

Line-shape analysis of speed-dependent collisional width inhomogeneities in CO broadened by Xe, N₂, and He

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We present high-resolution (10^{-4} cm⁻¹) and high signal-to-noise ratio (2000) infrared line shapes of CO perturbed by Xe, N₂, and He in the intermediate regime from Doppler to collision broadening. It is found that the pressure-broadened component of the line shape cannot be fit by a Lorentzian line shape, and the largest deviation occurs in the core of the line. A speed-dependent collisional width is required to fit the spectra broadened by the larger Xe perturber, for which the collision rate of a CO molecule is determined primarily by its own speed. A line-shape model based on the theory of Robert *et al.* [Phys. Rev. A **47**, R771 (1993)], folding in the effect of Dicke narrowing, is derived. The speed-dependent mechanism also appears to explain the measurements made by Duggan *et al.* [Phys. Rev. A **48**, 2077 (1993)] in a dilute CO:N₂ mixture, in which a non-Lorentzian collision broadening scheme was suggested.

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I. INTRODUCTION

Retrieval algorithms for satellite and ground-based infrared atmospheric sounders frequently depend upon precise line-shape information. Most of this work has been done using the Voigt model to describe the behavior in the intermediate region from pure Doppler to collision broadening. It has been noted that this is inadequate to describe dense regions of the spectrum in certain atmospheric applications, for example, in the Q branch, where line mixing has proven to be important [3]. Line mixing also appear to explain the nature of the complex water-vapor continuum [4]. For well-resolved lines, the model will also fail if the molecules are not free streaming over dimensions larger than the wavelength of light. Then the ordinary Doppler effect associated with the Voigt profile is to be replaced by a Dicke narrowed line [5] whose width is inversely proportional to density. This contribution of the translational motion to the spectral width has been extensively explored since the early molecular studies of Cooper *et al.* [6]. A third way in which the Voigt profile may fail is if the correlation function for the internal degrees does not decay exponentially with time. In a recent paper [2] we speculated that this might prove to be the reason for some anomalous line shapes in CO:N₂ mixtures. In frequency space this means that the underlying spectral profile associated with broadening and shifting is not Lorentzian.

To allow for Dicke narrowing of isolated lines, a number of authors have used a model in which the effects of collisions on the translational and on the internal degrees of freedom are assumed to be statistically uncorrelated. In correlation function language, the time correlation function for the line shape $C(t)$ is the product of a time correlation function $\chi(k, t)$, describing the translational contribution where k is the wave vector, and a part $\Phi(t)$, associated with the relaxation of the internal degrees of freedom. For $\chi(k, t)$, two common models are used,

requiring only the mass diffusion coefficient D_m as an added spectral parameter. These are the soft-collision model of Galatry [7], which assumes that individual collisions have a very small effect on the molecular velocity, and the hard-collision model of Nelkin and Ghatak [8], which considers individual collisions to scatter the molecule into a thermal distribution of velocities. For $\Phi(t)$ the standard speed-independent form $\Phi_{SI}(t) = \exp[-\Gamma t]$ leads to a Lorentzian profile with a width given by the real part of Γ and a shift given by the imaginary part. A common, but empirical, method of analysis is to fit for an "optical" diffusion coefficient D_{opt} , based on measurements of the translational, or a Doppler contribution to the line shape and compare the results to D_m . We use the term optical diffusion loosely, because in our previous paper [2] we argued that the physics of Dicke narrowing should be well described by D_m alone. In that paper we also studied the density dependence of the optical diffusion coefficient for CO perturbed by N₂. We found that the line shapes agreed with the hard- or soft-collision model at low density, where Doppler broadening is dominant, insofar as the value of D_{opt} agreed with D_m , and it scaled inversely with pressure, as expected. However, at higher density, where pressure broadening becomes the dominant line-shape mechanism, D_{opt} was found to diverge from D_m . At the highest measured pressure of 20 kPA, for which the translational contribution only accounts for 20% of the linewidth, D_{opt} was found to be 3 times smaller than D_m . Varghese and Hanson [9] also found that they required an optical diffusion coefficient much smaller than D_m to explain their measurements of HCN. The experimental line shapes were therefore found to be even narrower than the Dicke narrowed line shape computed from D_m would predict. Abandoning the approach of ascribing the difficulty of fitting the spectral profile to translational motion, we then showed that a departure of the order of a few percent from an exponential decay for $\Phi(t)$ would explain the observed line

shape. In this paper we propose a speed-dependent collisional width inhomogeneity as the exact mechanism associated with this nonexponential or non-Lorentzian behavior. We will then demonstrate that correcting the pressure-broadening model eliminates the discrepancy between the D_{opt} and D_m . Therefore the concept of a distinct optical diffusion coefficient is not required. Our model will be validated by comparing with observed line shapes for CO diluted in He, N₂, and Xe.

II. THEORY

A. General speed-dependent collision broadening

A speed-dependent collision-broadening mechanism was first observed in the atomic emission spectra of Ca by McCartan and Lwin [10] and was studied more precisely by Shannon *et al.* [11]. Recently Farrow *et al.* [12] observed asymmetry in stimulated Raman line shapes of molecular H₂ at high temperature (1000 K) and at densities well above the Doppler regime, particularly for the comparatively heavy perturber Ar. They attributed this behavior to an inhomogeneous shift mechanism which separates the line shape into contributions from different speed classes. With reasonable values of the shift cross section as a function of speed and the addition of a spectral narrowing effect due to speed changing collisions

analogous to that used to explain Dicke narrowing, they were able to explain this asymmetry. For this molecular system they determined that a reasonable approximation in the analysis is that only collisional line shifting, and not the width, is speed dependent.

The model of Farrow *et al.* was generalized by Robert *et al.* [1] in a manner analogous to that used by Rautian and Sobel'man [13], who considered the effect of velocity-altering collisions in the process of Dicke narrowing. In the model of Robert *et al.*, collision types are broken up into three phenomenological types—speed changing (SC), dephasing (D), and speed changing and dephasing (SCD)—and the effects of Doppler broadening are neglected. Although this model fails to describe the physics for the CO system studied here, it yields an insightful phenomenological view in terms of the above collision types and helps to relate this work to other speed-dependent studies. We will discuss the most general pressure-broadening line shape and then consider simplifications applicable to the present experiment. The line shape of Robert *et al.* [1] was derived from the Boltzmann equation for the radiating dipole, making the hard-collision approximation that the collision frequencies are independent of speed. The expression given by Robert *et al.* [1] for a speed-dependent $\Phi(t)$, in frequency space, is

$$\Phi_{\text{SD}}(\omega) = \pi^{-1} \text{Re} \left[\frac{\langle f(v, \omega) \rangle}{1 - \nu^{\text{SC}} \langle f(v, \omega) \rangle - \langle [\nu^{\text{SCD}} - \gamma^{\text{SCD}}(v) - i\delta^{\text{SCD}}(v)] [f(v, \omega)] \rangle} \right], \quad (1)$$

where $\langle \rangle$ means an average over the radiator speed and $\langle f(v, \omega) \rangle = \langle [i\omega + i\delta^{\text{D}}(v) + \nu^{\text{SCD}} + \nu^{\text{SC}} + \gamma^{\text{D}}(v)]^{-1} \rangle$, (2)

where ν , γ , and δ are the collision frequency, broadening, and shifting, respectively, for the given collision types and the broadening and shifting are assumed to be speed dependent. Note that the broadening and shifting parameters γ^{D} , γ^{SCD} , δ^{D} , and δ^{SCD} depend upon the speed of the optically active molecule even after averaging over the speed of the perturber. The speed dependence is particularly important for a light optically active molecule colliding with a heavy perturber. If the speed dependence of the various components is neglected, a homogeneous Lorentzian profile with a width $\gamma^{\text{D}} + \gamma^{\text{SCD}}$ and a shift, $\delta^{\text{D}} + \delta^{\text{SCD}}$ is recovered. The denominator of (1) expresses the coherent interference of wave packets from different speed classes before and after collisions and overall has the effect of narrowing the collision-broadened line shape. If the denominator is set to unity, the speed classes are separate and we obtain a classical speed-dependent inhomogeneous line shape as in the theory of Berman [14].

Applying this theory to the experimental results of Farrow *et al.* [12], Robert *et al.* have shown that the inclusion of SCD collisions improves the fit between theory and experiment. Note that the line shifting is comparable in size to the pressure broadening in the case of the Ra-

man H₂:Ar spectra and it is the dominant speed-dependent consideration. A purely inhomogeneous model [Eq. (1) with the denominator set to unity] predicts larger asymmetry than experimentally observed. Both SC and SCD collision types reduce the asymmetry by allowing the separate speed classes to interfere with each other tending to produce a more homogeneous line shape and are necessary to explain the results of Farrow *et al.* [12].

B. Approximations relevant to the CO system

We now make approximations which should be valid for CO. They differ markedly from those made for the H₂:Ar Raman spectra. The collisional dephasing rate γ^{D} (as estimated from the broadening at high density) is approximately 3 times larger than the velocity-changing rate as computed from the diffusion constant, which is necessarily larger than the speed-changing rate (ν^{SC}). By virtue of the relatively large dephasing to speed-changing ratio ($\gamma^{\text{D}}/\nu^{\text{SC}}$) only SCD and D collisions need be considered. Calculations done for the CO:He system show that collision broadening is completely dominated by rotationally inelastic transitions [15], as is true for most molecular systems of atmospheric interest. Thus the SCD collisions are completely dephasing. The interfer-

ence of the speed classes represented by the denominator of Eq. (1) cannot take place in light of the fact that speed-changing collisions are inelastic, implying that in this case the denominator is unity. However, the model of Robert *et al.* cannot rigorously produce the correct line shape in the case of hard dephasing SCD collisions. In this limit it predicts a Lorentzian line shape of an average width $\langle \gamma^{\text{SCD}}(v) \rangle$, whereas we would expect an inhomogeneous line shape due to the fact that the speed classes cannot interfere. This behavior comes from the hard-collision approximation of a speed-independent collision rate ν^{SCD} , which cannot be valid given a speed-dependent broadening $\gamma^{\text{SCD}}(v)$ for hard-dephasing collisions. We will therefore choose to express our line shape model as one which is completely inhomogeneous in speed, in contrast with what the model of Robert *et al.* would predict. A final simplification is to neglect the collisional shifting term as it is typically less than $5 \times 10^{-4} \text{ cm}^{-1}/\text{amagat}$, two orders of magnitude smaller than the collisional width of approximately $5 \times 10^{-2} \text{ cm}^{-1}/\text{amagat}$.

With these approximations, we obtain

$$\Phi_{SD}(\omega) = \pi^{-1} \text{Re} \langle [i\omega + \gamma^{\text{SCD}}(v) + \gamma^{\text{D}}(v)] \rangle, \quad (3)$$

which corresponds to a completely inhomogeneous classical model. Thus, in the time domain, speed dependence of the collisional broadening is incorporated by writing

$$\Phi_{SD}(t) = \int_0^\infty M(v) \exp[-\Gamma(v)t] dv, \quad (4)$$

where the collisional width from Eq. (3) is

$$\Gamma(v) = \gamma^{\text{SCD}}(v) + \gamma^{\text{D}}(v) \quad (5)$$

and $M(v)$ is the Maxwellian speed distribution, given by

$$M(v) = (\pi u^2)^{-3/2} \exp(-v^2/u^2) 4\pi v^2, \quad (6)$$

where u is the average active molecule speed. In the frequency domain, Eq. (4) is the sum of Lorentzians of varying width, weighted by the appropriate Maxwellian distribution. Speed dependence changes the line shape because this sum does not produce a simple Lorentzian with some average width, i.e., $\Phi_{SD}(t)$ does not decay exponentially.

C. Doppler effects

The discussion above refers to collision broadening; however, the CO data are at sufficiently low density that we must also include the Doppler effect and Dicke narrowing. To accommodate this we use a soft-collision model to express the translational motion and write the full correlation function as

$$C_{SD}(t) = \chi(k, t) \Phi_{SD}(t), \quad (7)$$

where $\chi(k, t)$ is the soft-collision correlation function with $k = 2\pi/\lambda$ and $\Phi_{SD}(t)$ represents collision broadening. For the soft-collision model

$$\chi(k, t) = \exp[(1 - z\tau - e^{-z\tau})/2z^2], \quad (8)$$

where τ is a dimensionless time defined by $\tau = t\alpha_D$, α_D

being the $1/e$ Doppler half width in rad/sec or $k(2k_B T/m)^{1/2}$. The relationship between the narrowing parameter z and the diffusion coefficient D is $z = k_B T/mD\alpha_D$. If we set z to zero, this is the free-streaming limit in which no Dicke narrowing is present and Eq. (8) becomes $\chi(k, t) = \exp(-\tau^2/4)$, which Fourier transforms to a Gaussian, as expected. Since D has an inverse pressure dependence, z is linear in pressure. Equation (7) states that there are no correlations between velocity-altering effect of collisions in Dicke narrowing and the associated collisional dephasing. This has been found to be a reasonable assumption in the D_2 -He system studied by Blackmore, Green, and Monchick [16], although the effect of correlations is unknown for the CO systems of interest.

We should note that several authors have predicted that Dicke narrowing should be suppressed for the case where velocity-changing collisions are also inelastic [13,17]. Nienhuis [17] writes the line shape as completely inhomogeneous in speed, as the Berman model [14] with the addition of a source term, which gives rise to both the speed class interference in collision broadening discussed previously and Dicke narrowing. Given that speed-changing collisions are also inelastic we have argued that this interference should not be included in collision broadening. We cannot give a valid argument why this interference should be retained for the Dicke narrowing. However, our experimental results indicate that the degree of Dicke narrowing is not reduced, but is exactly what would be expected from the mass diffusion coefficient and the soft-collision model.

In this paper we will ignore the fact that the translational correlation function is in fact speed dependent; the total correlation function should explicitly be written as

$$C_{SD}(t) = \int_0^\infty M(v) \chi(k, v, t) \exp[-\Gamma(v)t] dv. \quad (9)$$

This includes a correlation between the Doppler effect of the individual speed groups, including Dicke narrowing, and the associated collisional width. Integrating $\chi(k, v, t)$ over the Maxwellian distribution produces the total translational correlation function $\chi(k, t)$, as shown in Eq. (8). Preliminary work indicates that this correlation is important, but does not change the general speed-dependent nature of the studied line shapes. The difficulty lies in deriving an appropriate model for $\chi(k, v, t)$ including the effect of diffusion or Dicke narrowing.

From $I_{SD}(\omega)$, the Fourier transform of $C_{SD}(t)$, it is possible to recover the other models. Removing the speed dependence from Γ recovers the speed-independent profile $I_{SJ}(\omega)$. Letting the narrowing parameter z approach zero reduces $I_{SJ}(\omega)$ to the Voigt profile $I_V(\omega)$. Letting z go to zero in $I_{SD}(\omega)$ we derive an expression $\chi(k, v, t) = \text{Sinc}[v\tau/u]$, where u is the average active molecule speed, which produces a speed-dependent Voigt profile [14] when multiplied by $\Phi_{SD}(t)$. Our experiments exhibit some Dicke narrowing and our objective is to show that the spectral profiles are best explained in terms of $I_{SD}(\omega)$, with D_{opt} in agreement with the mass diffusion constant rather than $I_{SJ}(\omega)$ with a fictitious optical diffusion coefficient.

D. Molecular interactions

In order to compute $\Gamma(v)$ we use the simple model given by Berman [14], who considers collisional dephasing with the interaction between the active molecule and the perturber varying as r^{-n} and straight-line collision paths. For CO interacting with nonpolar molecules, the van der Waals and the permanent dipole-induced dipole interactions both vary as r^{-6} . In the general case the speed-dependent width is written as

$$\Gamma(v) = \gamma \int f_p(\mathbf{v}_p) |\mathbf{v} - \mathbf{v}_p|^\mu d\mathbf{v}_p \quad (10)$$

where $\mu = (n-3)/(n-1)$, n is the order of the potential \mathbf{v}_p is the perturber velocity, and $f_p(\mathbf{v}_p)$ is the perturber speed (v/u_p), is shown for r^{-6} and r^{-12} potentials in Fig. 1. It is clear from the figure that the speed-dependent inhomogeneity is significant for a light optically active molecule in a heavy perturber. We also show the speed-dependent cross section for a Lorentzian (speed-independent) model and a hard-sphere potential. In fitting data to the model we allow γ in Eq. (10) to be a free parameter of the fit. The higher speed molecules have a larger width and will contribute more to the wing of the line shape. The order n of the potential model changes the dephasing cross section with speed or alters the “softness” of the molecule. At low active molecule speeds the collision rate, or equivalently $\Gamma(v)$, is determined by the perturber speed, explaining its constancy. Even with a constant cross section, as in the hard-core potential, speed dependence is present simply because the collision rate is dependent on the active molecule speed.

E. Computation

We use the algorithm of Ouyang and Varghese [18] and perform a fast Fourier transform on the correlation function to obtain a line shape $I_{sd}(\omega)$. Numerically we divide v into 50 speed groups spaced quadratically so that we can cover most of the Maxwellian tail. The summation is much faster than performing the full integral in Eq. (6) at each time step of the correlation function.

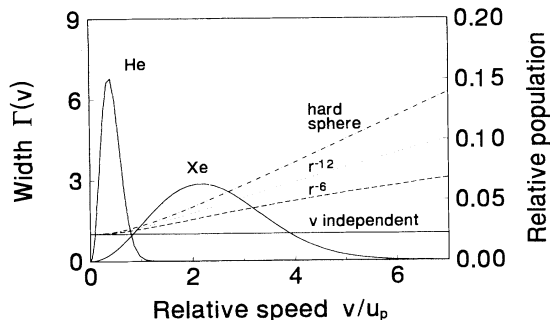


FIG. 1. Normalized collisional width for various models as a function of the speed of the radiating molecule normalized by the average perturber speed. The potential models are r^{-6} (dashed line), r^{-12} (dotted line), hard sphere (dash-dotted line), and Lorentzian speed independent (solid line). Also shown are the speed distributions of CO with He and Xe as the perturber.

III. RESULTS

Since the experimental apparatus and procedure has been described elsewhere [2], we go directly to the results. The results shown in this paper will be for the “extreme” cases of CO in Xe and He and for the intermediate mass N_2 perturber considered by Duggan *et al.* [2].

Figure 2(a) shows the absorption of the $P(7)$ CO line for a dilute mixture of CO in Xe (1:150) at 2.76 kPa and the difference between the experimental profile and a best fit for (i) the Voigt profile $I_V(\omega)$, (ii) the speed-dependent profile $I_{SD}(\omega)$ with an interaction varying as r^{-6} , and (iii) the speed-independent profile $I_{SI}(\omega)$. In cases (ii) and (iii) the diffusion constant was assumed to be the same as for N_2 :Xe mixtures [19] or $0.125 \text{ cm}^2/\text{sec}$. At this low density, speed dependence is not significant as Doppler broadening is dominant. For even lower pressures, a Gaussian would be sufficient, as the effect of collisions would be negligible. Figure 2(b) shows similar curves, but at 20 kPa. The Voigt model $I_V(\omega)$ is in error by approximately 1.5% in absorption at line center. The speed-independent profile $I_{SI}(\omega)$ demonstrates a distinct narrowing in the fit due to the inclusion of Dicke narrowing, but only the speed-dependent model with Dicke narrowing fits the profile within experimental noise limits. This indicates that both the correct Doppler and collisional broadening are required. If measurements were

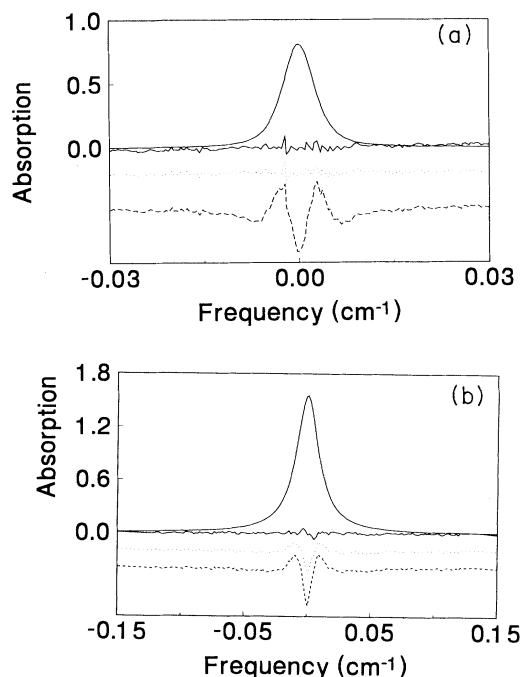


FIG. 2. (a) Sample absorption spectrum of the $P(7)$ CO line broadened by Xe (1:100 ratio) at 2.7 kPa and 298 K. From bottom to top are the residuals $[(\text{expt}) - (\text{fit})] (\times 10)$ for the Voigt model, the soft-collision translation with Lorentzian broadening, and the soft-collision translation and speed-dependent broadening. (b) Spectrum at 20 kPa and 298 K. From bottom to top are the residuals $[(\text{expt}) - (\text{fit})] (\times 20)$ for the Voigt model, the soft-collision translation with Lorentzian broadening and the soft-collision translation and speed-dependent broadening.

made at even higher density, translational effects could be ignored.

We would expect the derived value of D_{opt} to be the same as D_m if the correct model for collision broadening is used. We will use this as an indirect test of the molecular interaction models. Note that D_{opt} becomes more difficult to measure at high density because of the relatively larger contribution of collisional broadening in the line shape. Figure 3 shows the measured narrowing parameter as a function of pressure obtained by fitting to three different collision-broadening models for the CO:Xe system. All models fit the data equally well, with no structure in the residual, because D_{opt} is not fixed to D_m . The predicted narrowing parameter based on a D_m of $0.125 \text{ cm}^2/\text{sec}$ at 298 K and 1 atm is indicated by the solid line. The models used are (i) $I_{ST}(\omega)$, as used in [2], and $I_{SD}(\omega)$, as computed based on the theory of Berman [14] for (ii) r^{-6} and (iii) r^{-12} potentials. For (i) a result similar to that of the N_2 perturber is seen in which the narrowing parameter increases faster than linearly with pressure, or equivalently D_{opt} decreases below D_m with increasing pressure. In fact, at pressures beyond 15 kPa, the line shapes could not be fit by this model and are not shown. This indicates that for purely collision-broadened systems, a non-Lorentzian pressure broadening is required, as expected from the speed-dependent theory. The two other speed-dependent models are in better agreement with the data than the previous one because they can fit the higher-density data. Clearly the negative narrowing parameters associated with the higher density r^{-12} model cannot be associated with a corresponding physically meaningful diffusion coefficient. The r^{-6} model seems to indicate the closest correspondence with the physical diffusion coefficient, although even it does not agree within the 1σ error bounds. However, the agreement is satisfactory given the simplicity of the model for the speed-dependent widths.

In Fig. 4 we show the N_2 broadened data of Duggan *et al.* [2], as fit by $I_{ST}(\omega)$, and the r^{-6} and the r^{-12} speed-dependent model $I_{SD}(\omega)$ for the $P(7)$ and $R(18)$

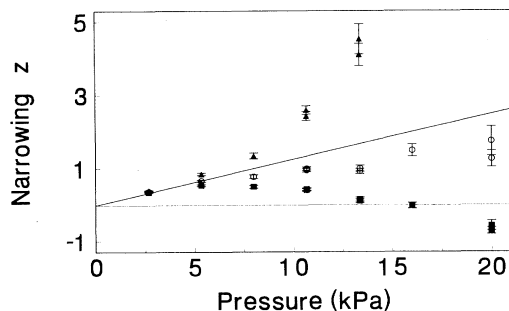


FIG. 3. Narrowing parameter z as a function of pressure for the CO:Xe data where the solid line indicates the expected narrowing based on the mass diffusion coefficient D_m . The collisional broadening has three forms: the triangles represent the Lorentzian model, the hollow circles represent the r^{-6} speed-dependent model, and the squares represent the r^{-12} speed-dependent model.

transitions. As with Xe, the narrowing parameter exhibits the best agreement for an r^{-6} model. Since N_2 has a larger mean speed than Xe, speed dependence is not as significant and the narrowing parameters do not vary as much for the different models.

As a null test of the speed-dependent mechanism we also analyzed spectra of CO in He for the $R(6)$ and $P(7)$ lines as a function of pressure (Fig. 5). We show the experimentally measured narrowing parameter and compare to the solid line computed using the measured mass diffusion coefficient of $0.718 \text{ cm}^2/\text{sec}$ at 1 atm and 298 K [19]. We used the Lorentzian model for the collisional broadening and obtain approximate agreement with the mass diffusion calculated narrowing. Applying an r^{-6} potential model alters the narrowing values by only 5% at the highest pressures. Clearly the reduced sensitivity of this system to speed-dependent broadening is demonstrated, as expected from Fig. 1.

The correlation between Doppler and pressure broadening expected from the proper evaluation of Eq. (9) has not been included in the fitting model, which may affect the best-fit potential model. However, ignoring this effect, we can speculate why the r^{-6} potential model appears to be the best. At small impact parameters, collisions of CO with the perturber will most likely result in inelastic collisions, removing population from the active quantum states irrespective of the details of the potential model. Distant collisions coupled by long-range forces

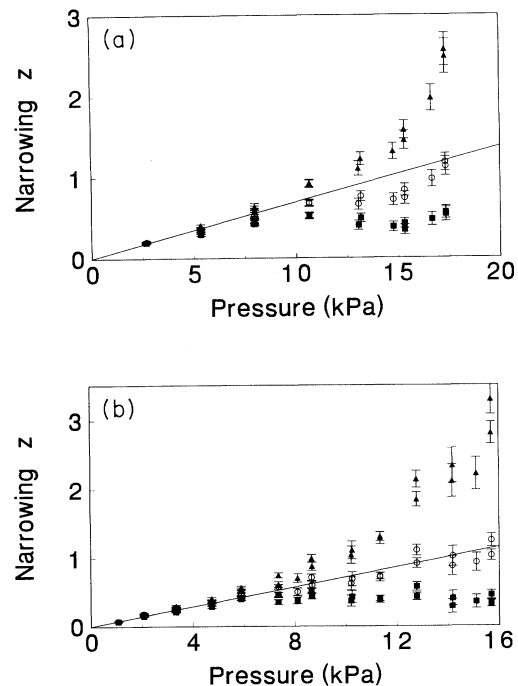


FIG. 4. Narrowing parameter z as a function of pressure for the CO: N_2 data for (a) $R(18)$ and (b) $P(7)$, where the solid line indicates the expected narrowing based on the mass diffusion coefficient D_m . The collisional broadening has three forms: the triangles represent the Lorentzian model, the hollow circles represent the r^{-6} speed-dependent model, and the squares represent the r^{-12} speed-dependent model.

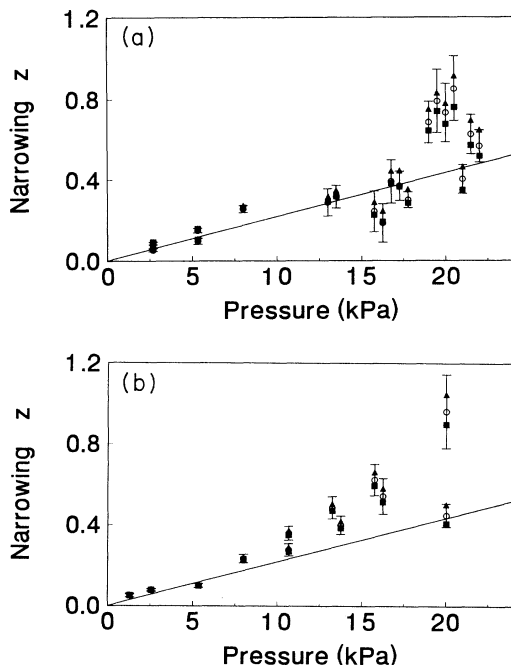


FIG. 5. Narrowing parameter z as a function of pressure in CO:He for (a) $R(6)$ and (b) $P(7)$, where the solid line indicates the expected narrowing based on the mass diffusion coefficient D_m . Collision broadening is expressed as a simple Lorentzian.

must be correctly modeled to yield collision broadening as a function of speed and these are mainly influenced by the r^{-6} intermolecular potential. However, this is an oversimplification of the complex and diverse nature of pressure broadening. Cross sections can increase or decrease as a function of collision energy and are sensitive to the particular transitions in question. Ideally, we would like to have theoretical pressure-broadening cross sections as a function of collision energy for a system sensitive to the speed-dependent mechanism, such as CO:Xe. The results presented in this paper only indicate a sensitivity of the line shape to speed-dependent broadening and to the nature of the intermolecular interaction.

In Fig. 6 we show the deviation of $\Phi_{SD}(t)$, the speed-dependent collision-broadening correlation function, from an exponential decay for the three perturber considered. Note that this is a best-fit exponential, minimizing the difference between the two models. The shape and amplitude of the deviations in N_2 are approximately the same as those predicted in Fig. 5 of Duggan *et al.* [2], based on values of the measured optical diffusion coefficients.

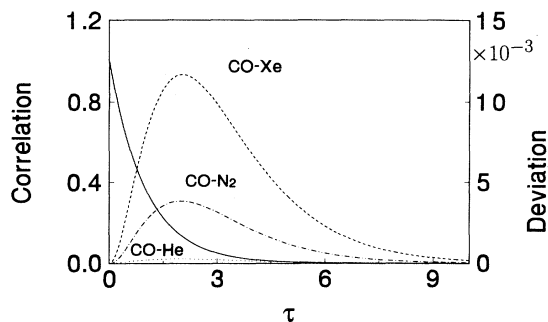


FIG. 6. Speed-dependent broadening in the time domain. Residuals [(speed-dependent)–(exponential decay)] are shown for the r^{-6} potential model for CO in He (dotted line), N_2 (dash-dotted line), and Xe (dashed line).

IV. CONCLUSION

A simple speed-dependent model applying an r^{-6} potential model in collision broadening appears to fit all our CO data within the current spectral resolution (10^{-4} cm^{-1}) and signal-to-noise ratio (2000) of our infrared spectrometer. This model requires no extra fitting parameter, such as an optical diffusion coefficient. Our interpretation of the theory of Robert *et al.* based on different collision types indicates that for cases where the collision-broadening cross section is larger than the kinetic cross section, a purely inhomogeneous collision-broadening model is appropriate. We feel that most atmospheric gases of interest would also be well characterized by this line shape and the speed-dependent effects will be greatest for light gases, such as methane. We are currently trying to develop a model that includes the correlation between Dicke narrowed Doppler broadening and speed-dependent collision broadening. The role of inelastic collisions on Dicke narrowing should also be investigated. To study the speed dependence alone, without including the added complexity of Doppler broadening and Dicke narrowing, higher-pressure data would be required. Theoretical calculations of pressure-broadening cross sections as a function of collision energy, such as those done on the CO:He system [20,21], which does not exhibit measurable speed dependence, would allow a more accurate comparison with experiment.

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