Testing the validity of the optical diffusion coefficient: Line-shape measurements of CO perturbed by N_2

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Using a high-resolution difference-frequency spectrometer, we have studied the shape of four infrared lines of CO, highly diluted in N_2. We have approached the analysis from two perspectives. In the first, the spectral profile of an isolated line is empirically represented by a variation from the "standard" model in which the mass-diffusion constant is replaced with a pressure- and line-dependent "optical" diffusion constant. In the second, we abandon the concept of an "optical" diffusion constant and replace it with a physically more tenable hypothesis that the departures from the standard model are due to a slight deviation from the usual exponential decay used to describe the collision broadening of spectral lines. This shifts the focus of the discussion from an analysis of the translational dynamics to an analysis of the dynamics of the internal degrees of freedom.

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INTRODUCTION

The absorption and emission of radiation in the infrared plays a significant role in the dynamics and energy balance of the atmosphere and is critically dependent upon line shapes. Consequently, to model the atmosphere, a knowledge of the spectral profiles of the optically active molecules is required for a number of perturbers (principally N_2) and over a wide range of temperature and subatmospheric pressures. Because of the complexity of the problem, it is not realistic to imagine calculating an entire spectrum from first principles. A computationally manageable code is required. Two problems must then be addressed. First, precise experimental profiles are required so that the underlying physics may be understood and second a model must be developed that includes all the important contributions to spectral band or line shapes. A common computational method uses a stick spectrum that has been broadened and shifted due to a combination of Doppler and collisional broadening and collisional shifts. Such a Voigt profile is known to be incorrect physically. If the molecular mean free path is small compared with the wavelength of the light being emitted or absorbed, the translational width is reduced. This is known as Dicke narrowing [1]. If the linewidths become comparable to the separation of lines, then quantum-mechanical line interference effects can significant modify the symmetry of lines and the absorption in the microwindows between lines [2]. This paper is concerned with the first of these, the proper blending together of the effects of collisions, on the internal molecular degrees of freedom and on the translational degrees of freedom. To address this problem it is convenient to work in time rather than frequency space.

A common blending model is one in which it is assumed that the effects of collisions on the two types of degrees of freedom are *statistically* uncorrelated. Consequently, the time correlation function for an isolated line consists of the product of a time correlation function, $\chi(k,t)$, for the contribution of the translational motion to the line shape [3] and a time correlation function, $\Phi(t)$, for the evolution of the optical coherence or internal degrees of freedom. One can think of two extreme cases: If the decay of $\Phi(t)$ is slow relative to the decay of $\chi(k,t)$, it forms a window in time over which the temporal evolution of $\chi(k,t)$ may be examined. Such an examination has recently been carried out by Forsman *et al.* [4] using the Raman spectrum of D_2. Small but predicted departures from the soft-collision model for $\chi(k,t)$ [5] were measured. Here we are concerned with the other extreme case, where $\chi(k,t)$ decays slowly relative to $\Phi(t)$ and provides a window in which to examine $\Phi(t)$. This is the situation often encountered in the atmosphere. We have examined four P and R lines in CO at room temperature, diluted in N_2.

APPARATUS AND TECHNIQUE

To observe what are nearly Doppler broadened lines we have built a difference-frequency spectrometer [6,7], depicted schematically in Fig. 1. Two laser beams, one from an argon-ion laser at 514.5 nm and the other from a coherent CR 699-29 dye laser tunable from 576–610 nm were mixed in a nonlinear $LiIO_3$ crystal thereby producing widely tunable infrared radiation from 3.3 to 5.5 μm. The frequency stability, governed by the input beams, was on the order of 1.5 MHz (5×10^{-5} cm^{-1}). The birefringence of the crystal is angle tuned and has a phase-matching angle of about 22° relative to the optic axis. As a result the nonlinear interaction length is reduced because the two input beams do not remain overlapped within the crystal, i.e., there is "walk off." Two 4-mm-long crystals were therefore used back to back in order to double the interaction length, thus quadrupling the IR power to approximately 4 nW. This is quite adequate for absorption spectroscopy.

The infrared beam emerging from the crystal is first collimated and then split with a wedged germanium beam

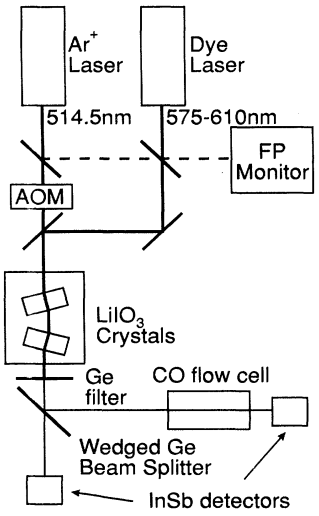

FIG. 1. The $LiIO_3$ based difference-frequency spectrometer. Relative frequencies are measured with the Fabry-Pérot (FP) monitor. The visible beams are combined with a dichroic mirror and blocked by the Ge filter after the infrared-generating $LiIO_3$ crystals. AOM denotes an acousto-optical modulator.

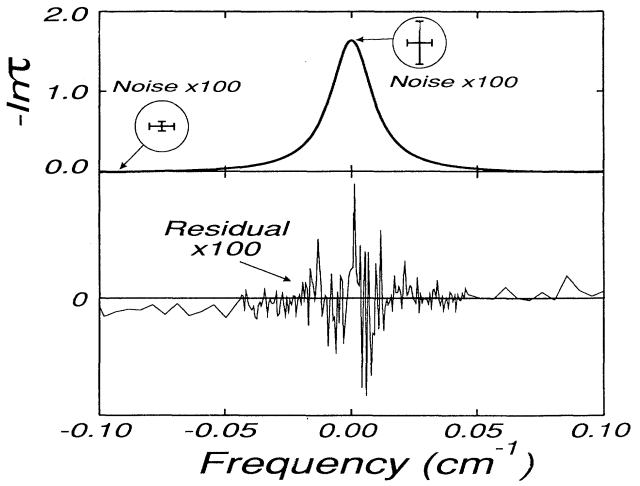

FIG. 2. Plot of minus the natural logarithm of the transmission of the $P(7)$ line of CO in N_2 at 16 kPa and of the deviation from a fitted profile vs relative frequency.

splitter. The beam going through the gas cell is focused onto the "signal" detector, the other is focused directly onto the "reference" detector. Both InSb detectors are 1 mm in diameter and liquid nitrogen cooled. The argon pump beam is modulated with an acousto-optic modulator at 80 kHz. Thus the infrared energy can be detected with a lock-in amplifier. The output is fed to an analog-to-digital converter (ADC). A monitoring confocal Fabry-Pérot interferometer determines the relative frequency shift of both the Ar^+ and the dye laser, which are also recorded via the ADC.

The 7-cm-long gas flow cell has CaF_2 windows, and the pressure is measured with a Baratron 107 capacitance manometer. Mass flow controllers set the ratio of CO to N_2, and the quantity of gas flowing through the cell. A large buffer volume prior to the cell prevents any high-frequency fluctuation of the mixture ratio resulting from the mass flow controllers. The flow prevents any possible problems associated with the adsorption of the gas by the cell walls. For this experiment the cell volume was approximately 50 cc and the flow rate was typically on the order of 20 standard cc per minute.

Typical peak signal-to-noise ratio in the wings was on the order of 2000:1 with a 4 sec integration time per spectral point. The reduction in transmitted signal, relative to the base-line electronic noise, reduced the ratio to about 500:1 near the peak in the absorption. Typically 200 spectral points were taken for each pressure with a higher density of points near line center, where the line shape varies more rapidly. The gas mixture ratio of N_2:CO was set between 40:1 and 250:1 and the total pressure from about 1 to 20 kPa. For these dilute samples the broadening is not sensitive to the mixture ratio. For an adequate signal-to-noise ratio we limited the minimum transmission at line center to about 20%. Figure 2 shows a sample spectral profile (minus the natural logarithm of the transmission versus the relative wave number). Note that the error bars have been multiplied by 100. Also shown is 100 times the deviation from a best-fit curve to be discussed below. The signal-to-noise ratio is about 1700 in the wing of the line. Such high-quality profiles have allowed us to critically examine the theory of models of IR line shapes in dilute gases.

RESULTS AND DISCUSSION

Like Forsman *et al.* [4] and many others, we have used as the reference or "standard" model for the spectral time correlation function, $C_m(t)$, a form given by $C_m(t)=\chi_{sc}(k,t)\Phi_m(t)$, where $\chi_{sc}(k,t)$ is the self-part of the intermediate scattering function for the soft-collision model [5]. Using the notation of Varghese and Hanson [8], we can write, $\chi_{sc}(k,t)=\exp[(1-z\tau-e^{-z\tau})/2z^2]$, where τ is a dimensionless time defined by $\tau=t\alpha_d$, α_d being half the $1/e$ Doppler width or $k(2k_BT/m)^{1/2}$. Here k is the wave vector or $2\pi/\lambda$ and the other symbols have their usual meaning. The rate of velocity changing collisions, $z\alpha_d$, is related to the mass-diffusion constant D by $z\alpha_d=k_BT/mD$. The narrowing parameter z is essentially the ratio of the Doppler width to the Dicke width k^2D. It is proportional to density since D is inversely proportional to density. To emphasize that $\chi_{sc}(k,t)$ is the standard model we shall write it as $\chi_{sc}(z_m,t)$, implying that the narrowing parameter is to be computed from the known mass-diffusion constant. In the same reduced variables, $\Phi_m(t)$, the standard model for the decay of the optical coherence has the usual form $\Phi_m(\tau)=\exp(-y\tau)$. Here $y\alpha_d$ is the half width at half maximum of the line (HWHM in radians per second). For low pressures, both y and z_m are proportional to the pressure [9]. In this paper we are not concerned with frequency shifts.

To fit the experimental profiles we have used an *empirical* correlation function, $C_{fit}(t)$, that has the same form as

the model correlation function, $C_m(t)$, except that the narrowing parameter was allowed to "float." This is equivalent to using a so-called "optical" diffusion constant. All of our time correlating functions were normalized to unity at $t=0$. At a given density, a fast Fourier transform was used to convert $C_{\text{fit}}(t)$ into frequency space. This was fitted to the spectral profile using the technique described in Ouyang and Varghese [10] and a value of y and z extracted. We are interested in y, the broadening parameter, z, the narrowing parameter, and how well the assumed profile fits the experimental profile.

The solid curve shown in Fig. 2 and the residue represent typical results of fitting the experimental profiles in frequency space. For a specific y and z the trial $C_{\text{fit}}(t)$ leads to a line shape that reproduces the experimental curve well within the noise. Over most of the range of densities explored, the spectral profiles are sensitive to both the value of y and z, more or less independently. Roughly speaking, in the density range explored, the part of the profile arising from the translational motion is nearly Gaussian and thus determined by the central part of the line profile. The Lorentzian wings determine the broadening. Thus y and z may be extracted from a fit to a single spectral profile at each density or pressure.

Figure 3 gives the width y of the $R(7)$ line as a function of pressure and 50 times the deviation of the measured widths from a straight line proportional to the pressure. No systematic deviations are seen. This is not surprising since at these pressures, we are well within the binary collision limit. A typical error in the widths (HWHM) is 4×10^{-5} cm^{-1}. Table I shows the broadening coefficient y^0 for all four lines, each value corresponding to the best fit of $y=y^0P$ to plots like Fig. 3. Here P is the pressure in atmospheres. The accuracy of our pressure transducer (2%) currently limits the precision of our broadening coefficients. They are in agreement with those deduced from the measurements of Nakazawa and Tanaka [11], which are also given in the table.

TABLE I. Broadening coefficients y^0(cm^{-1}/atm) for CO highly diluted in N_2 at 298 K.

	$10^{-2}y^0$	
Line	This work	Nakazawa and Tanaka [11]
$P(7)$	6.22(12)	6.37(5)
$P(17)$	5.43(10)	5.42(8)
$R(7)$	6.08(12)	6.23(11)
$R(18)$	5.21(10)	5.29(3)

We now consider the narrowing parameter. Figure 4 shows a plot of z as a function of density for the four lines observed. Also shown is a solid line, z_m, calculated from the measured value [12] of the mass-diffusion coefficient of CO in N_2 of 0.217 cm^2/sec at 298 K and 101.3 kPa. For pressures less than 5 kPa the agreement between the value of z extracted from the line shape and z_m is very good. However, above 5 kPa the "measured" value of z is greater than z_m becoming 2 to 3 times larger around 17 kPa. Furthermore the individual spectral lines do not exhibit identical behavior. From the expression given earlier for the narrowing parameter z, we could (but do not) deduce a line-dependent optical diffusion coefficient.

Using the same empirical form of analysis as that used here, Varghese and Hanson [8] measured an optical diffusion coefficient for HCN in N_2 which was approximately half of the mass-diffusion coefficient, i.e., a z two times larger than z_m. They attributed this behavior to

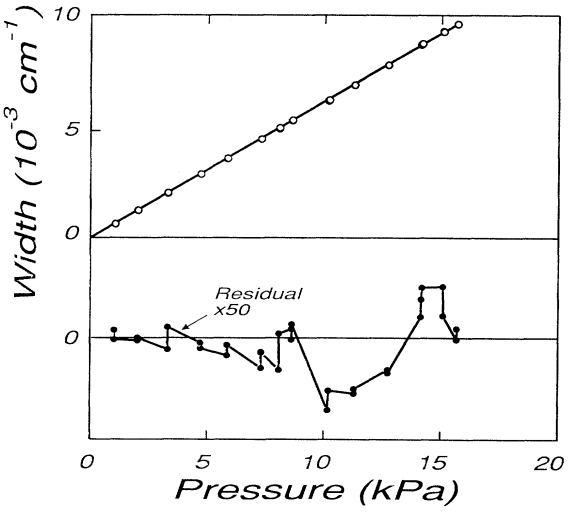

FIG. 3. Pressure broadened width (HWHM) of the $R(7)$ line vs pressure and deviation from a least-squares linear fit multiplied by 50. Note that the translational part of the width has been removed by fitting the spectra to an empirical soft-collision model.

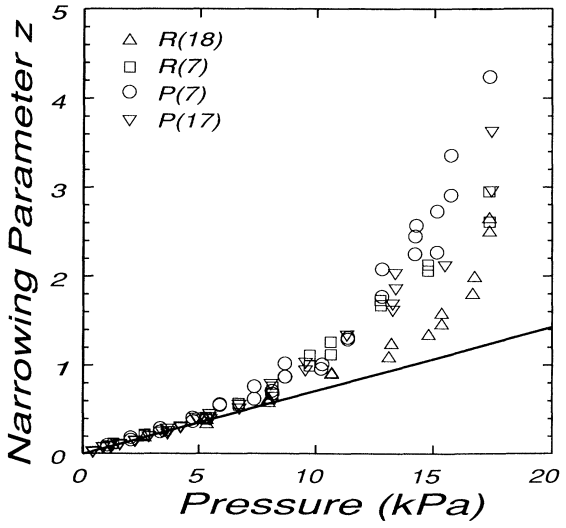

FIG. 4. Narrowing parameter derived from fitting the spectra with a floating narrowing parameter in $\chi_{sc}(k,t)$. The relative uncertainty in the individual points is approximately 10%. The straight line is the narrowing parameter, z_m, calculated from the mass-diffusion coefficient.

long-range forces which perturb the molecular velocity at high frequency relative to the kinetic collision rate. Pine [13], using a *hard-collision model* [14] for $\chi(k,t)$ to analyze the lines of HF broadened by Ne, obtained a nonlinear pressure dependence of the narrowing parameter similar to that reported here. He did not compare it to a narrowing parameter calculated from a mass-diffusion coefficient. We have also analyzed our spectra using the hard-collision model for the translational motion. Our conclusions are unaltered, which is not surprising since the two models for $\chi(k,t)$ are indistinguishable on our time scales. On the other hand, the nonlinear pressure or density dependence of the narrowing parameter is *not* seen in the recent Raman work of Forsman *et al.* [4] in D_2. Thus there are conflicting experimental results concerning the need to introduce the concept of an optical diffusion constant. Furthermore, to the best of our knowledge, none has given a plausible reason that would explain why the diffusion of the optical coherence or off-diagonal elements of the density matrix for CO diluted in N_2 should be a factor of 3 different from the diffusion of the population or diagonal elements of the density matrix, should have an abnormal dependence on density, and should be line dependent. In the following paragraphs we wish to present an entirely new view of this old problem which, above all, does not invoke the concept of an optical diffusion constant.

The reader is reminded that the empirical spectra computed with our measured values of y and z fit the experimental curves (at the level of 0.1% of the peak absorption) over the entire profile. Consequently, with these values of y and z we can generate, at each density, an analytic time correlation function, $C_{\text{fit}}(t)$, that accurately represents the experimental time correlation function $C_{\text{expt}}(t)$. The question is how do we partition this experimental time correlation function between $\chi_{\text{expt}}(k,t)$ and $\Phi_{\text{expt}}(t)$, the experimental translational and internal correlation functions? When we interpret the narrowing parameter in terms of an optical diffusion coefficient we are assigning all of the discrepancy between the model and experimental correlation function to the translational part. What we wish to consider are the consequences of laying the difficulty at the feet of the internal part. To answer that question we assume that $\chi_{\text{expt}}(k,t)$ is identical to $\chi_{\text{sc}}(k,t)$ for the soft-collision model with the *correct mass-diffusion constant,* i.e., it is identical to $\chi_{\text{sc}}(z_m,t)$. We can then determine $\Phi_{\text{expt}}(t)$ by dividing $C_{\text{fit}}(t)$ by $\chi_{\text{sc}}(z_m,t)$ and compare it with the standard model for the decay of the optical coherence, $\Phi_m(t)=\exp(-y\tau)$. At this stage of trying to unravel the problem, we use y^0P to calculate $\Phi_m(t)$, where y^0 is taken from our values in Table I. This specific choice of y will provide *some* measure of how far we have erred in assuming a simple exponential decay for the internal degrees of freedom. Later we will examine the consequence of choosing a different value of y.

Figure 5 shows a comparison of $\Phi_{\text{expt}}(t)$ and $\Phi_m(t)$ at 16 kPa. On the scale of the figure, the two curves for $\Phi(t)$ are not distinguishable. Also shown on the same scale is $[\Phi_{\text{expt}}(t)-\Phi_m(t)]$ multiplied by 100. This

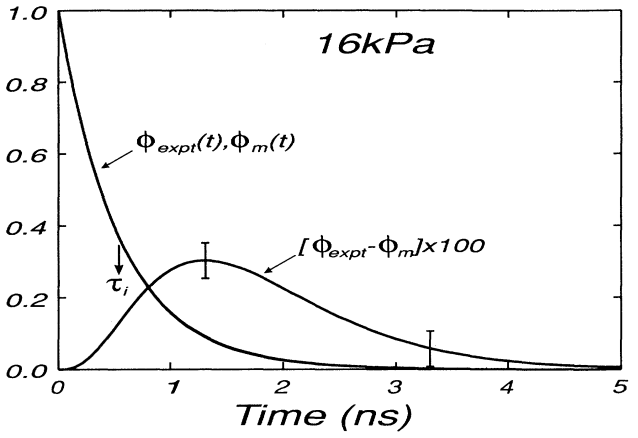

FIG. 5. Plot of the experimental and model correlation function for the decay of the dipole correlation function at 16 kPa; the two curves completely overlap. The difference $[\Phi_{\text{expt}}(t)-\Phi_m(t)]$ is shown multiplied by 100.

reaches a maximum of only 3×10^{-3} at about 1.3 ns or two and a half times τ_i, the relaxation time ($1/e$ point) of either function. We shall take as a measure of the deviation from an exponential the *maximum* value of $[\Phi_{\text{expt}}(t)-\Phi_m(t)]$ divided by the value of $\Phi_m(t)$ at that time point. Here it is about 0.003/0.1 or 3%. The maximum departure from an exponential decay exceeds the uncertainty in the departure by a factor of about 5. [The uncertainty or error bar shown in the figure was estimated from the size of the noise on the experimental profiles.]

We have carried out the same spectral analyses in the range of pressure from 5 to 17 kPa, the range of pressures in Fig. 4 where the narrowing parameter departs from a linear dependence on density. At each density, we find essentially the same shape for $[\Phi_{\text{expt}}(t)-\Phi_m(t)]$ as shown in Fig. 5, viz. a maximum deviation from an exponential decay of about 3%, located near $(2-3)\tau_i$. This is strong evidence that the departures from the standard model are indeed due to a slightly nonexponential decay of the dipole correlation function and not to "optical" diffusion. This is the main conclusion of this paper.

In the following paragraphs we wish to consider a number of factors that are useful in understanding the physical situation and for appreciating just what it is that the experiments are capable of examining. Figure 6 shows plots of $\chi_{\text{sc}}(z_m,t)$ and $\Phi(t)$ for pressures equal to 16, 5, and 1 kPa. On the scale of Fig. 6, $\Phi_m(t)$ and $\Phi_{\text{expt}}(t)$ are indistinguishable and we have dropped the subscript. The point to be made here is how one function $\Phi(t)$ or $\chi_{\text{sc}}(z_m,t)$ may obscure or filter the other and how the filtering changes with density or pressure. First we wish to point out that we are not instrumentally limited. The total width of the frequency scan for which our signal is above the noise level is about 0.2 cm^{-1}. Thus we can probe down to times on the order of 0.01 ns. This is very small compared to the time scale of Fig. 6. The separation in frequency space of our sampling sets an upper limit to the time scale of 10–20 ns. The resolution limit

of the spectrometer would permit us to extend this to hundreds of nanoseconds. Even so, the present measurements completely cover the time scales relevant to Fig. 6. Now consider the various correlation functions. At 16 kPa the translational function is much broader than the internal correlation function and we are able to observe the behavior of $\Phi(t)$ at times longer than the relaxation time τ_i. At 1 kPa the translational correlation function is sufficiently narrow to filter out all but the short-time behavior of $\Phi(t)$. At 5 kPa the two functions have comparable widths. This is the reason the experiments are sensitive to deviations from an exponential decay of the internal degrees of freedom only above 5 kPa. To further substantiate this conclusion, we analyzed our profiles for pressures *below* 5 kPa by adding a deviation of the form shown in Fig. 5 to an exponentially decaying function. Such a correlation function fitted the experimental curves below 5 kPa as well as a pure exponential. Thus the same slightly nonexponential form of $\Phi(t)$ (when multiplied by the soft-collision model with the correct mass-diffusion constant for the translational motion) will reproduce the experimental spectral profiles from 0 to 17 kPa.

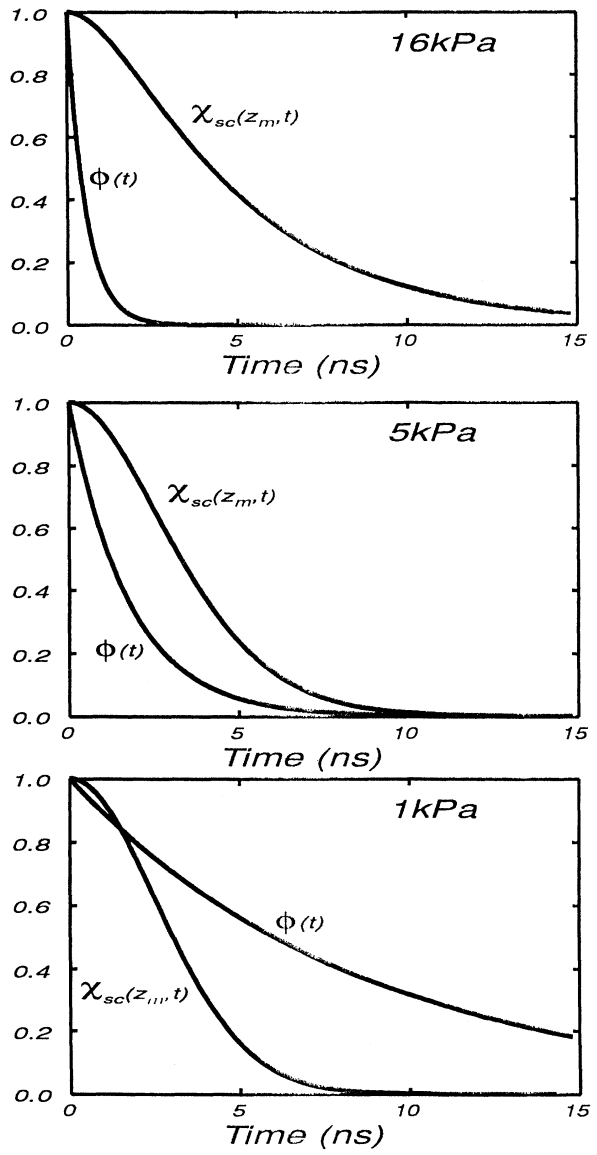

FIG. 6. Plots of the intermediate scattering function $\chi_{sc}(z_m,t)$ and $\Phi(t)$ for 16, 5, and 1 kPa.

In the discussion above we have used the difference between $\Phi_{expt}(t)$ and $\Phi_m(t)$ to measure the departure from an exponential decay. It reached a value of about 3% near t equal to $(2-3)\tau_i$. Thus it may seem surprising that the empirical fit to the spectral profile at say 16 kPa, using a pure exponential for $\Phi(t)$ and a floating value for the narrowing parameter in $\chi_{sc}(k,t)$, required a narrowing parameter 300% larger than that calculated from the mass-diffusion constant. (See Fig. 4 again.) However, this may be understood by examining the density and the time dependence of intermediate scattering function $\chi_{sc}(k,t)$. Figure 7 shows a plot of $\chi_{sc}(z_m,t)$ for pressures equal to 0, 16, and 45 kPa, where we have expressed time in units of τ_i, the relaxation time of the internal degrees of freedom at 16 kPa. [The 45 kPa curve is just the curve for the fitted (empirical) narrowing parameter shown at 16 kPa in Fig. 4.] In the region $(2-3)\tau_i$ where $[\Phi_{expt}(t)-\Phi_m(t)]$ is large, $\chi_{sc}(z_m,t)$ is constrained to be between a lower limit of (0.91–0.81), the free streaming or zero density value and 1, the limit reached asymptotically as the narrowing parameter or density approaches infinity. Note that $\chi_{sc}(z_m,t)_{45}$ is about (2–4)% higher than the correct $\chi_{sc}(z_m,t)_{16}$ at $(2-3)\tau_i$. The fact that the range (2–4)% brackets 3%, the modification required in $\Phi_m(t)$ in the same region of time, is convincing evidence that it is the nonlinear dependence of $\chi_{sc}(z_m,t)$ on density that is the reason it requires a large increase in the narrowing parameter to compensate for a small departure from an exponential decay for the internal degrees of freedom. This argument also explains why the broadest lines [narrowest correlation function $\Phi(t)$] require the

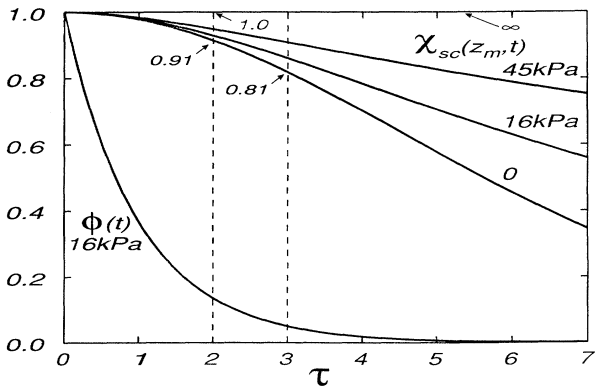

FIG. 7. Plots of the translational correlation function $\chi_{sc}(k,t)$ for 0, 16, and 45 kPa and the internal correlation function $\Phi(t)$ for 16 kPa, all in terms of the relaxation time τ_i of $\Phi(t)_{16}$.

largest modification of the narrowing parameter to fit the experimental results.

It was our original reaction to interpret our deviations from the standard model in the same manner as Forsman *et al.* [4]. We are now in a position to discuss why this is not possible. In that article, departures from the standard model were interpreted in terms of departures in $\chi(k,t)$ from $\chi_{sc}(k,t)$, the form of the intermediate scattering function given by the soft-collision model. The work of Desai [15], which is based on solutions of the Boltzmann equation for a given intermolecular potential, shows that such departures are both time and density dependent. The departures vanish at both low and high densities and at both short and long times. Noting that the hard-collision model [14] overestimates those departures by about a factor of say 2.5, we have estimated the density and time range where they would be important for CO by calculating $[\chi_{HC}(k,t)-\chi_{sc}(k,t)]/2.5$. We find that the range of pressures from 5 to 17 kPa covers the range where the departures from the soft-collision model are a maximum. At 10 kPa the departure has its peak value of about 0.02. However, the peak is reached at about 5 times the time between kinetic collisions τ_0. Since the optical cross section for CO is three times the kinetic cross section, the optical coherence at $5\tau_0$ has a value of $e^{-15}=3\times10^{-7}$ and any information on departures from the soft-collision model is filtered out of the spectrum. The situation is totally different in D_2. Here the optical cross section is about $\frac{1}{17}$ of the kinetic cross section. At $5\tau_0$, the optical coherence has decayed only to $e^{-0.3}=0.75$ and thus $\Phi(t)$ presents an open window in which departures from the soft-collision model may be observed. We conclude from this that there is no conflict between the two experiments and that the present experiments are insensitive to departures from the soft collision for the intermediate scattering function.

Throughout this paper, in the standard model for $\Phi_m(t)$, we have used the width derived from fitting the empirical model to the experimental line shape. There is no *a priori* reason to do this. Thus the reader should not attach deep significance to the shape of $[\Phi_{expt}(t)-\Phi_m(t)]$. To illustrate this point we have plotted in Fig. 8 the deviations from an exponential that result when we change the value of y appearing in $\Phi_m(t)$ by $\pm1\%$. Clearly the form of the departure from an exponential decay is an open question. The deviation could even occur at short times: It is only our insistence that all of the trial correlation functions be normalized to unity at zero time that forces the deviation to vanish at that point. Our form of analysis will not permit us to determine the form of the departure until we know what is the correct base or reference exponential decay. Fortunately, this limitation does not invalidate the conclusions reached above.

If spectral profiles are to be used to understand molecular dynamics or to measure intermolecular forces, then the physical nature of the departures from an exponential decay must be understood. While we have ruled out line mixing [16], we have not identified a specific reason why $\Phi(t)$, the dipole correlation function [17], should not decay exponentially. However, we offer a number of effects to be considered.

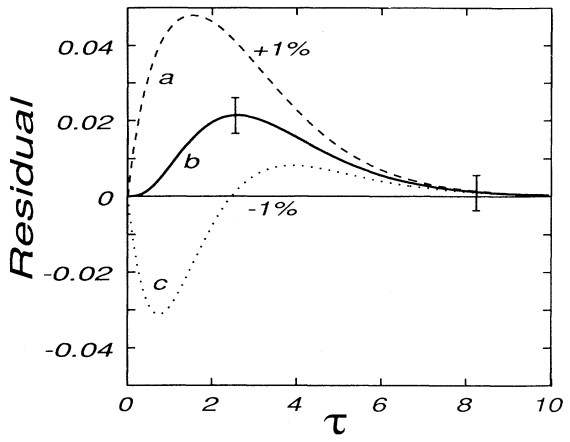

FIG. 8. Deviation from an exponential decay. The central curve *b* is the one used in the text. Curves *a* and *c* have the model width increased and decreased by 1%, respectively.

(a) The departure from exponential decay may be due to a failure of the impact approximation. If the duration of a collision is important it will affect the far wings of the line, i.e., it will affect the correlation function at times short compared to τ_i. To repeat a statement made above, our analysis conceals any possible short-time behavior since we have normalized all correlation functions to 1 at $t=0$, i.e., we have forced the departures to vanish at $t=0$.

(b) If there is any validity to the static theory, a theory that has been very successful in explaining the shift of the Raman lines in H_2 [18], then on some time scale each molecule has a slightly different frequency. The lines have a small vibrational inhomogeneous width in addition to the inhomogeneous width arising from the translational motion. As the density increases a molecule diffuses through the distribution of frequencies just as the velocity diffuses through the Boltzmann distribution. Like Dicke narrowing this averages out with increasing density and the line is narrower, or the correlation function decays more slowly. This sort of picture has been discussed by Burshtein, Zharikov, and Tempkin [19]. Like Anderson's exchange narrowing or motional narrowing in NMR it amounts to converting an inhomogeneous broadening to a narrower homogeneous case. The static model is a means of introducing some sort of inhomogeneous broadening or shifting to the picture.

(c) In contrast to the frequency modulation mentioned in (b), while Burshtein, Zharikov, and Tempkin argue that phase modulation leads to exponential decay, they fail to consider a third option, amplitude modulation. As it is the vector coupling between the optical field and the molecular dipole, reorientation of the angular momentum of the molecule will modulate the size of the coupling. It is not clear whether the statistics of such amplitude modulation can lead to a nonexponential decay.

(d) Speed dependent cross sections [20] have been shown to yield unusual line shapes. As in (c), it is not known if such effects are accompanied by a nonexponential decay of the optical coherence.

(e) There are effects such as transient dimer formation, three-body collisions, etc., which, while not likely candidates, may only be ruled out by a numerical evaluation.

(f) There is of course a question about the assumption of statistical independence of the evolution of the internal and translational degrees of freedom. We believe the question of statistical correlation can only be settled by a numerical molecular-dynamics simulation. For dilute gases, this is beyond present day computer power.

(g) It is generally recognized that no dipole correlation function can decay purely exponentially. Such a decay leads to a Lorentzian profile and infinite second and higher even spectral moments. This is not possible, these moments being related to physical and therefore finite effects [21]. Lines must thus be sub-Lorentzian in frequency space or decay more slowly than an exponential.

Such a list of theoretical possibilities is only limited by our imagination. Being already rather long it is not realistic to contemplate attacking them one at a time. Clearly what is required is a more complete experimental characterization of the effect. A fundamental question that should be answered is that of the exact shape of $\Phi(t)$. At higher density $\chi(k,t)$ becomes even less of a filter and $\Phi(t)$ becomes a narrower function of time. Thus experiments at higher density will permit us a clear view of $\Phi(t)$ over long times.

SUMMARY AND CONCLUSIONS

We have shown that the product of the soft-collision model for the intermediate scattering function for the translational motion and an exponentially decaying correlation function for the internal degrees of freedom provides an excellent description of the correlation function for the isolated lines of CO perturbed by N_2 provided the narrowing parameter is allowed to float. However, the empirical narrowing parameter does not scale with the mass-diffusion constant and must be adjusted for each specific density and each spectral line. From a pragmatic point of view one could use a lookup table to generate a synthetic profile suitable for describing the infrared emission of CO in the atmosphere. On the other hand, from the point of view of understanding the physical processes leading to the measured correlation function, we have suggested that the departures from the standard model should be ascribed to the decay of the internal degrees of freedom rather than to a nonphysical behavior of the narrowing parameter. By standard model we mean a soft-collision model for the translational degrees of freedom with the correct mass-diffusion constant and a simple exponential decay for the optical coherence. While the deviations from the standard model are small in the present case, until we understand the physical origin of the departures we can never be confident that they will remain small under all conditions.

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