
**THE ν_1 BAND CONTOUR IN RAMAN SPECTRA
OF METHANE AND ITS GASEOUS
MIXTURES WITH Kr AND Ar****B.T. KUYLIEV, N.D. ORLOVA¹, L.A. POZDNYAKOVA¹,
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We have carried out the investigations of the Raman scattering spectra of the ν_1 band of methane (CH_4) and its mixtures with Ar and Kr in the gaseous phase in the temperature interval 140–360 K under a pressure of 4–160 atm. At low pressures, the band represents an asymmetric contour typical of the Q -branch with a degraded discrete structure. Starting from ~ 50 Amagat and higher, the real contour is of Lorentzian shape. We have determined the broadening coefficients k of the band, which appears to be $k(\text{CH}_4+\text{CH}_4) \approx k(\text{CH}_4+\text{Kr}) > k(\text{CH}_4+\text{Ar})$ with increase in pressure. For all studied systems, k decreases first of all with increase in temperature, and then it starts to increase. The behavior of the ν_1 band of methane under the above-mentioned conditions is related to the vibrational relaxation process and the dephasing of vibrations. By calculations on the base of Gaussian98W software, the structure of isolated aggregates $\text{CH}_4\text{--Kr}$ is determined.

1. Introduction

The interaction of electromagnetic radiation with matter results in the fact that the light passed through a medium or the scattered light contains the information on the structure of a substance, vibrations of atoms in molecules, the interaction of molecules, etc.

The contours of the bands of vibrational spectra in the IR region, as well as in the region of Raman scattering spectra, represents the important and most comprehensive source of information on the molecular

dynamics and molecular relaxation in condensed media. However, the extraction of such information is a rather complex problem, whose solution can lead to various interpretations of the results. The reason is an imperfection of the theory which would be able to predict the shape of bands (and lines) in spectra of real molecular systems. The development of the theory meets difficulties which are conditioned by the insufficient knowledge of intermolecular interactions and a structure of matter. Meanwhile, the solution of the problem is of significant importance for molecular physics. Thus, experimental investigations remain actual as before. A specific interest is given to the investigations of variations of the bands' contours of vibrational spectra of substances in the transition from the states of practically free molecules to the states with a rising contribution of the intermolecular interaction and molecular collisions. Accordingly, we carried out the investigations of the isotropic RS spectra of pure methane (CH_4) and its mixtures with Ar and Kr in the gaseous phase in the temperature interval 140–360 K at a pressure of 4–160 atm. Partial pressure of methane in mixtures did not exceed 10 atm. In order to determine the peculiarities of intermolecular interactions, we carried out quantum-chemical calculations of interactions and the structure of molecular formations for an isolated monomer molecule, the aggregate of two CH_4 molecules, and the aggregate of a CH_4 molecule and a Kr atom.

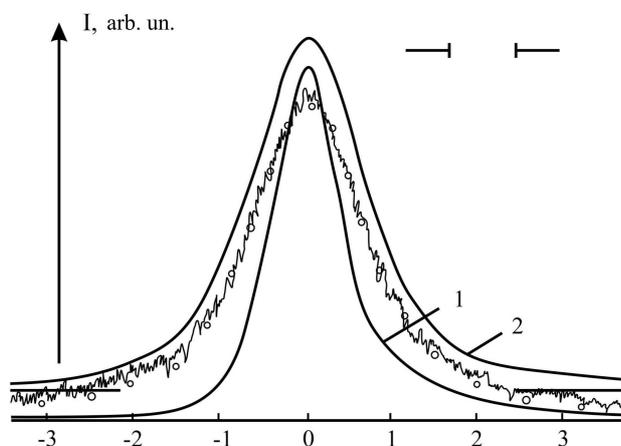


Fig. 1. Band $\nu_1 = 2916.5$ CH_4 contour at 295 K: 1 – $\rho = 20$ Amagat, 2 – 85 Amagat, 3 – observed contour at 118 Amagat (points denote the Voigt contour, being a result of the convolution of the true Lorentz contour, whose half-width is 1.5 cm^{-1} , with a Gaussian apparatus function, whose half-width is 0.8 cm^{-1})

2. Experimental Part and Calculations

The RS spectra of the ν_1 band of methane and its mixtures with Ar and Kr in the gaseous phase were studied with the help of a spectrometer DFS-24. The studies were carried out with using the cuvette of a special construction which was described earlier in [1]. Light scattering was excited by an Ar laser in the 90° -geometry of scattering. According to [2], the band which corresponds to the fully symmetric vibration ν_1 for methane is completely polarized, and that is why we did not use any polarization devices to extract polarized components of the band. The obtained experimental results were corrected for the apparatus distortion [3]. The positions of bands and their half-widths were determined to within $\pm 0.1 \text{ cm}^{-1}$.

The calculations of the bond's lengths, depolarization ratios of bands, as well as structures of molecular aggregates were carried out by Gaussian-98W software in RHF-6-31G(d,p) approximation [4]. On the base of this approximation, one cannot reach a complete agreement between the calculated vibration frequencies and the experimental data. To compare the calculated data with the experimental ones, it is necessary to introduce a scale factor $Sf = \nu_{\text{exp}}/\nu_{\text{calc}}$ which was equal to 0.92 in our case.

3. Results and Discussion

At the lowest studied densities, the band ν_1 of methane represented an asymmetric contour typical of the Q-

branch with a degraded discrete structure. With increase in the density, the band loses its asymmetry and is broadened (Fig. 1).

Starting from ~ 50 Amagat (and higher), the observed contour of the ν_1 band becomes symmetric and can be described in the scope of 3–4 half-widths of the Voigt curve (Fig. 1). We suppose that, under such conditions, the real contour of the band is of Lorentz's shape. At the lowest temperatures and high densities, the band is asymmetric again, but the character of asymmetry is different: the intensity of the low-frequency wing of the band increases with respect to the high-frequency one.

As a peculiarity, we note that the contour of the ν_1 band of CH_4 in the gaseous phase at densities up to 10 Amagat does not change its half-width for all studied systems. At higher densities, the half-width increases linearly with the density for all studied temperatures. However, the broadening coefficient k ($\text{cm}^{-1}/\text{Amagat}$) changes with variation in the temperature and the nature of a buffer gas. The magnitude of the broadening coefficient k is about $(0.6 \div 3.5) \times 10^{-2} \text{ cm}^{-1}/\text{Amagat}$. The linear broadening of the band ν_1 of CH_4 with increase in the pure gas density at room temperature was also observed earlier in [5–7]. At the same time, the magnitude of the broadening coefficient obtained in our work at room temperature is in good agreement with the results of previous studies in the limits of experimental errors. For all temperatures, there is the following relation between the broadening coefficients:

$$k(\text{CH}_4 + \text{CH}_4) \approx k(\text{CH}_4 + \text{Kr}) > k(\text{CH}_4 + \text{Ar}).$$

The variation of temperature leads to qualitatively the same change of the half-width for all studied systems. With increase in the temperature from 140 K to some T_{min} , k decreases and reaches the minimum at the temperature T_{min} which depends on a buffer gas. After that, the k starts to increase.

What is the reason of such a behavior of the ν_1 band of methane? Taking into account the previous investigations, theoretical predictions, and our studies of the ν_1 band contours of methane by isotropic Raman scattering, we can conclude that, side-by-side with rotational-inelastic collisions, there is a contribution to the broadening of the Q-branch contour from collisions which change the character of vibrational motion. Among them, we can indicate the following: 1) Collisions which occur without change of the vibrational energy and lead to the simple vibrational dephasing; 2) Collisions with losses of the vibrational energy; in this

case, a) the vibrational energy can be spent to excite the external degrees of freedom; b) there may occur the intermode energy exchange in a polyatomic molecule.

We made an attempt to investigate the nature of the vibrational broadening observed in the spectra of CH_4 . The closeness of the broadening coefficients in the spectra of CH_4 and the CH_4+Kr mixture allows us to suppose that the dispersion interactions are effective in vibrational disturbances (polarizabilities of CH_4 and Kr are close to each other). It is a rather simple thing to estimate the broadening coefficient which is related to the dephasing. According to [8], we calculated the broadening coefficients k which are related to the dephasing of vibrations under the influence of dispersive forces.

The calculated magnitudes of k for CH_4+CH_4 , CH_4+Ar , and CH_4+Kr are presented in Table 1. These magnitudes are several times less than those obtained in experiments.

We note that the Strekalov–Burshtein model [9] predicts a non-monotonic dependence of k of a vibrational band, which is related to the dephasing due to temperature. It was shown that the reason for such behavior can be an influence of the attraction forces, whose relative role is temperature-dependent, on the kinematics of collisions. The calculated dependence [9] of the broadening coefficients on temperature for pure methane does not provide the satisfactory numerical agreement with experiment. The qualitative behaviors of the theoretical and experimental curves are the same, but the calculations give a much weaker dependence than it occurs in experiment.

The above-presented arguments testify, at least qualitatively, that the dephasing under the influence of the dispersive interaction changes the magnitude of the broadening coefficient of the band of isotropic Raman scattering in methane. However, the observed quantitative differences in the theoretical estimations and experimental results make us suppose that this mechanism does not exhaust all features of the broadening effect.

In order to make clear the interactions of a CH_4 molecule with other particles, we carried out *ab initio* calculations on the base of the above-mentioned

Comparison of calculated [8] broadening coefficients k ($10^{-2} \text{ cm}^{-1}/\text{Amagat}$) of the CH_4 band with experimental results at 295 K

		Buffer gas			
CH_4+CH_4		CH_4+Kr		CH_4+Ar	
Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
1.1 ± 0.1	0.16	1.1 ± 0.1	0.23	0.7 ± 0.1	0.14

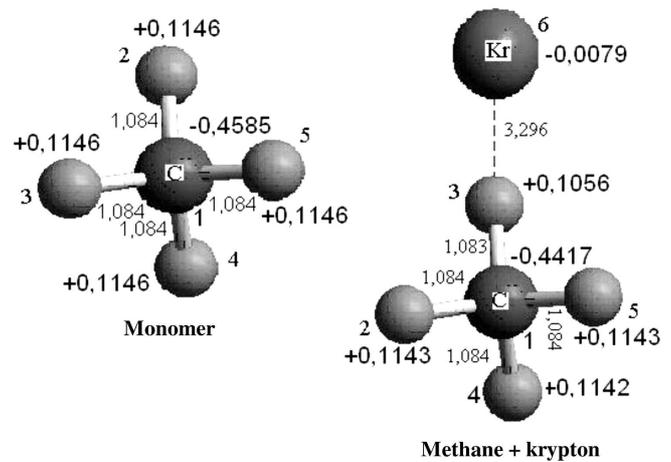


Fig. 2. Structure of a methane molecule and the methane-krypton aggregate (charges are given in electron charge units, distances in Å)

software. The calculations were carried out for an isolated monomer molecule, two interacting CH_4 molecules, and for an isolated methane molecule with one Kr atom. For a monomer methane molecule, the calculations gave the same length of the C–H bond: 1.084 Å (Fig. 2). The charges of all H atoms appeared to be equal to +0.1146; whereas the charge of a C atom appeared to be –0.4585 (in electron charge units). The fully symmetric vibration frequency was 3168.8 cm^{-1} (scaled factor $\text{Sf}=2916.5/3168.8=0.92$) with zero depolarization ratio. As was said above, the interaction of two CH_4 molecules must be of dispersion character. One of the C–H bonds of both interacting molecules appears to be different from other C–H bonds. The charges of H atoms of the bonds differ from the charges of other H atoms. For the aggregate of two CH_4 molecules, the vibration frequency ν_1 (3168.7 cm^{-1}) is not changed practically with the practically zero depolarization ratio (0.0004).

It is worth to note that there is an interaction between a CH_4 molecule and a Kr atom (Fig. 2). Due to the absence of dipoles both in CH_4 and Kr, the interaction must be of dispersion character. However, the interaction of CH_4 and Kr has some directedness. We note that the formation of complexes with the participation of atoms of inert gases was considered in [10]. In that work, the authors studied the problem of the formation of $\text{HF} \dots \text{Xe}$ complexes and their manifestation in infrared spectra. In our case, a Kr atom approaches a CH_4 molecule along one of the C–H bonds (H(3) in Fig. 2). The distance of C–H(3) ... Kr(6) is 3.296 Å. The H(3) atom, C(1) atom, and Kr(6) atom lie rather

linearly. The properties of the C—H(3) bond are slightly different from those of other three C—H-bonds: the C—H(3) bond is slightly shorter. The charge of the H(3) atom is also different from the charges of other three H atoms. In the process of interaction, the atom of Kr gains a small negative charge. The ν_1 vibration band with the wave number 3171.5 cm^{-1} corresponds to the CH₄—Kr aggregate. This is higher by 2.5 cm^{-1} than that for pure methane.

Really, the interaction of CH₄ molecules with Kr atoms must be much more complicated. Moreover, this complication must increase with increase in the medium density. At a higher pressure, two or more Kr atoms may appear near the given CH₄ molecule. In this case, the vibration frequency ν_1 may be changed (although insignificantly). This circumstance, obviously, should be accounted in the discussion of the contour's shape and its change with increase in the pressure. The ν_1 contour shape of methane under the application of an external pressure will be determined not only by the break of the rotational motion on a collision, the rotational energy relaxation, the shock dephasing, and the transfer of the energy of vibrations to the internal and external degrees of freedom, but also by the possible split of the band as a result of the formation of unstable aggregates.

For the formation of a dimer of two methane molecules and for the formation of a methane-krypton aggregate, the energy gain must be small. The thermal motion of particles will disturb such an orientation. Moreover, in compressed gases, one should take the environment of interacting molecules into account. Unfortunately, we could not do that. It is interesting that though the interaction energy is small, the calculations give the following magnitudes for the frequencies of mutual vibrations of molecules: for the formation of CH₄—Kr — 43.6 cm^{-1} , and for the formation of CH₄—CH₄ — 10.4 cm^{-1} .

4. Conclusions

1. The contour of the ν_1 band of methane and its gaseous mixtures with increase in the pressure loses, first of all, its discrete structure and then broadens. Starting from ~ 50 Amagat, the observed contour is described in the limits of 3–4 half-widths by the Voigt curve with the Lorentzian shape.

2. At all temperatures, the broadening of the band has linear character with the broadening coefficient $(0.6\text{--}3.5) \times 10^{-2} \text{ cm}^{-1}/\text{Amagat}$.

3. There is a qualitative agreement of the behavior of the broadening coefficient of the ν_1 band with the theoretical prediction; however, the numerical agreement is absent.

4. In the CH₄—Kr mixture, there is a weak directed interaction between a methane molecule and a Kr atom. The Kr atom approaches the CH₄ molecule along one of the C—H bonds.

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КОНТУР ПОЛОСИ ν_1 У СПЕКТРАХ КОМБІНАЦІЙНОГО РОЗСІЯННЯ МЕТАНУ ТА ЙОГО ГАЗОВИХ СУМІШЕЙ З Ar ТА Kr

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Р е з ю м е

Вивчено спектри комбінаційного розсіяння смуги ν_1 чистого метану CH₄ та його сумішей з Ar та Kr у газовій фазі в інтервалі температур 160–360 К та тисків 4–160 атм. За низьких тисків смуга має типовий для Q-вітки асиметричний контур з розмитотою дискретною структурою. Починаючи від густини близько 50 Амага і вище, контур має форму Лоренца. Визначено коефіцієнти розширення k смуги, значення яких із збільшенням тиску задовольняють співвідношення $k(\text{CH}_4 + \text{CH}_4) \approx k(\text{CH}_4 + \text{Kr}) > k(\text{CH}_4 + \text{Ar})$. Для всіх вивчених систем із збільшенням температури коефіцієнт розширення смуг спочатку зменшується, а потім збільшується. Поведінку смуги ν_1 метану в досліджених умовах пояснено коливальним релаксаційним процесом та дефазуванням коливань. За програмою Gaussian 98W розраховано структуру ізольованих агрегатів CH₄—Kr.