Evidence of rotational and vibrational relaxation in the isotropic Raman spectra of CO and N_2

N. S. Golubev, N. D. Orlova, and L. A. Platonova
Scientific-Research Institute of Physics, A. A. Zhdanov Leningrad State University

(Submitted 2 December 1981)

Pis'ma Zh. Eksp. Teor. Fiz. **35**, No. 2, 65–68 (20 January 1982)

The theoretically predicted relationship between the width of the isotropic Raman-scattering band and the angular-momentum correlation time has been tested experimentally for the first time. The correlation time was measured by an NMR method. Experiments were carried out on CO and N_2 in various gas mixtures. A vibrational broadening is exhibited by CO in CO_2; the mechanism for this broadening is not clear.

PACS numbers: 33.20.Fb, 33.25.Bn, 33.70.Jg, 51.70. + f

The mechanism primarily responsible for shaping the isotropic-scattering bands of compressed gases is generally believed to be the "collisional contraction" which results from an interference of vibrational-rotational lines caused by rotationally inelastic collisions. This effect has been observed in several experiments[1-3] and discussed theoretically.[4-6] Temkin and Burshteĭn[5] have predicted a relationship between the half-width and the correlation time of the angular momentum of the molecule. As will be shown below, however, this theory may not be sufficient to explain the experimental results.

We studied the shapes of the isotropic bands of CO and N_2, for both the pure gases (at 295 K) and mixtures with CF_4 (273 K) and CO_2 (323 K), over the total density range ~7-380 amagat. The experimental apparatus is described in Ref. 7. We also recorded NMR spectra of ^{13}C and ^{15}N in the same systems, containing the molecules ^{13}CO and $^{15}N_2$. The experimental procedure is described in Ref. 8. The widths of the NMR lines, set in the present case by spin-rotational relaxation under conditions of a pronounced contraction, are[9]

Table I

System	CO	CO в CF$_4$	CO в CO$_2$	N$_2$	N$_2$ в CO$_2$
σ_J, A^2	46 ± 2	45 ± 2	25 ± 2	31 ± 2	14 ± 2

$$T_2^{-1} = \frac{4}{3}(IkT/\hbar^2)(2\pi C)^2\tau_J \ ,$$

where I is the moment of inertia, C is the spin-rotational interaction constant,[10,11] and τ_J is the angular-momentum correlation time. The measurements were carried out at densities up to ~100 amagat. In all cases, τ_J^{-1} varied linearly with the density; i.e., we found τ_J^{-1}, where n is the gas density, v is the average relative velocity of the molecules, and τ_J is the cross section for the rotationally inelastic collisions. We used the measured cross sections (Table I) to extrapolate τ_J^{-1} to higher densities, where the width of the NMR lines could not be determined because of the finite resolution of the particular spectrometer used (a Bruker HX-90).

At low densities, under our experimental conditions, the CO and N$_2$ vibrational bands have the asymmetric shape with a shading on the low-frequency side which is typical of isotropic-scattering bands. Because of the low resolution (the instrumental half-width of the apparatus was 0.3–0.8 cm^{-1}), we did not observe a discrete rotational structure. Figure 1 shows the dependence of the half-width $\Delta\nu_{1/2}$ on the gas density. The values of $\Delta\nu_{1/2}$ have been corrected for the finite resolution of the apparatus. The half-width decreases with increasing density in all systems except CO + CO$_2$, where the half-width remains essentially constant. May *et al.*[1] have studied the effect of pressure on the shapes of the isotropic CO and N$_2$ bands at room temperature at densities up to ~600 amagat, but they did not report data for CO in the interval 1–123 amagat, to which the data from the present experiments correspond. Our results on the N$_2$ spectrum at densities up to ~145 amagat agree with the data reported by May *et al.*[1] Figure 2 shows the dependence of the band half-width on the experimental values of τ_J^{-1} at the same densities. Here the results are plotted in terms of the dimensionless quan-

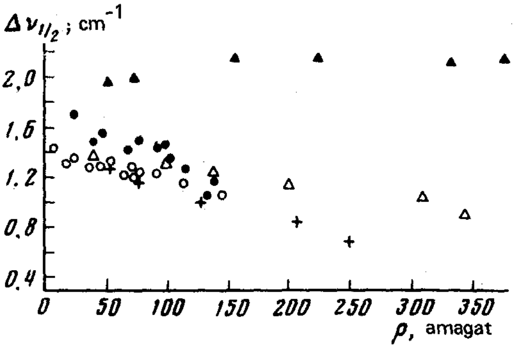

FIG. 1. Dependence of the half-width of the isotropic bands on the density. ●–CO, 295 K; +–CO in CF$_4$, 273 K; ▲–CO in CO$_2$, 323 K; ○–N$_2$, 295 K; △–N$_2$ in CO$_2$, 323 K. The error in the measurement of the half-width is ±0.2 cm^{-1}.

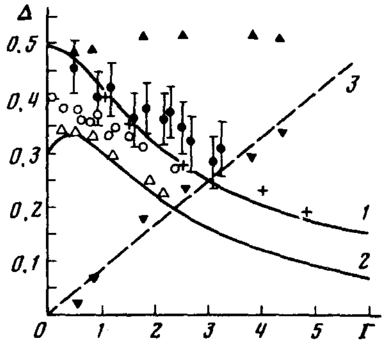

FIG. 2. Dependence of the band half-width on the experimental values of τ_J^{-1}. 1,2–Theoretical curves for strong and weak collisions, respectively.[5] The experimental points have the same meaning as in Fig. 1; Δ–Difference between the values of Δ for CO in CO_2 and curve 1. The error in all cases is approximately the same as that indicated for CO.

tities Δ and Γ, which are $\Delta\nu_{1/2}$ and τ_J^{-1} expressed in units of $\bar{\omega}_a = a_e T/T^*$, where $\bar{\omega}$ is the frequency of the centroid of the band, α_e is the vibrational-rotational interaction constant, and $T^* = \hbar^2/2cI$. The solid curves show the theoretical predictions of Ref. 5 for the cases of strong (1) and weak (2) collisions. If line interference is the only mechanism shaping the band, the experimental points should fall in the corridor defined by these curves. This is in fact what we find, within the experimental errors, except for the system of CO with CO_2. The points for CO lie closer to the strong-collision curve than do those for N_2, and this seems a reasonable result since the interacting lines in the nitrogen band are next-nearest lines, rather than nearest lines as in the case of CO. For all the systems studied, except $CO + CO_2$, the theory thus gives a generally correct description of the transformation of the shape of the isotropic-scattering band with increasing gas density. The situation remains uncertain at low densities, however, where the theory predicts very different values of Δ for the models of strong and weak interactions (curves 1 and 2 at $\Gamma \simeq 0$). This result seems faulty on physical grounds. The present experiments cannot clarify the situation because of the comparatively large error in the determination of the half-width.

In the spectrum of the mixture with CO_2, the CO band retains the same width up to ~380 amagat, but its shape changes form initially asymmetric to symmetric. It is natural to suggest that the collapse of the rotational structure in this system is accompanied by a simultaneous broadening of the band caused by a loss of vibrational phase coherence. If we assume that these mechanisms make additive contributions to the band half-width, we can find the vibrational broadening from the theoretical results in Fig. 2. By analogy with the behavior of the spectrum of CO in other systems, we assume that the effect of the rotational relaxation can be described by curve 1, and we subtract the corresponding values from the experimental values of Δ. The vibrational contribution found as a result turns out to be a linear function of the density, with a broadening coefficient $\sim 0.45 \times 10^{-2}$ cm^{-1} amagat^{-1}. The vibrational broadening in gas spectra has been measured previously for two systems: for the ν_1 band of methane[12] and the ν_3 band of N_2O (Ref. 7). In the first of these two cases the broadening was attributed to an intramolecular energy transfer between ν_1 and ν_3 (Ref. 13), while in the second case it was attributed to resonant dipole-dipole interactions.[7] For the $CO + CO_2$ system we have not been able to find a mechanism to explain this pronounced vibrational broadening. It should be noted that the nitrogen band exhibits only the effect of rotational relaxation under the same conditions, despite the similar properties of the N_2 and CO molecules. In the course of searching for a mechanism to explain the observed effect, we examined the theories of the loss of vibrational phase coherence which have been developed for the liquid phase,[14] since no theory for the vibrational broadening of gas bands exists. The correct theory will undoubtedly differ from the liquid-phase theory, however, since it will have to take into account the slightly perturbed rotation and the possible nonadditive rotational and vibrational contributions to the band shape.

1. A. D. May, J. C. Stryland, and G. Varghese, Can. J. Phys. **48**, 2331 (1970).
2. T. Witkowitcz and A. D. May, Can. J. Phys. **54**, 575 (1976).
3. V. V. Smirnov and V. I. Fabelinskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **27**, 131 (1978) [JETP Lett. **27**, 123 (1978)].
4. V. A. Alekseev and I. I. Sobel'man, Zh. Eksp. Teor. Fiz. **55**, 1874 (1968) [Sov. Phys. JETP **28**, 991 (1969)].
5. S. I. Temkin and A. I. Burshteĭn, Pis'ma Zh. Eksp. Teor. Fiz. **24**, 99 (1978) [JETP Lett. **24**, 86 (1978)]; Chem. Phys. Lett. **66**, 52 (1979).
6. A. P. Kouzov, Opt. Spektrosk. **49**, 1013 (1980) [Opt. Spectrosc. **49**, 554 (1980)].
7. N. D. Orlova and L. A. Platonova, Pis'ma Astron. Zh. **51**, 746 (1981) [Sov. Astron. Lett. (to be published)].
8. N. S. Golubev, A. I. Burhnteĭn, and S. I. Temkin, Chem. Phys. Lett. (to be published).
9. R. G. Gordon, J. Chem. Phys. **44**, 228 (1966).
10. I. Ozier, L. M. Crapo, and N. F. Ramsey, J. Chem. Phys. **49**, 2314 (1968).
11. L. M. Ishol, T. A. Scott, and M. Goldblatt, J. Magn. Res. **23**, 313 (1976).
12. N. D. Orlova and L. A. Platonova, Pis'ma Zh. Eksp. Teor. Fiz. **31**, 10 (1980) [JETP Lett. **31**, 8 (1980)].
13. N. D. Orlova and L. A. Platonova, Opt. Spektrosk. **51**, 15 (1981) [Opt. Spectrosc. (USSR) (to be published)].
14. D. W. Oxtoby, Adv. Chem. Phys. **40**, 1 (1979).

Translated by Dave Parsons
Edited by S. J. Amoretty