

PRESSURE BROADENING OF NO₂, CF₂Cl₂, HDO AND HOOH BY O₂ AND N₂ IN THE MILLIMETER WAVE REGION

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Abstract—The pressure-broadening coefficients of four molecules of atmospheric significance (NO₂, CF₂Cl₂, HDO and HOOH) have been measured in the millimeter wave region. For each species, two transitions near 230 GHz were broadened by both N₂ and O₂, for a total of 16 different pressure-broadening measurements. Intercomparisons among the results of these measurements, as well as our recent more extensive measurements on HNO₃, are considered.

INTRODUCTION

Although there has been a multitude of papers which address both experimental and theoretical aspects of pressure broadening, the complexity of the problem is such that for many fundamental species the pressure-broadening parameters of only a few transitions are known to be better than 10%. For other important species, even less is known. However, because of both the fundamental significance of collisional processes and the practical application of their results to the deconvolution of remote sensing data, there has been significant recent activity and progress. Of recent measurements in the microwave region applicable to atmospheric study, the measurement of the oxygen (O₂) and nitrogen (N₂) broadening of four transitions of ozone (O₃) near 100 GHz, the 119 and 425 GHz O₂ transitions, and the 183 and 380 GHz transitions in water (H₂O) are especially useful.¹⁻⁴ In a recent paper, we have reported the pressure-broadening parameters of nitric acid (HNO₃) by both O₂ and N₂ for 16 different transitions over a range of quantum states and have observed systematic variations and trends.⁵ In this work, it was found that significant deviations from earlier calculations⁶ existed.

In this paper, we report O₂ and N₂ pressure-broadening parameters for selected transitions of four molecules of atmospheric significance. Although the number of states covered for each species is not so large as in our study of nitric acid, the work reported here provides selected points to compare with theory, as well as an intercomparison of pressure-broadening parameters from different species. Comparison with theory is important because it is well known that the availability of a few experimental data points can make possible a significant improvement in calculated values. This adjustment is ordinarily accomplished by judicious changes of the parameters in the theory. Comparisons of data for different species are useful because it is also well known that pressure-broadening measurements can be fraught with systematic errors. Although our values could also contain systematic errors, relative systematic errors among our measurements are believed to be << 5%. Thus, these measurements provide a means for intercomparison of more extensive sets of measurements on individual species.

All of the lines selected for measurement are in the general region of 230 GHz. This choice was made partly for experimental convenience, partly to hold constant any systematic errors that might be frequency dependent, and partly because this is an atmospheric window which is used for field observations.

EXPERIMENTAL STUDIES

We have recently described in some detail the broadband millimeter and submillimeter spectrometer used to make these pressure-broadening measurements as well as the signal recovery

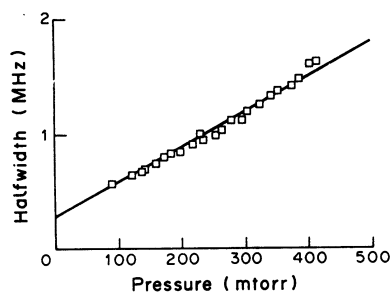


Fig. 1. Measured linewidths of the NO_2 transition at 247,355.37 MHz as a function of pressure.

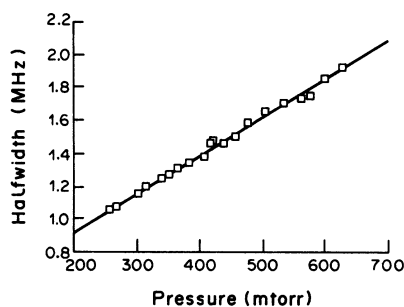


Fig. 2. Measured linewidths of the HDO transition at 241,561.55 MHz as a function of pressure.

and processing techniques used.⁵ For each of the 16 pressure-broadening measurements reported here, approximately 25 linewidths were measured in the pressure region between 100 and 400 mtorr. For each of these measurements, about 25 mtorr of spectroscopic sample was first admitted to the cell and the foreign gas added incrementally. The Pyrex cell was 10 cm in diameter, 1 m long, with polyethylene end caps. During the several minutes duration of data collection for each point, no changes in gas composition or pressure were observed. For the relatively unstable hydrogen peroxide, its slow decomposition caused no detectable problems. All measurements were done at room temperature (~ 295 K). Figure 1, the NO_2 transition at 247,355.37 MHz, and Fig. 2, the HDO transition at 241,561.55 MHz, are representative of the better and poorer data which were measured in this work.

RESULTS

In addition to their relevance to atmospheric science, the four species discussed in this paper and HNO_3 were chosen because they are representative of several spectral types of small, fundamental molecular species. The simplest spectroscopically is CF_2Cl_2 . It is a relatively heavy asymmetric rotor with small rotational constants, a high density of energy levels, and minimal centrifugal distortion. As such it is fairly easy to model with standard asymmetric rotor theory. HNO_3 is a lighter species, with more widely spaced levels and larger centrifugal distortion effects. HDO is the lightest of the three asymmetric rotors, has large centrifugal distortion effects, and widely spaced levels. HOOH has a much more complicated spectrum due to its internal rotation. Because of this, the calculation of its energy levels is more difficult and the existence of low lying thermally populated torsional levels further complicates any calculation. However, these are not fundamental issues associated with collisional theory and merely make the calculation of the energy levels, selection rules, and transition moments more complicated. The electronic spin associated with NO_2 is more interesting theoretically. In the ground electronic state the energy splittings due to the electron spin are small in comparison to the rotational level spacing and certainly small in comparison to the thermal energy. In the i.r. they are often unresolved. Because of the small energies associated with this fine and hyperfine structure, it would appear to be a good approximation to simply ignore them. In the microwave measurement of Meier discussed below, the different components were all observed to have the same pressure broadening coefficient.⁷ However, not all electronic effects are negligible. In the case of NO it has been observed that the broadenings of the transitions in the $^2\Pi_{3/2}$ state are $\sim 7\%$ larger than the broadenings in the $^2\Pi_{1/2}$ state.⁸

NO_2

Nitrogen dioxide uniquely combines in a single, chemically stable molecule an unpaired electronic spin and an asymmetric rotor with large rotational constants. Because of this feature, it has become a favorite testing ground for theory and has acquired an extensive literature and following among spectroscopists. Of the species studied here, it has the smallest dipole moment (0.316 D). In an earlier paper on the mm/submm spectrum of this species, we have reviewed the spectroscopy that is pertinent to this pressure-broadening study.⁹

The interaction with the electron spin splits a single rotational level into a doublet, each of which is further subdivided into a triplet by a nuclear hyperfine interaction with the $I = 1$ nitrogen nucleus. At the high resolution available in the mm/submm, the selection rules for strong transitions produce a six line pattern. In this experiment two lines were observed, the $F = 11/2 - F' = 11/2$, $J = 9/2 - J' = 9/2$ of the $N_{Kp,Ko} = 4_{0,4} - N'_{Kp,Ko} = 4_{1,3}$ at 231,229.96 MHz and the $F = 23/2 - F' = 23/2$, $J = 21/2 - J' = 21/2$ of the $N_{Kp,Ko} = 10_{0,10} - N'_{Kp,Ko} = 10_{1,9}$ at 247,355.37 MHz. Because the energy of the interaction that produces the splittings is very small in comparison to the rotational energy, it is expected that the pressure broadening coefficients will be the same for all fine and hyperfine components. For self broadening, this has been investigated experimentally by Meier who looked at the self broadening of the six components of the $26_{1,25} - 25_{2,24}$ transition at 94 GHz and found the broadening coefficients to be the same to within experimental error.⁷

Table 1 shows our experimental results. The statistical uncertainties listed are those that result from the fit to the experimental data. Since it is well known that systematic effects are common in pressure broadening experiments, these should be used more as a guide to the relative quality of the experimental data rather than a measure of the absolute accuracy of the results. In the case of N_2 broadening, the coefficients are essentially the same for both rotational transitions to within this statistical uncertainty. Malathy Devi et al have measured 7 lines in the ν_3 band at $12 \mu\text{m}$.¹⁰ The pressure broadening parameters that they reported for these lines were 3.0 MHz/torr to within the $\sim 10\%$ experimental error. Table 1 shows that the microwave measurements fall within the same range of values. Although it would be tempting from this to conclude that the pressure broadening coefficients for $\text{NO}_2 - N_2$ collisions are relatively constant, all of the observed transitions fall well within the thermally populated rotational manifold and it would be dangerous to extrapolate these results to more highly excited rotational states. It is, however, reassuring that the microwave and i.r. results are in general agreement. Our results for the O_2 pressure broadening parameters show a somewhat larger variation between the two lines, about 10%. Although not absolutely conclusive, we believe that this decrease with increasing J is probably real.

Tejwani and Yeung have published two papers that use Anderson theory to calculate the pressure broadening coefficients for $\text{NO}_2 - N_2$ collisions.^{11,12} In the first they considered only interactions between the quadrupole moment of N_2 and the electric dipole moment of NO_2 . They obtained a value of 1.78 MHz/torr for the $10_{0,10} - 10_{1,9}$ observed in this work, with little state-to-state variation apparent for other calculated transitions. This is much lower than either the microwave or i.r. measurements. In their later work, they noted that interactions with the electric quadrupole moment of NO_2 are very important due to the low electric dipole moment of NO_2 and calculated an average over the thermally populated states of 2.69 MHz/torr, a value in much better agreement with the numbers then being used to interpret experimental data.^{13,14}

Table 1. Broadening parameters of selected molecules.

Molecule	μ (Debye)	Transition frequency [†] (MHz)	$\gamma(N_2)$ (MHz/Torr) [‡]	$\gamma(O_2)$ (MHz/Torr)
NO ₂	0.32	231229.96	3.20 (3)	2.97 (3)
		247355.37	3.10 (5)	2.64 (4)
CF ₂ Cl ₂	0.51	239247.21	4.08 (7)	3.50 (9)
		231979.45	3.99 (27)	3.73 (22)
HDO	1.84	241561.55	4.31 (9)	2.33 (3)
		225896.72	4.28 (12)	2.22 (8)
HOOH	1.58	223100.95	4.87 (12)	2.85 (12)
		229785.93	4.22 (6)	2.79 (9)
HNO ₃	2.17	231777.61	4.96(9)	3.24(4)
		231627.28	4.57(9)	2.97(6)

[†] See text for complete state labels and references.
[‡] Uncertainties are one standard deviation from the fit.

CF₂Cl₂

Difluorodichloromethane (Freon 12) has received relatively little spectroscopic attention. It is an asymmetric rotor with small rotational constants. As a result, it has a dense spectrum, ordinarily not rotationally resolved in the i.r., and its rotational levels are thermally populated to large values of J and K . In an earlier study of the rotational spectrum of this species, we have discussed the spectral properties of this molecule in more detail.¹⁵ At high J in a species such as CF_2Cl_2 , the K degeneracy is often not broken by the asymmetry and many of the strong transitions are degenerate pairs.

The pressure broadening parameters of two such pairs, the $30_{26,5}-29_{25,4}/30_{26,4}-29_{25,5}$ and the $53_{1,52}-52_{2,51}/53_{2,52}-52_{1,51}$, are shown in Table 1. Calculations based on our earlier analysis give the frequencies of these transitions as 231,979.45 and 239,247.21 MHz respectively. Because of the resulting large partition function and relatively small dipole moment, 0.51 D, the mm/submm spectrum of CF_2Cl_2 is weaker than the other species reported here. The larger statistical uncertainties on these lines, especially the weaker $30_{26,5}-29_{25,4}$, reflect this fact. To within this uncertainty, the measured pressure broadening parameters for both O_2 and N_2 do not vary between the two transitions. The i.r. spectrum of CF_2Cl_2 is relatively dense and so far as we know, no i.r. pressure broadening parameters for this species have been reported.

HDO

Water has received perhaps more spectroscopic attention than any other molecule. Its singly deuterated form, HDO is a light asymmetric rotor with a relatively large dipole moment of 1.8 D. As a consequence it has a strong, relatively sparse spectrum. It has been extensively studied in both the i.r. and the microwave, and we have previously discussed much of its extensive literature in the context of our earlier work on its mm/submm spectrum.^{16,17}

The pressure broadening parameters for the $2_{11}-2_{12}$ and $3_{12}-2_{21}$ transitions which we have previously reported at 241,561.55 and 225,896.72 MHz respectively are shown in Table 1. Malathy Devi et al have reported i.r. pressure broadening measurements on 31 transitions in the ν_2 band of HDO that lie between 1260 and 1345 cm^{-1} .¹⁸ The measured pressure broadening parameters reported in that work for HDO- N_2 collisions range from ~ 2.5 to ~ 4.5 MHz/torr with a strong systematic trend towards the larger values for lower energy states. The observed values for the four measurements of states whose quantum numbers are less than or equal to three all lie within about 0.3 of their average of 4.1 MHz/torr. Thus we see that the HDO values reported in Table 1 fall within the range of values observed in the i.r. for low lying states. As in the other species, the oxygen pressure broadening parameters are about the same for the two states studied and smaller than the nitrogen broadening parameters.

HOOH

Hydrogen peroxide is a spectroscopically complex molecule owing to its combination of internal rotation and large centrifugal distortion effects. It has a large rotational constant, widely spaced rotational levels, and a relatively large dipole moment of 1.6 D. We have previously discussed its spectroscopy in the millimeter and submillimeter spectral region.^{18,19}

The pressure-broadening parameters for the $8_{08}(\tau = 1)-7_{16}(\tau = 3)$ and $15_{1,15}(\tau = 3)-14_{2,13}(\tau = 1)$ at observed frequencies of 223,100.95 and 229,785.93 MHz, respectively, are shown in Table 1. Here a significant difference exists between the two pressure broadening parameters for collisions with N_2 . But as would be expected, the higher lying state has the smaller pressure broadening parameter. For the oxygen broadening parameters we once again measured nearly identical values which were smaller than the nitrogen broadening values.

HNO₃

As has been discussed, we have recently completed a much more extensive series of measurements on the pressure-broadening parameters of nitric acid. Nitric acid is an ordinary asymmetric rotor with a 2.2 D dipole moment and without the complications of unpaired electronic spin or internal rotation. In the hierarchy of rotational constants, it falls between CF_2Cl_2 and HDO. Two representative transitions, the $14_{4,10}-13_{4,9}$ and the $18_{0,18}-17_{0,17}$ at 231,777.61 and 231,627.28 MHz,

respectively, are included in Table 1 so that they can be compared with the other measurements reported here. These were selected because they are two strong transitions at similar frequencies to the others reported here and also well within the thermally populated rotational manifold. It is worth noting that over the much wider range of states studied that the nitrogen broadening parameters varied from 3.90 to 5.30 MHz/torr and the oxygen parameters varied from 2.97 to 3.54 MHz/torr. Again, the trend is toward lower values for the higher lying states.

DISCUSSION

Since only a limited number of states were observed for each of these species, caution must be used in any attempt to interpret results in terms of basic molecular properties. However, because all observed states were selected to be well within the thermally populated rotational manifold and to have similar transition frequencies, much of this state to state variation should be minimized. Even for the species which showed the largest variation, HOOH, the difference is not much more than 10% and that comparison involves states with one of the larger differences in energy. In addition, the basic agreement discussed above between our results and the results of i.r. studies makes it seem reasonable to consider these systematic trends.

First let us consider nitrogen broadening. Nitrogen has a substantially larger quadrupole moment than oxygen and it is expected that the dipole-quadrupole interaction along with variations in molecular velocity should be important. In this case, the size of the electric dipole moment of the spectroscopically active species should be a first order cause of variation among the species. Inspection of Table 1 shows this generally to be the case, with the larger dipole moment species having the larger pressure broadening parameters. In addition, the largest state to state variations should be expected for the species with the larger dipole moments because the selection rules of the dipole-quadrupole interaction should make a significant contribution above and beyond the less selective close encounter interactions associated with the higher order terms in the multipole expansion.

Next let us consider oxygen broadening. In addition to having no electric dipole moment, oxygen has only a very small electric quadrupole moment. The physical significance of this is perhaps best understood in the context of theoretical calculations. In these calculations, the dipole-quadrupole interaction is often so small that the calculations predict essentially the same pressure broadening coefficient for all transitions, a coefficient that is simply related to the assumed hard shell geometrical size,⁵ according to the relation $\gamma = (nv/2c)b^2$, where γ is the broadening parameter, n is the number density of colliding molecules, v is the mean collision velocity, and b is the effective molecular diameter. Thus we should expect for the O₂ a different ordering, one related to the physical size of the molecule allowing for velocity effects. Although the general concept of a physical size of a molecule is nebulous, the ordering for the five species in Table 1 is fairly clear: CF₂Cl₂ is largest, followed by HNO₃, NO₂, HOOH and HDO in order. Only the relative size of NO₂ and HOOH is questionable, and their measured pressure broadening parameters overlap.

The nature of the interaction in NO₂ is worthy of special note at this point. Of the five species discussed here, it has the smallest electric dipole moment, 0.316 D. In the context of interactions based upon multipole expansions, the dipole-quadrupole interaction is ordinarily expected to be the largest contributor to the linewidth. However, in Tejwani and Yeung's second paper¹² they found that because of the small value of the dipole moment of NO₂ that the quadrupole-quadrupole interaction was dominant. The most obvious experimental manifestation of this can be seen in Table 1; the pressure broadening coefficients for NO₂ are the smallest of the four species and the difference between O₂ and N₂ broadening is the least.

SUMMARY

Oxygen and nitrogen pressure-broadening parameters for transitions of NO₂, CF₂Cl₂, HDO and HOOH have been observed in the region near 230 GHz. These results are compared with our recent more extensive measurements on HNO₃. Since all of these measurements were made in the same frequency region, all involved states within the thermally populated rotational manifold, and all data were obtained with the same experimental techniques, they provide an unusual opportunity

for the intercomparison of pressure-broadening studies on different species. For the N₂ parameters, a systematic trend with the dipole moment of the spectroscopically active gas was found, presumably due to the dominance of the dipole-quadrupole interaction. However, for O₂ broadening, it was found that the parameters were more closely related to the size of the spectroscopically active gas. It would appear that in the case of O₂ broadening, the small size of the quadrupole moment of O₂ causes the higher order interactions which are important at shorter range to be dominant.

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