

RECENT ADVANCES IN PRESSURE BROADENING: EXPERIMENT AND THEORY^{*,**}

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ABSTRACT

Recent measurements of pressure broadened linewidths at both ambient and cryogenic temperatures are presented. For simple systems, such as CO broadened by He, accurate molecular scattering theory calculations give quantitative agreement. Results for more complex systems, which are not yet amenable to accurate calculations, are discussed in the context of Anderson-like theories; these suggest that a short-range cutoff procedure based on the infinite order sudden scattering approximation might prove useful.

INTRODUCTION

The venerable field of pressure broadening has long provided information that is both of practical importance for technological applications and of fundamental interest for understanding molecular interactions and dynamics. Practical applications include the transmission of radiation through planetary atmospheres, especially greenhouse effects, and a host of spectroscopically based remote sensing applications including observations of upper atmospheric chemistry and temperature; analyses of pressure, temperature, and composition in the atmospheres of the other planets; and temperature and pressure probes in flames and combustion engines. Pressure broadening also provides fundamental information about molecular collisional excitation rates and intermolecular forces. Now seems like an appropriate time to address this subject, with an emphasis on the experimental and theoretical opportunities and challenges presented by the wide temperature range both of the current applications and available laboratory data.

In microwave and infrared spectra, pressure broadening is dominated by

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collisional excitation among the many thermally populated molecular rotational levels. There are typically very many open collision channels, with fast transition rates and contributions to these rates from many levels. The connection between the macroscopic phenomena and the microscopic processes, however, is complex enough that a proper understanding has been hampered; it is difficult to infer collisional excitation rates or intermolecular forces from line width data, and, on the other hand, it is difficult to calculate accurate broadening parameters from first principles. This complicates both the experimental and the theoretical problems, as well as the inversion of experimental results to obtain molecular information.

In this paper we review experimental techniques that have been used, with particular attention paid to a new technique that allows pressure broadening measurements to be made at very low temperatures. Under these conditions, only a few molecular rotational levels are energetically accessible, simplifying the connection between experiment and theory and making accurate, *ab initio* calculations possible. Next, we will review the results of several ambient temperature experiments for guidance about appropriate approaches in this theoretically more complex regime. These experimental results include observations of pressure broadening dominated by long range dipole-dipole interactions and also measurements of pressure broadening due to collisions with N_2 , O_2 , and He. We are particularly interested in theoretical methods that properly invest their effort on those parts of the problem that make the largest contributions, and in techniques that allow the information obtained from a limited number of experimental measurements to be incorporated in the calculation of the pressure broadening parameters for the entire rotational manifold.

EXPERIMENTAL

Pressure broadening measurements require a combination of a spectroscopic method of sufficient resolution and measurement accuracy to characterize the line profile and a sample handling system which provides an environment in which the temperature and pressure of the sample are well characterized. For completeness, we will briefly discuss the methods used for the work discussed in this paper. Since most of it is a relatively straightforward implementation of techniques previously described, this is done briefly. However, the technique which we have developed to extend pressure broadening measurements to very low temperatures and some of the characteristics of spectroscopy in this temperature regime are described in more detail.

The techniques which we have developed for the millimeter and submillimeter spectral region have been previously described [1,2]. Briefly, klystrons in the 35–60 GHz region are phase locked to a frequency synthesizer and their power matched onto harmonic generators [3]. The output of these harmonic generators is propagated quasi-optically through the pressure broadening cell

and detected with a 1.5 K InSb detector. The frequency of the system is swept by the microprocessor controlled synthesizer at a repetition rate between 20 and 100 Hz and the output of the detector digitized synchronously with this sweep. The bandwidth of the detector and electronics are adequate to reproduce the true lineshape. For ambient pressure broadening measurements, the spectroscopic cell is typically a simple glass pipe, 10 cm in diameter and 1 m long. Pressure is measured with an MKS capacitance manometer [4].

In previous papers we have shown that a simple collisional cooling technique allows macroscopic samples of spectroscopically active gas to be cooled to very low temperatures (≤ 4 K) and studied under essentially equilibrium conditions [5,6]. This technique is complementary to the well-developed method of free expansion jets and shares many of its attributes; however, its geometry and molecular densities are more suitable for many experiments – especially pressure broadening. Because with this method the collisions take place essentially in thermal equilibrium and because the temperature can be easily measured and varied, the calculation of pressure broadening parameters from experimental data is greatly simplified.

Figure 1 shows a cross section of the experiment. Within the vacuum chamber is a shield at 77 K, a shield maintained at ~ 25 K by a cryocooler, and a three-liter liquid helium container. The pressure broadening cell is located inside the liquid helium reservoir. Figure 2 shows the cell in more detail. The temperature is varied by pumping on the helium bath through a vacuum regulator valve, which accurately controls the pressure of the bath, and is measured directly with a germanium thermometer. The cell is first filled with a static pressure of helium which rapidly equilibrates with the wall temperature. Warm, spectroscopically active gas is then injected into the cell via a vacuum insulated tube. The warm gas cools very rapidly as it collides with the cold

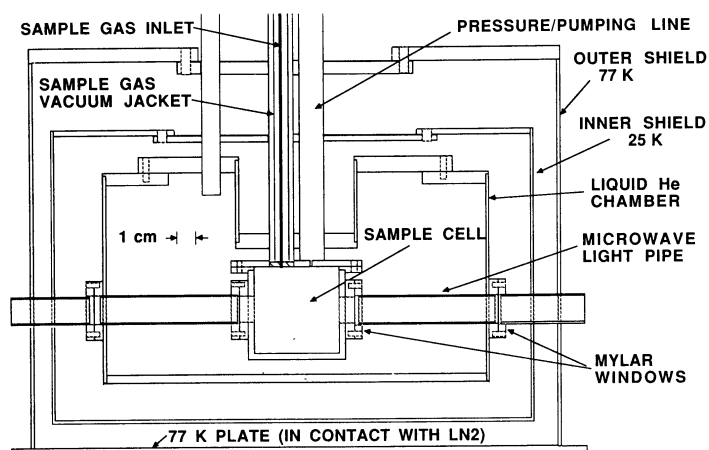


Fig. 1. Very low temperature spectroscopy system.

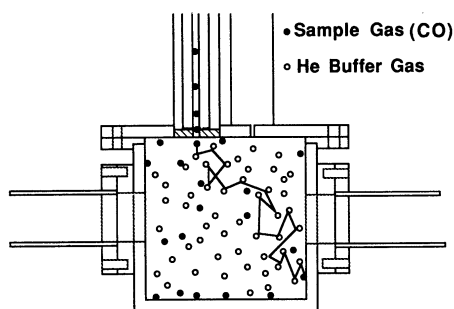


Fig. 2. Collisionally cooled sample cell.

buffer gas, requiring many fewer than 100 collisions to reach essentially thermal equilibrium. On the other hand, at 10 mtorr, about 10 000 collisions are required before the gas reaches the walls and is frozen out. The very large absorption coefficients, which are characteristic of very low temperature spectroscopy, allow the concentration of the spectroscopic gas to be so small that it has negligible influence on the temperature of the buffer gas, making this a very general experimental technique.

It is worth investigating the strengths and characteristics of molecular absorptions as a function of temperature. In the mm/submm spectral region, experiments are typically carried out at or near the doppler broadened limit; thus, linewidths at 4 K are typically an order of magnitude narrower and correspondingly greater resolution and measurement accuracy are possible. In addition, several temperature dependent factors strongly affect molecular absorption coefficients, which are given by

$$\alpha = [8\pi^2\nu/3ch] \cdot | \langle m | \mu | n \rangle |^2 \cdot [N / \Delta\nu] \cdot [1 - e^{-h\nu/kT}] \cdot [1/Q_r]$$

where $\langle m | \mu | n \rangle$ is the transition moment, N the number density of the absorber, $\Delta\nu$ the linewidth, and Q_r the rotational partition function. Although the behavior of $N / \Delta\nu$ depends upon the details of the pressure broadening, simple theory gives $N / \Delta\nu \propto T^{-1/2}$. For the molecules of interest, Q_r is typically 100–1000 at 300 K, but it approaches unity in the low temperature limit. The term $[1 - e^{-h\nu/kT}]$, which represents the difference between induced absorption and emission, is $\sim 1/100$ for transitions near 100 GHz at 300 K, but again approaches unity in the limit $h\nu \gg kT$. Together, these factors represent a four or five order of magnitude increase in the absorption coefficient. The dilution ratio of the spectroscopic gas in the cooling gas will reduce this gain for stable species, but the reduced pressure broadening parameters associated with helium will add to the overall system gains. To give two typical examples, the absorption coefficients for the $J=0-1$ transitions of gas phase CO and HCN at 4 K are 25 cm^{-1} and $10\,000 \text{ cm}^{-1}$, respectively. This expectation has been

confirmed in our work on CO and CH₃F. Molecules with very small dilution ratios ($< 1/1000$) are easily observable on an oscilloscope screen in real time. With modest flow rates, absorptions that approach 100 % of the incident power are observable for CH₃F.

RESULTS AND DISCUSSION

Because pressure broadening parameters are needed for many spectral lines and often for a range of temperatures, it would be extremely useful to have a theoretical framework which would facilitate interpolation and extrapolation of measured values (as a function of both temperature and quantum number). Ideally this framework would accept input from *ab initio* predictions and also clarify the relation with state-to-state collision rates. In principle, at least within the standard impact approximation, this can be done by relating pressure broadening parameters to the intermolecular potential via collision dynamics. The difficulties are well known: the intermolecular potential is a complicated, multidimensional function which is difficult to obtain, and the molecular scattering problem is quite arduous. Therefore the theoretical framework that is used in almost all current studies dates to the early work of Anderson [7] who introduced a number of simplifying approximations: only the long-range (multiple) part of the intermolecular potential is considered and collision dynamics are treated with time-dependent, second-order perturbation theory based on straight-line trajectories. A large body of work has made incremental improvements within this general framework, but these still suffer from unrealistic treatment of hard (short-range) collisions and use of low-order perturbation theory.

The present work focuses on two points. First, for some simple but non-trivial systems it is currently possible to obtain the intermolecular potential and solve the collision problem by purely *ab initio* methods. Second, a molecular scattering approximation which has proved to be very useful in the last decade for describing collisions of short-range systems might be a good way of handling the "cutoff" problem, which has been the bane of Anderson-like theories.

The CO-He system provides an excellent example of the current abilities of *ab initio* calculations. Owing to the interest of radio astronomers in low temperature state-to-state excitation rates [8], an *ab initio* (SCF-CI) intermolecular potential was computed by Thomas et al. [9] and accurate scattering calculations using this potential were done. These agreed well with earlier microwave pressure broadening measurements from 77 to 300 K [10] and also with infrared measurements at room temperature [11]. It was noted in ref. 10 that low temperature experimental data, which depend on only a few state-to-state rates rather than a sum over many, would provide a more stringent test of the accuracy of the potential. However, until recently there had been no

experimental test of these results in the very low temperature regime of direct interest to astronomy. Figure 3 shows results which were recently obtained with the collisional cooling technique discussed above [6]. This figure shows the excellent agreement of the ab initio calculations [12] with these experimental results. At the very lowest temperatures measured to date (~ 1.7 K) it appears that the theory may be high by about 20%. This discrepancy, in fact, accords with the expectation that the ab initio potential has too deep a well owing to basis set superposition errors (BSSE) [13]. The effect of reducing the attractive well by half is also shown in Fig. 3 [14]. Since BSSE errors for similar systems suggest that the error is more likely to be 20% of the well depth rather than half, this would account for the apparent discrepancy. Measurements at still lower temperatures should help clarify this. This increased sensitivity of the pressure broadening parameter to the details of the potential with decreasing temperature was also shown in an earlier study in which it was noted that all reasonable choices of potential yielded essentially the same pressure broadening parameters at high temperature, but that significant differences occurred at low temperature [10].

The cryogenic CO-He results were somewhat surprising. Pressure broadening cross sections are approximately related to the total inelastic collision rate, and it was initially assumed that these rates would decrease strongly as the available collision energy was lowered to values near or below the rotational energy spacings. The experimental results, however, indicated that the pressure broadening cross section remained constant and perhaps increased somewhat at the lowest energies. The accurate scattering calculations discussed above clearly indicated that resonance structure at low energies, owing to the attractive well, is responsible for this behavior. In fact, interactions with He have atypically small potential wells, and, in general, we expect pressure broadening cross sections for other systems to increase strongly at low temperatures. It will be quite interesting to test this conjecture experimentally.

More recently we have begun an experimental study of CH₃F-He collisions

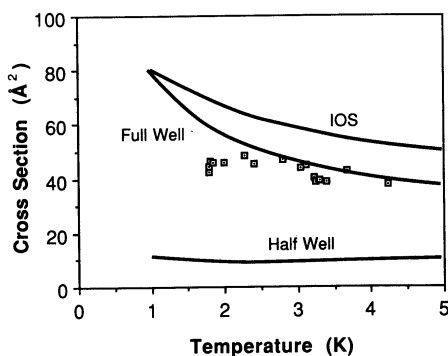


Fig. 3. Cross section for CO-He pressure broadening below 5 K.

at very low temperature [15]. This system should have a slightly deeper well than CO-He as CH₃F has a larger dipole and polarizability. Preliminary results at 1.9 K show a pressure broadening parameter of 47 MHz/torr for both the $K=0$ and $K=1$ components of the $J=1-2$ transition. This result corresponds to about the same pressure broadening cross section as at room temperature. However, measurements at 3.9 K give 48 MHz/torr for the $K=0$ component and 43 MHz/torr for the $K=1$ component. These values at 1.9 K represent about a 30% drop in the cross section between 3.9 K and 1.9 K.

Another system which illustrates the power of current ab initio methods is H₂CO-He. Anderson theory calculations [16] (see Table 1) correctly indicated little variation from line to line (i.e., they were all dominated by the short-range cutoff), but they were a factor of two too small; by comparison, accurate scattering calculations on a theoretical (SCF-CI) potential with no adjustable parameters were all within experimental error [17]. See Table 1.

Thus, we conclude for relatively simple collision systems (especially at low temperature) that, although sometimes computationally arduous, theoretical methods exist which can give good results. It will be interesting to consider future comparisons between results of these theoretical techniques and experimental data in the very low temperature regime. This regime contains many of the interesting effects, provides the most stringent tests of intermolecular potentials, and makes possible the most exact calculations, especially for the more complicated collisional systems.

Next we would like to consider the calculation of pressure broadening parameters in circumstances when the use of the most exact ab initio methods is inappropriate. This includes systems with complex intermolecular potentials

TABLE 1

Broadening parameters of H₂CO at 300 K (MHz/torr)^a

Transition	Self broadening				Helium		
	Exper.	AT1	AT2	AT3	Exper.	AT	CS ^b
1 ₀₁ -2 ₀₂	22.6(7)	29.1	26.0	22.6	2.38(22)	1.43	2.2
1 ₁₁ -2 ₁₂	28.9(6)	33.0	29.1	27.2	2.59(25)	1.56	2.4
1 ₁₀ -2 ₁₁	28.6(6)	33.0	28.9	27.2	2.50(22)	1.56	2.4
2 ₀₂ -3 ₀₃	20.8(4)	26.2	23.1	20.9	2.36(22)	1.41	2.1
2 ₁₂ -3 ₁₃	24.3(5)	28.8	25.7	23.6	2.44(22)	1.50	2.3
2 ₁₁ -3 ₁₂	24.5(6)	28.8	25.7	23.6	2.48(22)	1.50	2.3
2 ₂₁ -3 ₂₂	30.2(6)	35.4	31.2	30.0	2.55(22)	1.54	
2 ₂₀ -3 ₂₁	30.7(8)	35.4	31.2	30.0	2.56(22)	1.54	
3 ₁₃ -4 ₁₄	23.0(7)	27.8	24.6	22.7	2.38(25)	1.46	
3 ₁₂ -4 ₁₃	23.1(7)	28.5	25.2	23.1	2.40(25)	1.46	

^aExperimental results and Anderson theory calculations from ref. 16.

^bCoupled States calculations from ref. 17.

and many thermally populated levels, where the computational expense rapidly becomes prohibitive. For example, calculations involving molecular perturbers currently seem beyond reach. Furthermore, in systems dominated by long-range interactions simpler alternative methods should be considered.

Anderson theory works best for systems dominated by long-range forces (e.g., strong dipole-dipole interactions) and often gives good predictions for both the magnitude of the broadening and its variation with quantum number. Yet even for the strongly dipolar H_2CO self-broadening, different choices of the (arbitrary) cutoff procedures yield results that vary significantly as shown in Table 1. Inspection shows that the agreement between experiment and the Anderson-like calculations can vary from excellent agreement to a systematic difference of about 30%, depending upon the cutoff procedure adopted.

For dipole-quadrupole systems, which have the next longest range interactions, Anderson-like theories [18] begin to have more severe problems as demonstrated by recent results for nitric acid [4]. Figure 4 shows that for $\text{HNO}_3\text{-N}_2$ Anderson-like predictions give some estimate of the line to line variation but are systematically too large. However, because of the very small quadrupole moment of O_2 , the $\text{HNO}_3\text{-O}_2$ interaction is of very much shorter range and, as shown in Fig. 5, neither the magnitude nor the variation with line is well reproduced by the theory.

An approximation which has found much use in recent molecular scattering calculations is the infinite order sudden (IOS) method [19]. It can be derived from the full quantum close coupling scattering formalism by (1) approximating the collisional angular momentum operator, ignoring some Coriolis couplings, to decouple different partial waves, and (2) ignoring rotational energy spacings compared with the collision kinetic energy. This allows significant reductions in the computation of collision cross sections. Perhaps more important, however, it indicates relationships between various state-to-state and relaxation cross sections. In particular within the IOS approximation the en-

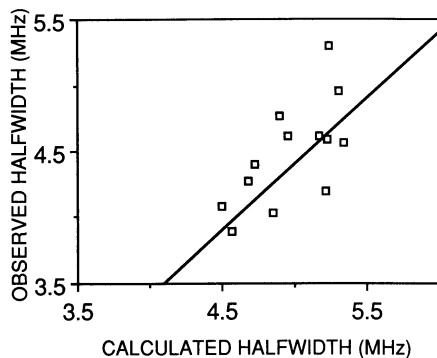


Fig. 4. A comparison of experimental and theoretical pressure broadening coefficients for $\text{HNO}_3\text{-N}_2$.

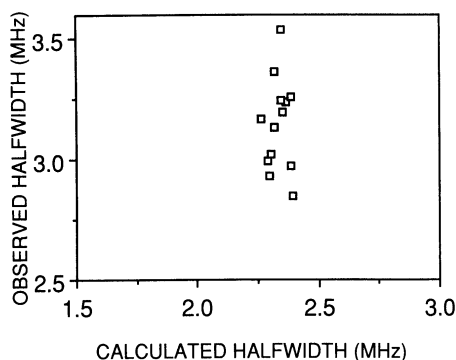


Fig. 5. A comparison of experimental and theoretical pressure broadening coefficients for $\text{HNO}_3\text{-O}_2$.

tire matrix of state-to-state rates, as well as pressure broadening parameters and other relaxation rates, can be computed from knowledge of the rates out of the lowest level. This is strictly true for linear and symmetric top rigid rotors in collisions with atoms; the relations are similar, but a little more involved, for more complex systems.

The IOS approximation is not expected to be accurate at energies where only a few levels are accessible or for systems in which long-range forces are important. Nonetheless, it often does remarkably well. IOS values for CO-He at cryogenic temperatures are compared in Fig. 3 with the accurate close-coupling results; they are seen to be reasonable even at very low temperatures. However, caution should be used in generalizing this result. It is likely that approximations in the IOS method lead to an underestimate of the contributions of the resonances and an overestimate of the contributions of inelastic collisions at very low temperatures which effectively cancel in the case of CO-He .

Since the IOS approximation is expected to be accurate for short-range collisions and since it leads to fairly tractable calculations (given an intermolecular potential) and to pressure broadening cross sections which depend on only a few parameters (i.e., the $0 \rightarrow j$ rates), it might provide a useful method to handle the "cutoff" problem in Anderson-like calculations. Expressed differently, it might be useful to develop a hybrid method which uses the IOS approximation for short-range (small impact parameter) collisions and Anderson-like theory for long-range collisions. This might be most easily implemented in a quantum framework where the integration over impact parameter is replaced by a sum over partial waves. The quantum version of Anderson theory is essentially the Born approximation [20]; the distorted wave Born approximation corresponds to use of curved trajectories. The utility of this mixed approach will depend on the existence of a range of partial waves for which the

TABLE 2

Broadening parameters of selected molecules (MHz/torr)

Species ^a	μ^b	Frequency	$\gamma(\text{N}_2)^c$	$\gamma(\text{N}_2)/\mu$	$\gamma(\text{O}_2)^c$	$[\gamma(\text{N}_2) - \gamma(\text{O}_2)]/\mu$
NO ₂	0.32	231229.96	3.20(3)	10.0	2.97(3)	0.72(15)
		247355.37	3.10(5)	9.7	2.64(4)	1.40(22)
CF ₂ Cl ₂	0.51	239247.21	4.08(7)	8.0	3.50(9)	1.13(23)
		231979.45	3.99(27)	7.8	3.73(22)	0.51(69)
HDO	1.84	241561.55	4.31(9)	2.3	2.33(3)	1.07(5)
		225896.72	4.28(12)	2.3	2.22(8)	1.12(8)
HOOH	1.58	223100.95	4.87(12)	3.1	2.85(12)	1.28(11)
		229785.93	4.22(6)	2.7	2.79(9)	0.91(7)
HNO ₃	2.17	231777.61	4.96(9)	2.3	3.24(4)	0.79(5)
		231627.28	4.57(9)	2.1	2.97(6)	0.73(5)

^aSee ref. 20 for complete state labels and references.^bDebye.^cMHz/torr (uncertainties are one standard deviation from the fit).

two methods give similar results, i.e., the final result must be insensitive to the partial wave where the switch from short- to long-range is made.

This theoretical framework would clearly meet our stated goal of allowing for ab initio input; given a potential energy surface it provides a clear computational framework, which can be tested against more accurate calculations. It also meets our goal of providing a relation to state-to-state cross sections. For most systems, while the multipole moments are known and the long-range component could be calculated, the short-range potential is not well known and the IOS part would be left as parameters to be fit to experimental data. For systems with reasonably long-range forces, this method would simply give a somewhat more sophisticated treatment of the short-range cutoff within an essentially Anderson-like theory; but, it would allow for a smooth transition to systems with weak long-range forces.

Recent measurements of several medium sized species broadened by N₂ and O₂ will help illustrate these ideas [21]. First, consider broadening due to molecular oxygen, which has only a very small electric quadrupole moment. The physical significance is perhaps best understood in the context of Anderson-like calculations which, as shown in Fig. 5, predict essentially the same pressure broadening coefficient for all transitions of HNO₃, a coefficient that is simply related to the geometrical size corresponding to the chosen cutoff impact parameter. Thus we should expect an ordering related to the physical size

of the molecule for O₂ broadening. Although the physical size of a molecule is a fairly ambiguous quantity, the ordering for the five species in Table 2 is clear: CF₂Cl₂ is largest, followed in order by HNO₃, NO₂, HOOH, and HDO. Only the relative size of NO₂ and HOOH is questionable, and their measured pressure broadening parameters overlap. Next consider nitrogen broadening. Nitrogen has a fairly large quadrupole moment and it is expected that the dipole-quadrupole interaction 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. However, as shown in column five of Table 2, the broadening coefficients do not really correlate with the dipole moment. This is because the short-range (geometric) parts, which are not influenced by the dipole moment, make a substantial contribution. Since N₂ and O₂ have about the same "size", to a first approximation we might take the O₂ broadening as a measure of the short-range contribution to each transition. The difference between the N₂ and O₂ broadening then represents the long-range part, and this does, in fact, correlate extremely well with the dipole moments of the observed species, as shown in the last column of Table 2. The variation in this last column is little more than the shown 1 σ propagated errors (which are almost surely optimistic measures of the uncertainties) in the experimental measurements. It is noteworthy in this exercise that the short-range contributions represent more than half of the N₂ broadening in these systems, emphasizing the need for a more careful treatment than is usual in Anderson-like theories.

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