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Profile of the ν_1 Raman Band of Pure CD_4 and Its Mixtures with Ar and Kr in the Gas Phase

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ABSTRACT The ν_1 band profile of isotropic Raman spectrum of pure CD_4 and its mixtures with Ar and Kr is recorded in the temperature range 140–360 K at pressure of pure CD_4 ranging from 4 to 20 atm and at total pressure of gas mixtures in the interval 4–160 atm. The dependences of the band shape on temperature and density are analyzed. The coefficients of the CD_4 band broadening by Ar and Kr are determined, and the decisive role of vibrational contributions, in particular of the intramolecular energy transfer, is pointed out.

KEYWORDS band profile of Raman spectra, broadening by rare gases, broadening coefficients, CD_4

INTRODUCTION

Formation of Raman spectral band shapes of polyatomic molecules in the gas phase is the result of an interplay of many processes involving intermolecular interactions and intramolecular coupling of different degrees of freedom. Consequently, experimental information on the band shape characteristics can be useful in understanding these processes. However, at present, there exists no comprehensive theory necessary to correctly interpret the results of observations. The experimental findings are often scarce because recording such spectra presents significant technical difficulties. Thus, it is desirable to increase the amount of data derived, in particular, from specially designed experiments, which can be used to test the theoretical approaches.

In our previous paper,^[1] we reported the results of a study of the ν_1 Raman band of CH_4 in the gas phase. The Raman spectra of pure methane and its mixtures with Ar and Kr were studied, and the changes in the ν_1 band shape with variation of temperature and density were discussed. Although methane belongs to the compounds extensively investigated by the spectroscopic methods, specific features of the ν_1 band profile of Raman scattering by this molecule under different experimental conditions are studied insufficiently. Among the most interesting studies devoted to this problem we can mention those reported in Refs. 2 and 3. In Ref. 2, the shape of the ν_1 Raman Q branch of CH_4 in mixtures with Ar and He was studied by the method of

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stimulated Raman spectroscopy at room temperature and at relatively low pressures. It was shown that under these conditions, the Q branch is largely influenced by collision-induced energy transfer between the rotational states. The model proposed in this paper and based on the line mixing effect predicts the spectral shape in good agreement with the experiment. In Ref. 3, the shape of the ν_1 Raman band of CH_4 in mixtures with He was studied by the method of inverse Raman spectroscopy at CH_4 pressure fixed at 30 atm and He pressure varying from 5 to 50 atm. It was found that in this pressure region, the band width is a linear function of the foreign gas pressure, and the broadening coefficient was determined.

In the current paper, we study the behavior of the ν_1 Raman band of CD_4 under conditions similar to those of the experiment of Ref. 1. The objective of this experiment is to study the effect of isotope substitution on the band shape. It is of interest because the intermolecular interaction is insensitive to such substitution, but the position of intramolecular vibrational levels can change drastically.

MATERIALS AND METHODS

The Raman spectra of pure CD_4 and its mixtures with Ar and Kr in the region of the ν_1 band were recorded with a DFS-24 spectrometer in the temperature interval 140–360 K using a cell described in detail in Refs. 1 and 4. Each recorded spectrum is the convolution of a real spectrum of the Lorentzian type with a Gaussian instrumental function whose half width at half maximum was about 0.8 cm^{-1} . The pressure of pure deuteromethane was varied from 4 to 20 atm. The total pressure of gas mixtures was varied from 4 to 160 atm with a partial pressure of CD_4 not higher than 10 atm. The main focus of this experiment is on the region of higher pressures where the collisional perturbations of vibrational states are most important for the band shape formation. The gas sample of CD_4 with a purity of 98% (Institute of Applied chemistry, Russia) contained admixtures of CH_4 and deuterioethanes.

RESULTS AND DISCUSSION

Figure 1 displays the typical Raman spectra of pure CD_4 at 4 Amagat and a mixture CD_4/Ar at 144

Amagat in the region of the $\nu_1 = 2102\text{ cm}^{-1}$. One can see in the figure that weak bands are superimposed on the low-frequency wing of the ν_1 band of deuteromethane. We assign these weak bands to totally symmetric vibrational modes of C_2HD_5 (at 2093 cm^{-1}) and C_2D_6 (at 2083 cm^{-1}). For pure CD_4 , the width of experimental spectra is virtually constant within the experimental error limits at pressures up to 20 atm and at all temperatures. Note that the narrowing of Q branch in the Raman spectra of molecules was predicted in Ref. 5 for a certain region of increasing density. This effect in spectra of the C_2H_2 , CO_2 , and N_2 molecules was observed in Refs. 6 and 7. In our studies, we did not reveal any narrowing of the ν_1 band of methane in the region of low densities. A similar result was obtained in Ref. 2 for CH_4 . An appreciable vibrational broadening and instrumental distortion of the band shape can explain why this subtle effect has not been observed in our experiments. At higher densities, the band width increases noticeably with density according to the law

$$b = b_0 + \xi \cdot \rho,$$

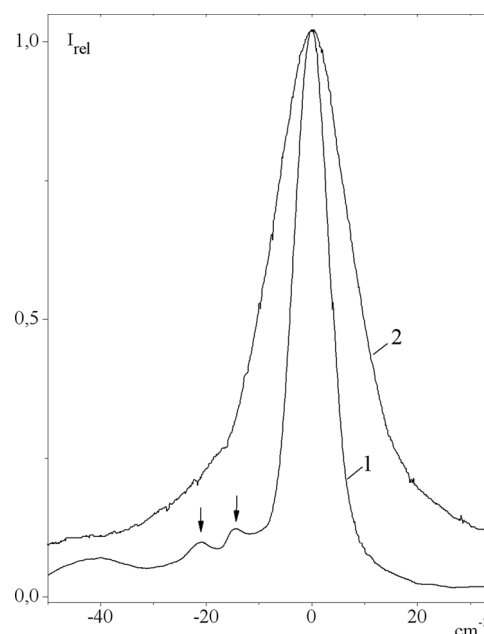


FIGURE 1 Raman spectra of CD_4 in the region of the ν_1 band at 295 K and at density of 4 Amagat (pure CD_4 , curve 1) and 144 Amagat (CD_4/Ar mixture, curve 2). I_{rel} is the scattering intensity in relative units. The spectral features indicated by arrows in curve 1 are associated with C_2HD_5 and C_2D_6 .

TABLE 1 Parameters of the Broadening of the ν_1 Band of CD_4 in Ar and Kr at Different Temperatures and Densities

| T (K) | ρ (Amagat) | B^* (cm ⁻¹) | b_0 (cm ⁻¹) | ξ (cm ⁻¹ /Amagat) |
|----------|--------------------|------------------------------|------------------------------|-------------------------------------|
| Ar | | | | |
| 140 | 31 | 7.2 | 6.5 ± 1.1 | 0.035 ± 0.013 |
| | 48 | 9.0 | | |
| | 107 | 9.3 | | |
| 200 | 30 | 7.9 | 7.1 ± 0.5 | 0.024 ± 0.003 |
| | 97 | 9.3 | | |
| | 194 | 12.3 | | |
| | 218 | 12.0 | 7.6 ± 0.3 | 0.026 ± 0.003 |
| | 26 | 8.3 | | |
| | 30 | 8.1 | | |
| 44 | 8.5 | | | |
| 83 | 9.6 | | | |
| 144 | 87 | 10.4 | | |
| | 11.0 | | | |
| Kr | | | | |
| 250 | 31 | 8.3 | 6.9 ± 0.1 | 0.047 ± 0.002 |
| | 58 | 9.7 | | |
| | 88 | 11.0 | | |
| | 115 | 12.3 | | |
| 292 | 35 | 8.9 | 7.5 ± 0.6 | 0.034 ± 0.010 |
| | 57 | 9.4 | | |
| | 70 | 9.6 | | |
| | 83 | 10.7 | | |
| 350 | 12 | 7.4 | — | 0.055 ± 0.008 |
| | 30 | 9.0 | | |
| | 41 | 9.3 | | |
| | 61 | 10.2 | | |

$$*b = b_0 + \xi \cdot \rho.$$

where b is the full width at half maximum in cm^{-1} , b_0 and ξ are constants, and ρ is the foreign gas density in Amagat. Note that an analogous density dependence of the ν_1 band width ($b = 0.78 + 0.0024 \cdot p$) was found in Ref. 3 for a mixture of CH_4 with He. In this case, p is the He pressure in atm. Values of the broadening coefficients ξ obtained in our studies at different temperatures lie in the range 0.024 to 0.055 $\text{cm}^{-1}/\text{Amagat}$. It should be noted that, with the same perturbing gas, the broadening coefficient of the CD_4 band is larger than that of the CH_4 band.^[1] Also of interest is the dependence of ξ on temperature. For deuteromethane, as in the case of CH_4 , the broadening coefficient initially decreases with temperature and then increases (see Table 1). This effect is more pronounced for a mixture of CD_4 with Kr.

The behavior of the ν_1 band of CD_4 with variation of temperature and density is, apparently, governed by several factors, the most important of which are the collisional changes in the rotational and vibrational states of molecules. At sufficiently high densities, the band becomes symmetric and rapidly broadens with increasing density. After the rotational structure has collapsed, the broadening of the ν_1 band at higher densities is primarily associated with the collisional changes in the vibrational states of molecules. Among these processes one should distinguish the collisions that cause the vibrational dephasing without changing the vibrational energy and the collisions that give rise to relaxation of the vibrational energy. In the latter case, the energy of vibrations can be expended for exciting external degrees of freedom. The contribution of dephasing to the broadening coefficient is readily estimated. Such estimates made in Ref. 1 for CH_4 showed that, although the temperature dependencies of the experimental broadening coefficients and of the calculated values related to the vibrational dephasing are in qualitative agreement, the theoretical values are too small. These results suggest that the dephasing caused by the intermolecular interaction affects the broadening coefficient of the isotropic Raman band of methane, but other mechanisms of broadening should also be taken into account.

It is known that the intramolecular energy transfer between different vibrational modes affects significantly the width of isotropic Raman spectra of polyatomic molecules. According to Ref. 8, the rates of such transfer processes can be high if the vibrational energy levels of molecules are closely spaced and the corresponding normal modes involve displacements of atoms of the same molecular fragments. For pure CH_4 , the rate of energy transfer between the ν_1 and ν_3 modes, whose fundamental frequencies are 2916 and 3020 cm^{-1} , respectively, was derived from the experimental data in Ref. 8. According to estimates of Ref. 8, this value of $\beta = (1.2 \pm 0.3) \mu\text{s}^{-1} \text{cm}^{-1}/\text{torr}$ should correspond with a broadening coefficient value of $(0.010 \pm 0.002) \text{cm}^{-1}/\text{Amagat}$, which virtually coincides with the result of our experiment.^[1] We are not aware of similar estimates made for other systems. But we believe that the larger values of the broadening coefficients for CD_4 as compared with those for CH_4 ^[1] are accounted for by smaller energy differences between

the vibrational levels of CD_4 in the region of the first excited state of the ν_1 mode. Indeed, the distances between this level and the $2\nu_2$ and $\nu_2 + \nu_4$ levels in CD_4 are almost twice as small as the corresponding distances in CH_4 .^[9]

Thus, in this study the ν_1 band shapes of isotropic Raman spectrum of pure CD_4 and its mixtures with Ar and Kr were recorded in a wide range of pressures and temperatures. The main results were obtained at high densities of gas mixtures. At these densities, the vibrational contributions to the band shape are predominant. Comparison of the results obtained here for CD_4 with the data derived earlier for CH_4 ^[1] allows us to estimate the effect of vibrational dephasing and to show the decisive role of the intermode energy relaxation. However, both these vibrational effects cannot explain the temperature behavior of broadening of methane Raman spectra by heavy foreign gases. In our opinion, this calls for the development of more sophisticated approaches for describing the band shape formation at higher densities of gas mixtures.

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