yields the pressure boadening parameter $\Gamma_p=\beta/2\pi$ for the halfwidth of the line. The values of Γ_p are given in Table 3. This table also contains the values for the pressure broadening parameters predicted by use of the modified Murphy-Boggs (MB)-theory [17] with consideration of long-range (dipole-, quadrupole-, induction- and dispersion-) intermolecular interaction. The molecular parameters used for the intermolecular potential in the calculations were 0.1608 D for the electric dipole moment [19], −7.3 DÅ for the electric quadrupole moment [20], 12.89 eV for the ionization potential [21], 3.0 Å^3 for the average polarizability [22] and 2.79 Å^3 for the anisotropy of polarizability [22]. It should be noticed that the used quadrupole moment is twice the value given in [23]. The pressure dependence Γ_p for the l-type doublet transition with $J=16$ is plotted in Figure 1. In Fig. 2 we present the J-dependence of the self-broadening linewidth parameters for the l-type doublet transitions. The quoted errors are the standard deviations from the linear least squares fit. Shifts in temperature (< 2 K) and inaccuracies for the pressures (< 0.1 mTorr) are not reflected in these errors. The pressure broadening parameter is descreasing with increasing rotational quantum number J for the experi-

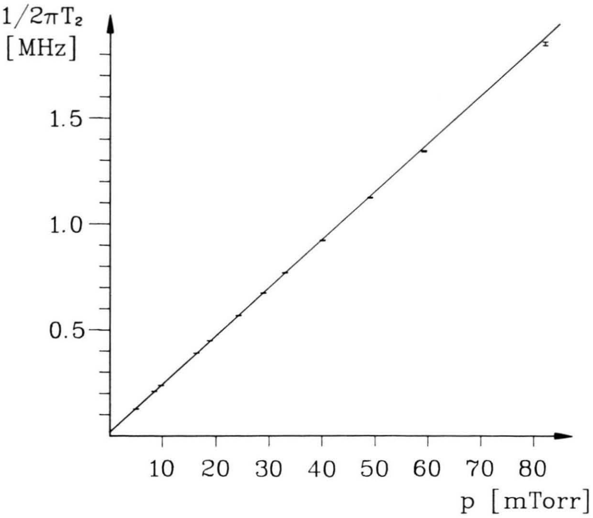

Fig. 1. Pressure dependence of the pressure broadened halfwidth $1/2\pi T_2$ for the l-type doublet transition in the vibrational state $v_2=1$ of $^{15}N_2O$ with $J=16$ at room temperature.

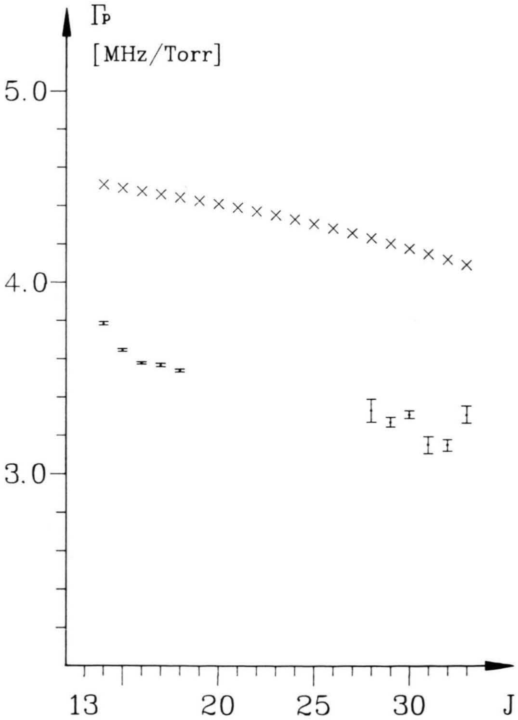

Fig. 2. J-dependence of the self-broadening linewidth parameters Γ_p for the l-type doublet transitions in the vibrational state $v_2=1$ of $^{15}N_2O$ at room temperature. The given errors for the experimental values (●) are the single standard deviations from the least squares fits. The theoretical values (×), calculated using the modified Murphy-Boggs theory, are given without errors.

mental and for the theoretical values which are 15% to 30% larger than the experimental values. Former investigations [2, 3, 6] showed the same discrepancies between experimental and theoretical values for linewidth parameters due to self-broadening.

The fraction $f(J_p)$ of perturber molecules with rotational quantum number J_p is the weighting factor for the calculation of the self-broadening parameter Γ_p from the parameters $\Gamma_p^{J_p}$ which reflect the broadening caused by perturber molecules in rotational state J_p according to

$$\Gamma_p = \sum_{J_p} f(J_p)\, \Gamma_p^{J_p} \,. \tag{4}$$

In former investigations [2, 3, 6] the J_p-dependence of $\Gamma_p^{J_p}$ for different l-type doublet transitions with the rotational quantum numbers J were shown in figures. The curves $\Gamma_p^{J_p}$ were always more or less sharply peaked around $J_p = J$. This fact was always explained by the first order dipole-type collisional selection rules $\Delta J = 0, \pm 1, \Delta J_p = 0, \mp 1$ [24] and the dominant contribution from collisions with near resonant exchange of rotational energy to the broadening of the lines. Thus, according to (4) the pressure broadening parameter J_p peaks around the J-value which corresponds to the maximum of the Boltzmann distribution $f(J_p)$.

For nitrous oxide the observed J-dependence of the self-broadening parameter is also mostly caused by the Boltzmann distribution of the population of perturber rotational energy levels. However, N_2O has by far the smallest dipole moment and the largest quadrupole moment in comparison with previously studied molecules [2, 3, 6]. From calculations based on the MB-theory it can be shown that collision-induced transitions caused by quadrupole-quadrupole interaction predominantly contribute to the linewidth. The quadrupole-type collisional selection rules are $\Delta J = 0, \pm 1, \pm 2, \Delta J_p = 0, \mp 2$ for J_p in the vibrational ground state. Reflecting the combination of different interactions, the peaks in the curves $\Gamma_p^{J_p}$ are broadened and not very significant. Therefore, corresponding figures for depicting the J_p-dependence of $\Gamma_p^{J_p}$ are not presented in this paper.

The maximum of the Boltzmann distribution curve is at about $J = 14$ at room temperature. For this J quantum number the broadening of the line should be at maximum. It was not possible to test this fact because the transition frequencies for the l-type doublet transitions with $J \leq 13$ were out of the range of our spectrometers.

5. Conclusion

Summarizing our results from the centrifugal distortion analysis, we conclude that the centrifugal distortion constants are accurately determined up to second order. The agreement between experimental and theoretical resonance frequencies is better than the resolution of the spectrometer. For some of the transitions we alo determined linewidth parameters from the pressure dependence of transient emission decay rates. We explained the observed J-dependence of the pressure broadening parameters qualitatively with a Boltzmann population distribution of the perturber rotational states. The results are compared with calculations by means of the modified Murphy-Boggs theory. Differences between the experimental and the theoretical values are believed to be due to insufficiencies of the used theory to treat binary collisions. The interpretation of the J-dependence of linewidth parameters is complicated by the large molecular quadrupole moment of N_2O.

Acknowledgements

We thank all members of the group for help and discussions. This work was supported by funds from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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