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THE PRESSURE BROADENING OF NO_2 IN THE MILLIMETER AND SUBMILLIMETER WAVE SPECTRAL REGION

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Abstract—Pressure-broadening parameters for 19 transitions of the millimeter and submillimeter wave spectrum of NO_2 have been obtained experimentally. Results for broadening by N_2, O_2 and He are presented and compared with earlier theoretical calculations of the N_2 and O_2 parameters. A discussion of the relation between theoretical calculations and experimental measurements is presented.

INTRODUCTION

Pressure-broadening coefficients, which are intimately related to intermolecular potentials and collision dynamics, are of practical importance because they are necessary for the interpretation of data which involve the emission, absorption, and propagation of electromagnetic radiation. However, because of the theoretical complexity of the problem and the general difficulty of the experimental measurements, the broadening parameters of molecular species are less well known than their transition frequencies, with relatively few of the pressure-broadening parameters known even to 10%. In a previous paper, we have reported[1] the O_2 and N_2 pressure-broadening parameters of HNO_3 for 16 transitions over a range of quantum states and have found significant deviations from earlier calculations. We also have reported the O_2 and N_2 pressure-broadening parameters of two transitions in NO_2 as well as of a number of other species.[2] In this paper, we present a much more extensive study of NO_2, which includes the parameters for 17 distinct rotational transitions in addition to the two previously reported and extends the collision partners to include He as well as O_2 and N_2. These transitions cover a wide range of quantum states and make possible a comparison with earlier theoretical calculations which used the theory of Anderson.

EXPERIMENTAL DETAILS

We have recently described a computer-controlled millimeter and submillimeter spectrometer which was used to make these pressure-broadening measurements, as well as the signal recovery and processing techniques that were used.[3] For each transition, approx. 30 mtorr of NO_2 were introduced into a 1 m long Pyrex cell of 10-cm dia with polyethylene end caps. The foreign gas was added incrementally through a computer-controlled valve. The computer was also used to monitor the cell pressure and record the data. Typically, for each pressure-broadening parameter, three series of incremental additions of the broadening gas to the initial fill of NO_2 were made. All measurements were made at room temperature ($\sim$295 K). Pressures were measured with a capacitance manometer.

RESULTS

Linewidth measurements were made for each transition at about 25 different pressures between 100 and 1000 mtorr. The high-pressure limit was imposed because of the increasing difficulty of deconvoluting the broader lines from power fluctuations in the system and in some cases by overlap

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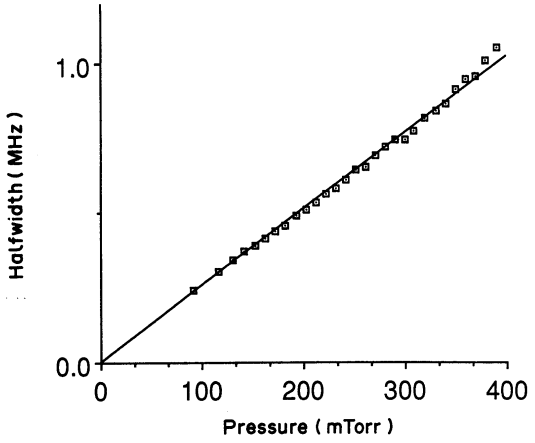

Fig. 1. Measured linewidth as a function of N_2 pressure for the 2_{02}–2_{11} transition.

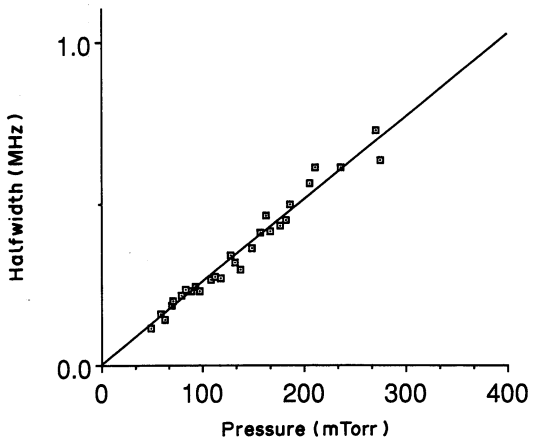

Fig. 2. Measured linewidth as a function of N_2 pressure for the 26_{026}–26_{125} transition.

with adjacent hyperfine structure. Figures 1 and 2 are representative of the best and worst of these data. Each pressure-broadening coefficient was obtained from a least-squares fit to the data with the data points weighted inversely with the square of the pressure. This is based on the assumption that the accuracy of the measured halfwidth is inversely proportional to the linewidth.

Table 1 shows the experimental results. Except for the 17_{117}–18_{018} transition, only a single hyperfine component of each rotational transition was measured. For this transition two hyperfine components were observed. As expected, to within experimental uncertainty, the same pressure-broadening parameters were obtained for each component. The listed uncertainties in Table 1 are 1σ errors from the least-squares fit to the data. Since these are quite small ($\sim$1–5%) and it is well known that systematic errors can be important in measurements of this type, these should be considered only as indicators of the relative quality of the data. The results for oxygen and nitrogen broadening are plotted vs the N quantum number in Figs. 3 and 4 along with the values from previous theoretical work carried out by Tejwani and Yeung[4,5] using Anderson–Tsao–Curnutte (ATC) theory. Their calculations included the interaction of the quadrupole moment of N_2 or O_2

Table 1. Broadening parameters of NO_2 broadened by N_2, O_2 and He.†‡

$N'_{K'_-K'_+}$ - $N''_{K''_-K''_+}$	J′ - J″	F′ - F″	Frequency (MHz)	$\gamma(O_2)$	$\gamma(N_2)$	γ(He)
0_{00} - 1_{11}	1/2 - 3/2	3/2 - 5/2	253383.12	2.73 (7)	3.97 (14)	2.28 (8)
2_{02} - 2_{11}	5/2 - 5/2	7/2 - 7/2	229067.49	2.39 (9)	2.56 (10)	2.07 (8)
4_{04} - 4_{13}	9/2 - 9/2	11/2 - 11/2	231229.96	2.97 (3)	3.20 (3)	2.37 (3)
6_{06} - 6_{15}	13/2 - 13/2	15/2 - 15/2	235030.76	2.93 (5)	2.95 (6)	2.28 (6)
8_{08} - 8_{17}	17/2 - 17/2	19/2 - 19/2	240393.93	2.70 (4)	2.96 (8)	2.16 (7)
10_{010} - 10_{19}	21/2 - 21/2	23/2 - 23/2	247355.37	2.64 (4)	3.10 (5)	2.39 (4)
12_{012} - 12_{111}	25/2 - 25/2	27/2 - 27/2	255989.05	2.52 (2)	2.82 (3)	2.41 (3)
12_{111} - 11_{210}	25/2 - 23/2	27/2 - 25/2	350699.56	2.17 (5)	2.37 (5)	1.98 (5)
14_{014} - 14_{113}	29/2 - 29/2	31/2 - 31/2	266391.99	2.41 (6)	2.79 (5)	2.25 (4)
15_{115} - 14_{212}	29/2 - 27/2	27/2 - 25/2	345754.84	2.52 (4)	2.70 (6)	2.36 (4)
16_{016} - 16_{115}	33/2 - 33/2	35/2 - 35/2	278677.88	2.33 (3)	2.58 (4)	2.12 (3)
16_{115} - 15_{214}	33/2 - 31/2	35/2 - 33/2	229782.05	2.63 (7)	2.79 (7)	2.44 (7)
17_{117} - 18_{018}	35/2 - 37/2	37/2 - 39/2	275010.50	2.09 (3)	2.29 (3)	1.98 (4)
17_{117} - 18_{018}	35/2 - 37/2	35/2 - 37/2	275006.21	2.19 (5)	2.39 (6)	1.88 (4)
19_{119} - 18_{216}	39/2 - 37/2	41/2 - 39/2	276052.51	2.44 (5)	2.25 (5)	2.20 (6)
20_{020} - 20_{119}	41/2 - 41/2	43/2 - 43/2	309411.88	2.25 (4)	2.67 (5)	2.26 (4)
24_{024} - 24_{123}	49/2 - 49/2	51/2 - 51/2	349264.58	1.86 (2)	2.63 (3)	2.10 (2)
26_{026} - 26_{125}	53/2 - 53/2	55/2 - 55/2	372936.11	2.10 (2)	2.57 (2)	2.02 (2)
26_{224} - 25_{323}	53/2 - 51/2	55/2 - 53/2	452774.59	2.14 (7)	2.73 (10)	1.92 (7)
32_{032} - 32_{131}	65/2 - 65/2	67/2 - 67/2	460117.85	2.22 (3)	2.30 (3)	1.97 (2)

† Broadening parameters are given in MHz/Torr.

‡ Experimental uncertainty is one standard deviation taken from fit.

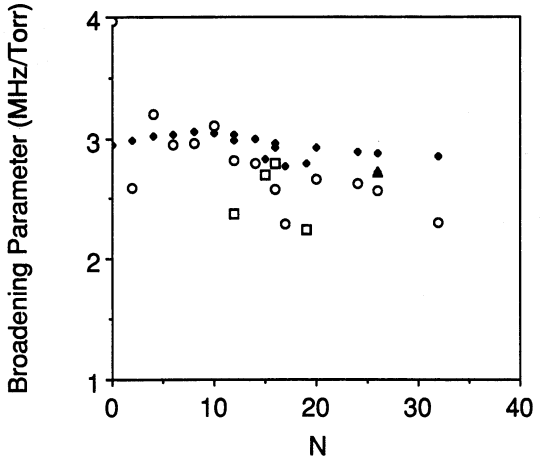

Fig. 3. Nitrogen pressure-broadening of NO_2. For the experimental measurements, open circles refer to the $K = 0$–1 branch, open squares to the $K = 1$–2 branch, and the triangle to the $K = 2$–3 branch. The solid diamonds are theoretical results (Ref. 5).

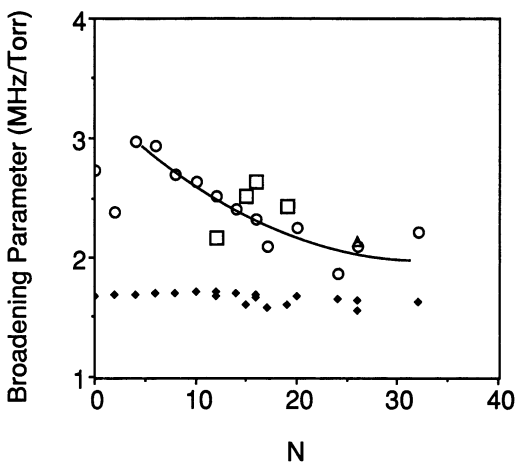

Fig. 4. Oxygen pressure-broadening of NO_2. For the experimental measurements, open circles refer to the $K = 0$–1 branch, open squares to the $K = 1$–2 branch, and the triangle to the $K = 2$–3 branch. The solid diamonds are theoretical results (Ref. 5).

with the dipole and quadrupole moments of NO_2. In the figures, open circles represent the $K = 0$–1 branch, open squares the $K = 1$–2 branch and triangles the $K = 2$–3 branch. The calculated values are plotted as solid diamonds. For both collision partners, the most notable features of the experimental data are the relatively large state to state variations at low N, followed by a general decline in pressure-broadening parameter with increasing N. Much of the scatter in the points at high N result from the existence of data from several different branches. Since the N_2 data has larger state to state variations, this is most notable in the data for O_2 broadening. For example, a relatively simple, smooth empirical curve can be drawn to within about $\pm 5\%$ of the oxygen broadening data above $N = 4$ of the $K = 0$–1 branch. We conclude that this is a reasonable measure of the relative accuracy of the data and that state to state variations larger than this amount are experimentally significant.

The N_2 broadening parameters obtained in this mm/submm work and those from the i.r. work of Devi et al[6,7] are plotted vs N in Fig. 5 as solid and open circles respectively. Although the parameters should have some functional dependence on other quantum numbers, it can be seen that a relatively smooth progression exists and that there is a smooth transition between the measurements from the two spectral regions. This smooth progression and overlap is consistent with the expectation that both data sets are good to better than 10%.

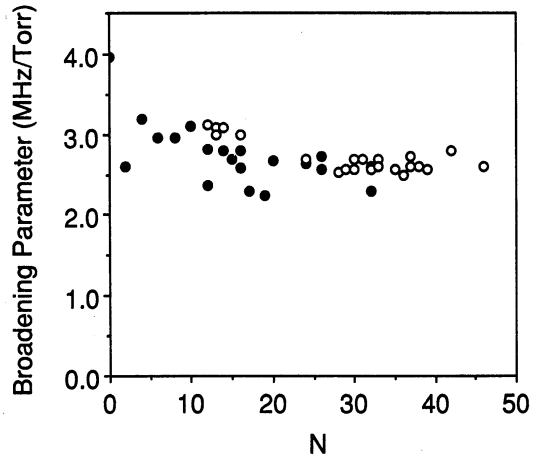

Fig. 5. Nitrogen pressure-broadening measurements of NO_2 from mm/submm (●) and i.r. (○) measurements (Refs. 6,7).

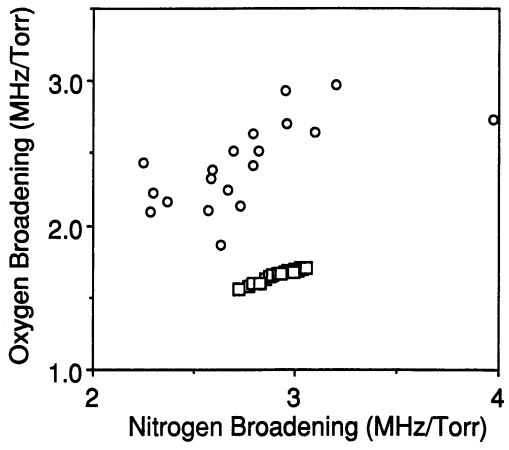

Fig. 6. The relation between nitrogen and oxygen broadening of NO_2 for the experimental measurements (○) and from the theoretical results (□, Ref. 5).

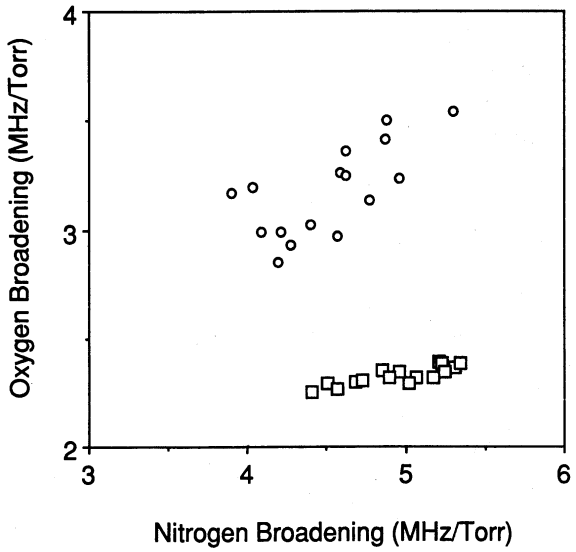

Fig. 7. The relation between nitrogen and oxygen broadening of HNO_3 for the experimental measurements (○) and from the theoretical results (□, Ref. 5).

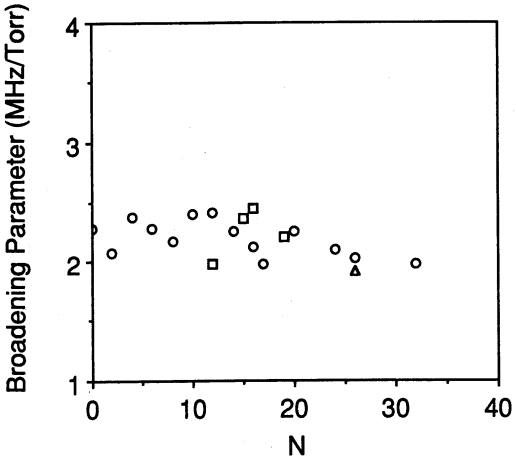

Fig. 8. Helium pressure-broadening of NO_2. For the experimental measurements, open circles refer to the $K = 0$–1 branch, open boxes to the $K = 1$–2 branch, and the triangle to the $K = 2$–3 branch.

DISCUSSION

Figures 3 and 4 show the comparison between our experimental results and the calculations of Tejwani and Yeung.[5] The most obvious results of this comparison are that the experimental data show significantly more state to state variation than do the theoretical calculations, and the theoretical calculations for O_2 are significantly smaller than the experimental values. We have previously reported a similar difference between the experimental and theoretical pressure-broadening parameters of HNO_3.[1]

Figure 6 shows a comparison between the experimentally observed pressure-broadening parameters for N_2 and O_2 (open circles) as well as a comparison for the theoretical calculations (open squares). It is remarkable how similar the experimental measurements for collisions with the two different collision partners are, not only in magnitude, but also in state to state variation. The similarity for the cross sections is even greater since the slightly smaller reduced mass of the N_2–NO_2 system lowers its cross section relative to that of O_2–NO_2. The smoothness of the theoretical comparison is a manifestation of the small calculated state to state variation, but the figure shows that the calculated N_2 values are almost 100% larger than those of O_2. This is easy to understand; the calculation of the interaction is via the much smaller quadrupole moment of O_2. Thus, we conclude that the actual collisions between either O_2 or N_2 and NO_2 are much more alike than predicted by a theory in which the quadrupole moment of the diatomic is the principal measure of its collisional interactions.

Figure 7 shows a similar comparison for HNO_3 broadened with O_2 and N_2. Since HNO_3 has a much larger dipole moment than NO_2, its calculated pressure-broadening parameters are also significantly larger; and again, the calculated N_2 parameters are about 100% larger than the calculated O_2 parameters. However, a larger difference between the measured O_2 and N_2 broadening was found than for the case of NO_2. In fact, for a number of species including NO_2, we have previously noted that because O_2 has such a small quadrupole moment its pressure-broadening parameter is a useful measure of the range of hard collisions and that the difference between the O_2 and the N_2 parameters can be simply related to the interaction between the quadrupole moment of the N_2 and the dipole moment of its collision partner.[8] Thus, the small difference between the O_2 and the N_2 parameters observed in our measurements is simply a consequence of the small dipole moment of the NO_2.

Finally, the broadening of NO_2 by He, shown in Fig. 8, should be considered. For this case, no systematic trend with N is observed, a result that is expected because its high velocity is efficient in overcoming energy defects. However, it is worth noting that the magnitude of the He broadening

is close to that of the O_2 broadening at high N, with the O_2 broadening becoming only $\sim 20\%$ larger at low N. Since helium has no quadrupole moment, this result is suggestive that the pressure-broadening due to O_2 should be associated with a multiplicity of short range forces rather than the single quadrupole–(dipole + quadrupole) interaction. This is consistent with our earlier suggestion that because of its lack of a dipole moment and small quadrupole moment, O_2 can be considered as a probe of the "hard sphere" diameter of its collision partners.[8]

SUMMARY

The pressure-broadening parameters for a number of transitions of NO_2 broadened by N_2, O_2, and He have been observed. In regions of overlap, good agreement was obtained with N_2-broadening parameters derived from infrared measurements. In comparison with previous theoretical calculations, substantially more state to state variation was observed. This result is similar to earlier comparisons between experiment and theory for other species. In addition, although the absolute magnitude of the calculated nitrogen pressure-broadening parameters fell within the range of experimentally-observed values, the observed parameters were found to be about 100% larger than the calculated parameters for oxygen. It therefore appears that the small quadrupole moment of oxygen alone does not provide a good representation of its collisional interactions.

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