

# "Anomalous" behavior of the profile of the $\nu_1$ band of $\text{CH}_4$ as a result of varying the gas density

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The behavior of the band of isotropic scattering of a multiatomic molecule (methane) as a result of varying the pressure is investigated for the first time. It is found that the band transformation is inconsistent with the predictions of the theories which to date have described correctly the effect in the investigated systems.

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In recent years in connection with the development of Raman scattering techniques (RS) studies of the profiles of bands and lines in the spectra of gases have become possible, and new effects have been studied. Thus, when the pressure was increased from several atmospheres to  $\sim 100$ – $650$  atm, a narrowing of the  $Q$  branch was observed in the isotropic scattering bands of the molecules  $\text{N}_2$ ,  $\text{CO}$ ,<sup>(1)</sup>  $\text{HF}$ ,<sup>(4)</sup>  $\text{HD}$ ,<sup>(3,4)</sup> and  $\text{N}_2\text{O}$ .<sup>(5)</sup> The theory developed in Refs. 6–8 describes these experimental facts as a "narrowing due to collisions," which shows that they are caused by nonadiabatic interaction that lead to an interference of the overlapping lines. An analogous behavior was predicted for the band profiles of fully symmetric vibrations of tetrahedral molecules such as  $\text{CH}_4$ , etc.<sup>(7)</sup>

In this paper we investigate the structure of the  $\nu_1(A_1)$  band of pure methane

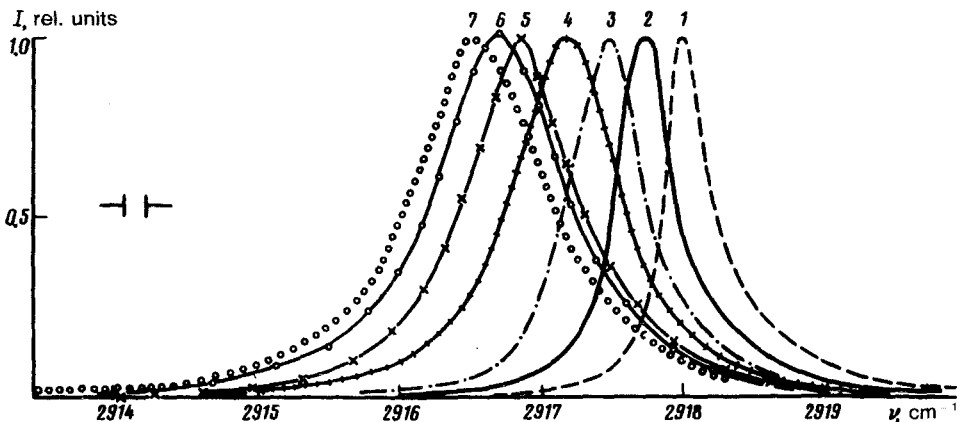


FIG. 1. Spectrum of Raman scattering in the region of the  $\nu_1$  band for methane at different pressures. Pure gas: 1—1 atm; 2—7 atm; 3—14 atm; mixture of 14 atm  $\text{CH}_4$  with  $\text{N}_2$ : 4—45 atm; 5—65 atm; 6—90 atm; 7—110 atm.

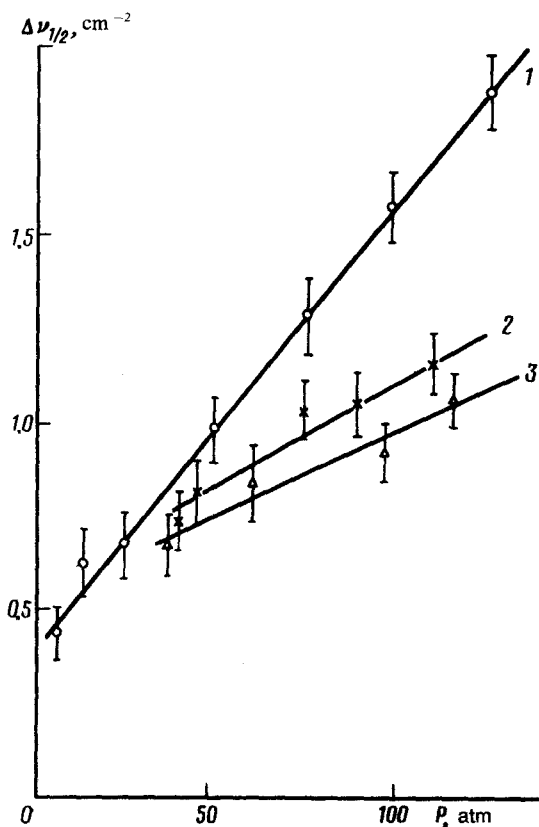


FIG. 2. Dependence of halfwidth of the  $\nu_1$  band for  $\text{CH}_4$  on gas pressure: 1— $\text{CH}_4$ ; 2— $\text{CH}_4 + \text{N}_2$ ; 3— $\text{CH}_4 + \text{Ar}$ . The partial pressure of  $\text{CH}_4$  in the mixtures is 14 atm.

( $\text{CH}_4$ ) and with  $\text{N}_2$  and Ar impurities at pressures up to 125 atm at room temperature. The partial pressure of  $\text{CH}_4$  in the mixtures was 0.14 atm. A high-pressure vessel was used.<sup>19)</sup> The spectra were recorded by a Speks Ramalog-8 spectrometer, and the 165-08 Spectra Physics argon-ion laser with a power of about 0.5 W in the 5145 Å line was used. The width of the instrumental function in different experiments, which was 0.16–1.0  $\text{cm}^{-1}$ , was measured along the line profile of the Tyndall scattering. The halfwidths given below were corrected for the effect of the instrument.

Under all conditions we observed a band devoid of fine structure, whose width varied from  $\sim 0.26$  to  $\sim 2 \text{ cm}^{-1}$  in the investigated pressure range. Figure 1 illustrates the band transformation as the gas density is varied. At the lowest pressures the band has the usual shape of the envelope of the  $Q$  branch for the isotropic scattering band. It is asymmetric with a deflection toward the high-frequency side. Its width increases with increasing pressure. Starting at approximately 20 atm (in pure gas), the band is almost symmetric. Its shape resembles a dispersion shape. The maximum of the band shifts toward lower frequencies. Figure 2 shows the dependence of the band halfwidth on the pressure for the investigated systems. Within the limits of experimental accuracy, this dependence turned out to be linear with broadening coefficients of  $0.012 \pm 0.002$ ,  $0.006 \pm 0.001$ , and  $0.005 \pm 0.001 \text{ cm}^{-1}/\text{atm}$ , respectively, for pure methane and for that with nitrogen and argon impurities. In our work the displace-

ment of the band was determined very imprecisely. It was about  $0.02 \text{ cm}^{-1}/\text{atm}$  for the pure gas and  $\sim 0.01 \text{ cm}^{-1}/\text{atm}$  for the impurities. The value for pure methane agrees with the value of  $0.017 \text{ cm}^{-1}/\text{atm}$ , which can be obtained from the results of studying  $\nu_1$  for methane in a broader range of density variation.<sup>(10)</sup> Thus, in contrast to what is observed in the spectra of two-atom molecules, as the pressure is increased from 1 to 125 atm, the isotropic scattering band for methane broadens and shifts toward the low-frequency side rather than toward the band center.<sup>(7)</sup>

The greater complexity of the  $\nu_1$  band for methane contributes to large differences between it and the two-atom molecular bands, for which a narrowing effect was observed. In the spectra of  $\text{N}_2$ ,  $\text{CO}$ , and other molecules the band consists of a set of lines whose frequencies are determined by the difference of the rotational constants in the two vibrational states  $a_e$  and  $\nu = a_e J(J+1)$ , and the separation between the lines is relatively large. For  $\text{N}_2$ ,  $a_e = 0.017 \text{ cm}^{-1}$ , and for  $\text{HD}$ ,  $a_e = 1.99 \text{ cm}^{-1}$ . The equation for the line frequencies of the  $\nu_1$  band for methane is much more complex due to the splitting of the rotational terms because of the decrease in the symmetry of the molecule arising from the centrifugal force. As a result, the distances between the lines are determined not only by  $a_e$ . As seen from the CARS spectrum with high resolution, the distances are much smaller.<sup>(11)</sup> It might therefore be assumed that a "collapse" of the rotational structure in the methane spectrum occurs in regions of lower pressure than for the bands of the two-atom molecules. However, it can be seen from the CARS<sup>(12)</sup>  $\nu_1$  spectra for methane at pressures from 200 Torr to 4.3 atm, that as the pressure increases there is a smearing of certain band details (because of the relatively low resolution, individual vibrational-rotational lines were not observed in this work), followed by a gradual broadening. In addition, as was noted earlier, under our experimental conditions a change is observed in the band profile: from an asymmetrical with a deflection toward the high-frequency wing, the band becomes symmetrical as the pressure increases, and it broadens.

Evidently, the behavior of the band profile for isotropic scattering of methane is not described by simple theory of spectral transformation due to collisions, developed for two-atom molecules.

The band profiles for the isotropic scattering of multiatomic gases in the region of comparatively high pressures where line overlapping occurs, were studied only for the  $\nu_1$  and  $\nu_3$  bands of  $\text{N}_2\text{O}$  in a mixture with  $\text{Ar}$ .<sup>(15)</sup> The structure of these bands in a spectrum of rarified gas and its behavior with increasing pressure do not differ qualitatively from the effects in the spectra of two-atom molecules. Therefore, it is now difficult to determine whether the deviations from such behavior observed in this paper are common for complex molecules or whether they are related strictly to the properties of molecular dynamics of methane. In principle, for a multiatomic molecule with a complex spectrum, that corresponds to the interaction among the anharmonic vibrations, it is natural to expect that the narrowing of the band because of nonadiabatic rotational collisions occurs simultaneously with the broadening of the vibrational-rotational terms due to vibrational relaxation (phase and energy), for which conditions may change with changing density. It was shown<sup>(13)</sup> that the Fermi resonance with  $A_1$ -type components of the  $2\nu_2$  and  $2\nu_4$  levels, and also the weak Coriolis interaction with  $F_1$ -type sublevels for the vibration  $\nu_2 + \nu_4$ , have an effect on the  $\nu_1$  band structure of

methane. A theory capable of predicting the effect of these factors on deformation of the vibrational-rotational band profiles under the influence of intermolecular interactions does not exist. A collapse of the rotational structure occurs in the  $\nu_1$  vibrational band for  $N_2O$ , which is in Fermi resonance with  $2\nu_2$  as the pressure is increased.

Thus, in formulating a theory for description of the behavior of the isotropic scattering bands for multiatomic molecules as a function of density, we must take into account other mechanisms for perturbing the spectrum in addition to the rotational relaxation, among these are mechanisms that reflect the specifics of a complex molecule as a set of interacting oscillators.

<sup>1</sup>A.D. May and J.C. Strayland, *Can. J. Phys.* **48**, 2331 (1970).

<sup>2</sup>J. Le Duff and W. Holzer, *Chem. Phys. Lett.* **24**, 219 (1974).

<sup>3</sup>P. Dion and A.D. May, *Can. J. Phys.* **51**, 36 (1973).

<sup>4</sup>T. Witkowitz and A.D. May, *ibid.* **54**, 575 (1976).

<sup>5</sup>R. Ouillon, *Chem. Phys. Lett.* **35**, 63 (1975).

<sup>6</sup>A.D. Alekseev and I.I. Sobel'man, *Zh. Eksp. Teor. Fiz.* **55**, 1874 (1968) [*Sov. Phys. JETP* **28**, 991 (1968)].

<sup>7</sup>S.I. Temkin and A.I. Burshtein, *Pis'ma Zh. Eksp. Teor. Fiz.* **24**, 99 (1976) [*JETP Lett.* **24**, 86 (1976)].

<sup>8</sup>S.I. Temkin and A.I. Burshtein, *ibid.* **28**, 583 (1978) [*ibid.* **28**, 538 (1978)].

<sup>9</sup>N.D. Orlova, L.A. Pozdnyakova, and E.B. Khodos, *Sb. Molekulyarnaya spektroskopiya (Molecular Spectroscopy)*, LGU, Leningrad (1975).

<sup>10</sup>A.D. May, J.C. Strayland, and H.L. Welsh, *J. Chem. Phys.* **30**, 109 (1959).

<sup>11</sup>A. Owyong, C.W. Patterson, and R.S. McDowell, *Chem. Phys. Lett.* **59**, 156 (1978).

<sup>12</sup>A.D. May, M.H. Hensian, and R.L. Byer, *Can. J. Phys.* **56**, 248 (1978).

<sup>13</sup>J.E. Lock and A.G. Robiette, *Chem. Phys. Lett.* **64**, 195 (1979).