Interference of fine-structure components in the IR absorption spectra of polyatomic molecules

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The collisional broadening of the absorption spectra of SF_6 and CF_2Cl_2 molecules has been studied by diode-laser spectroscopy in a previously inaccessible pressure range. The Weisskopf cross section is observed to decrease with increasing frequency of kinetic collisions. The effect of the structure of the colliding molecules on this process is discussed.

1. The highly coherent output and widely tunable frequency of diode lasers in the mid-IR range make these diodes suitable for studying the broadening of the absorption lines of molecules. Correlation methods for analyzing the spectra obtained with diode lasers allow such studies to be extended to the case of polyatomic molecules whose spectra are densely packed with narrow, partially overlapping absorption lines.[1] In studies of collisional broadening, it has proved possible to study pressure regions in which the line overlap is significant. It thus becomes possible to study the interference of absorption lines that occurs in the case of such an overlap. Effects of this type, manifested by a nonlinear increase in the line width with the pressure, are well known in the Raman spectroscopy of diatomic molecules, e.g., N_2 and O_2 (Refs. 2 and 3), and are observed at high pressures, ~ 100 atm. For polyatomic molecules such as SF_6 and CF_2Cl_2, interference effects may be manifested at much lower pressures, ~ 10–100 Torr, but these effects have not previously been observed because of difficulties in measuring line widths under these conditions.

2. We have now used a diode-laser spectrometer to measure the average coefficients of collisional broadening of the absorption lines of molecules $^{32}SF_6$ and CF_2Cl_2. In the case of SF_6 we studied the interval 949.8–950.4 cm^{-1}, which includes lines of the R branch of the v_3 vibrational-rotational transition with $J \sim 40$. As buffer gases we used H_2, N_2, CO, He, Ne, Ar, Kr, Xe, $^{32}SF_6$, and $^{34}SF_6$. The broadening of the CF_2Cl_2 lines by air was studied in the interval ~ 929.6–930.1 cm^{-1} on the R branch of the v_6 vibrational–rotational transition with $J \sim 40$. The partial pressure of the SF_6 and CF_2Cl_2 was ~ 0.2 Torr. Figure 1A shows transmission spectra of CF_2Cl_2 at various air pressures, and Fig. 1B shows autocorrelation functions of their logarithmic derivatives. From the width of the correlation function at the zero level we determined the widths of the absorption lines averaged over the spectrum. An average width of this type may be thought of as a characteristic of the collision matrix averaged over all possible transitions.[4] Figure 2 shows the line width versus the buffer-gas pressure. In all cases except the SF_6:He system the broadening coefficient $k = d\gamma/dp$ decreases with increasing pressure of the buffer gas. The change in k occurs at those pressures at which the widths of the various spectral components become comparable to the fine
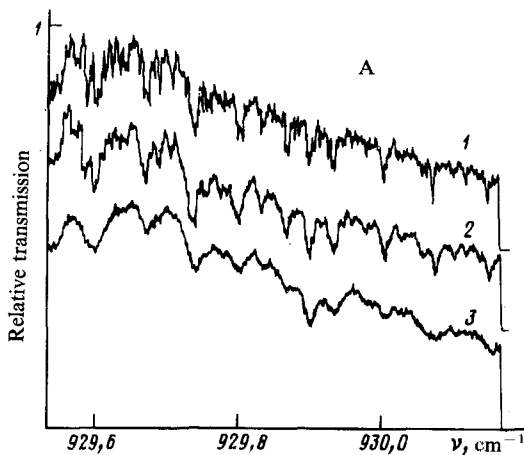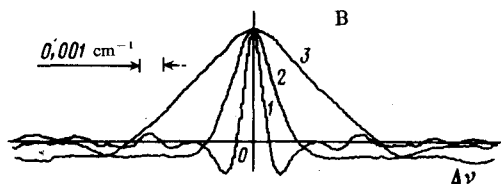
FIG. 1. A: Transmission spectra of CF_2Cl_2 at various air pressures. 1—0 Torr; 2—12 Torr; 3—55 Torr. B: Correlation functions of the derivatives of these spectra.

splitting averaged over the spectrum. This behavior of k with increasing buffer-gas pressure can be logically attributed to interference effects.
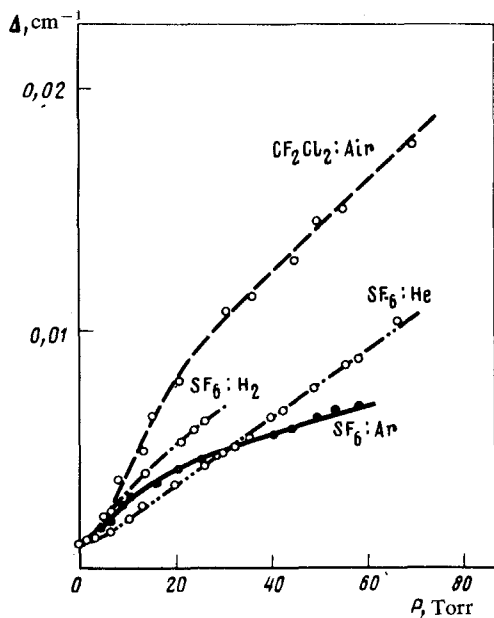

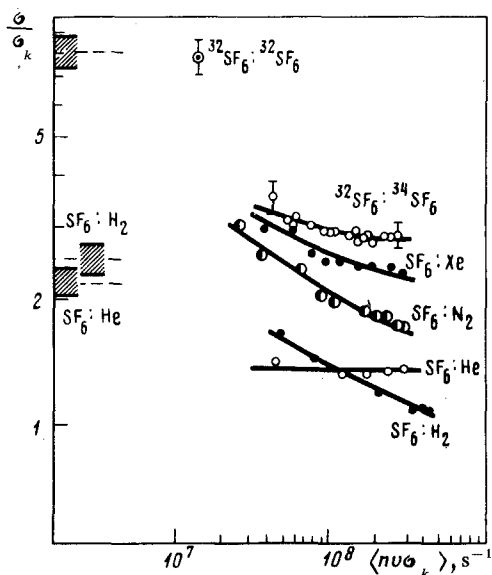FIG. 2. Line width versus the buffer-gas pressure.

FIG. 3. The cross-section ratio $\langle\sigma_W\rangle/\langle\sigma_k\rangle$ versus the frequency of kinetic collisions. The hatched regions show data from Ref. 5.

3. Figure 3 shows the most typical experimental results on the behavior of the ratio of the Weisskopf cross section for the collisional broadening, $\langle\sigma_W\rangle$, to the kinetic cross section $\langle\sigma_k\rangle$ as a function of the kinetic collision rate $\langle nv\sigma_k\rangle$. The cross section $\langle\sigma_W\rangle$ was determined from the Lorentzian contribution to the line width: $\langle\sigma_B\rangle = \gamma\pi/n\langle v\rangle$, where γ is the collisional broadening measured at the half-maximum of the lines, n is the density of molecules, and v is the relative velocity of the colliding particles. The curves for the systems with Ne, Kr, Ar, and CO are similar to those for the systems with N_2, Xe, and $^{34}SF_6$ and are bracketed by the latter.

At low kinetic collision rates, the ratio $\langle\sigma_W\rangle/\langle\sigma_k\rangle$ depends only slightly on the structure of the molecules. Collisions with lighter particles are not as efficient; this result can be explained on the basis that the angular momentum of the relative motion of the colliding molecules is not sufficient for transitions involving a change in J. The difference in the broadening efficiencies observed in the cases of H_2 and He, on the other hand, can be attributed to the additional angular momentum of hydrogen, associated with the internal rotation. Particularly noteworthy is the increase in the efficiency of the line broadening which stems from the resonant transfer of an excitation in collisions between $^{32}SF_6$ molecules. Our results at low pressures agree reasonably well with data from photon-echo experiments.[5]

With increasing frequency of kinetic collisions, the Weisskopf cross section begins to decrease; this effect can be attributed to an interference of spectral lines, which causes some relaxation channels to cease to contribute to the broadening. Since it is primarily the closest components in the spectrum that overlap in the broadening, the relaxation processes that are initially "turned off" are apparently those involving a change in the rotational quantum number and in the projection of the rotation onto the axis of the molecule. After nearest neighbors have interfered, there remain collisional-relaxation channels corresponding to a transition to other branches of the spectrum. The most probable channels appear to be those for which the total angular

momentum is conserved (for SF_6, these are transitions between Coriolis sublevels). Experimentally, we observe a monotonic increase in the cross sections for these processes with increasing mass of the buffer molecule. This effect can tentatively be attributed to the inverse proportionality between the cross section and the velocity.

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