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# VIBRATIONAL-ROTATIONAL INTERACTION IN MOLECULES OF THE SPHERICAL TOP TYPE

*We show that, in the Raman spectrum of very low-density gases, the Q branch of the $nu_1$ band of methane and deuteromethane has asymmetric contour. With increase in the gas density, the band contour becomes more symmetric and broadens. The band shape is described by the Voigt curve. Possible mechanisms of the vibrational broadening of $\nu_1$ – dephasing and intermode exchange of vibrational energy – are analyzed. Both mechanisms may be efficient in the band broadening.*

*K e y w o r d s:* Raman spectra, spherical top, vibrational-translational interaction.

## 1. Introduction

In recent years, a number of methods for studying the structure of molecules have been developed. The results are of a very general meaning, and the application of theories and principles that have been made on the basis of these studies, marks a new phase in the development of physics, chemistry, and biology. Spectroscopic studies of the patterns of the interaction of electromagnetic waves with matter accompanied by the processes of absorption, emission, and scattering of light gave a lot in understanding the structure and intermolecular interactions in liquid media. As objects of spectroscopic investigations, a variety of substances found in all states of aggregation can be used. In the simplest case of a rarefied gas, the average distance between molecules is so large that they can be regarded as isolated from one another. The most complex cases are condensed substances, in which each particle is influenced by the forces of intermolecular interaction (IMI). From spectroscopic data, it is possible to obtain information about the structure and properties of molecules and intermolecular interactions and, hence, about the structure of matter in general. In particular, the vibrational-rotational spectra of molecules are the only source of complete and reliable data about the internal states and physico-chemical properties of molecules. They carry information about the structure, intramolecular dynamics, and electrooptical properties of molecules, which are widely used in solving the problems of the interaction of radiation with matter. Extracting this information from experimental high-precision studies is one of the fundamental problems of molecular spectroscopy [1].

The contours of bands of the isotropic Raman scattering (RS) of molecular gases contain a lot of information about the vibrational-rotational energy states of molecules and about intra- and intermolecular interactions. This situation points to the need for a further study of isotropic RS spectra. The accumulation of experimental data establishing the correlation between shapes and contours of the parameters characterizing the properties of the medium and their comparison with the available theories is of significant interest. Here, we present the results of experimental investigations of the band contours in the isotropic Raman spectra of dense gases for spherical top molecules of methane and deuteromethane ($CH_4$, $CD_4$) and address the factors influencing the formation of the band contour.

## 2. Experimental

The Raman spectra of the investigated systems were recorded by a DFS-24 spectrometer. We used a high-pressure cell thermostat. The light source for the excitation of Raman spectra were argon lasers with a

power of $0.1 \div 0.5$ W in the line at 488.0 nm. In recording the spectra, the instrumental function half-width varied in the interval $0.8 \div 4$ cm$^{-1}$ depending on the object under study. The experiment was conducted over a wide temperature interval $140 \div 360$ K at pressures of 4–160 atm.

## 3. Results and Discussion

It is known that the molecules of the spherical top and homonuclear diatomic molecules cannot give a pure rotational spectrum in the Raman spectra. The polarizability tensor of a rigid spherical top is isotropic. Therefore, the pure rotational spectrum of spontaneous Raman scattering is forbidden. For the first time, the spherical top molecules, for which the Raman spectrum was investigated with high resolution, were molecules of methane [2]. The spectrum of methane in the infrared region was also studied with high resolution, thus providing the majority of the fundamental tones of molecular vibrations, many overtones of these vibrations, and composite frequencies. Despite the numerous studies of scattering spectra and the infrared absorption, the results were so complex that a reliable analysis of all fine details have not yet carried out.

In [3], the authors attempted to resolve the structure of the band $\nu_1$ (2916 cm$^{-1}$) of methane, but the goal was not achieved. In [2], the structure of the band was first resolved, and the authors gave its theoretical interpretation. It was also indicated the possibility of observing the pure rotational spectra of a spherical top in the CARS method.

The frequencies of $Q(J)$ lines, corresponding to the transitions with $\Delta J = 0$, in the spectra of linear and spherical molecules are described in the first approximation by the following relation:

$$\nu_{\mathrm{Q(J)}} = \nu_0 - \alpha_1 J(J+1),$$

where $\nu_0$ is the frequency of a pure vibrational transition, and $\alpha_1$ is the constant of the vibration-rotation interaction.

The structure of the isotropic $Q$ branch is such that, in the case of $\alpha > 0$, the band has a shading toward lower frequencies. When $\alpha < 0$, the shading occurs in the direction of high frequencies.

The bands $\nu_1$ of CH$_4$ and CD$_4$ have the structure [4–7], which is more complex than that predicted by the theory for molecules that are a randomly spherical top. This structure is associated with a tetrahedral
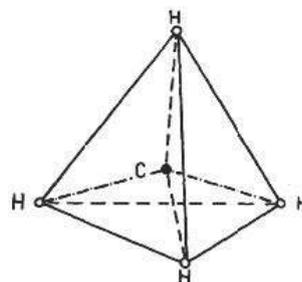


***Fig. 1.*** Structure of methane molecule

splitting of degenerate rotational states. The structure of a methane molecule is particularly important for the whole organic chemistry, as it is connected with the main ideas regarding carbon atoms.

Since the work by Pasteur, van't Hoff, and Lebel, it has been common idea of the tetrahedral structure of a methane molecule for many years. It was assumed that the carbon atom is at the center of the tetrahedron, and four hydrogen atoms are at the tops of the tetrahedron (Fig. 1) [8].

The interpretation of the observed lines with regard for the tetrahedral splitting and the centrifugal tension has led to a constant $\alpha_1 = -0.009$ cm$^{-1}$ for CH$_4$ and $\alpha_1 = -0.223$ cm$^{-1}$ for CD$_4$, which qualitatively explains the direction of shading of the $Q$ branch and the bandwidth at relatively low gas densities. Later, it was shown that, with a proper identification of the band structure, whose characteristics are not in conflict with properties of the force field of the molecule, it is necessary to consider the interaction of Coriolis oscillations $\nu_1(A_1)$ with $(\nu_2 + \nu_4)(F_1 + F_2)$ and the Fermi resonance between the oscillations $\nu_1(A_1)$, $2\nu_2(A_1)$ and $2\nu_4(A_1)$. The true value of $\alpha$ was found to be $0.038$ cm$^{-1}$ for CH$_4$ and $0.0138$ for CD$_4$.

In our experiment at the lowest densities, the investigated band was typical of the $Q$ branch with the asymmetric contour and a fuzzy discrete structure that becomes more symmetric and broadens, as the density increases (Figs. 2–4).

At high densities ranging from 50 Amagat units (and above), the observed contour of the $\nu_1$ band was symmetric and described by the Voigt curve.

In all the systems studied, the contour of the $\nu_1$ band broadens with increase in the density.

Possible mechanisms of the vibrational broadening of the $\nu_1$ band in the isotropic RS of CH$_4$ and CD$_4$ are dephasing and intermode exchange of vibrational
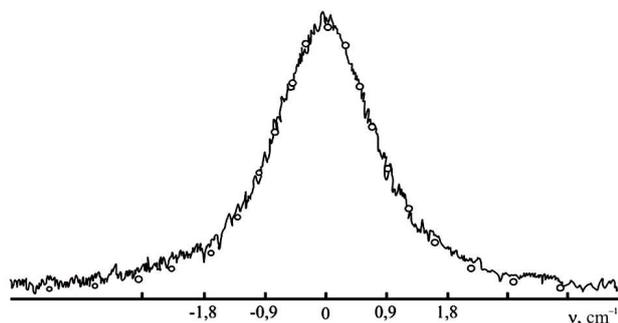
**Fig. 2.** Observed contour of band $v1$ of $CH_4$ at $\rho = 118$ Amagat units and $T = 295$ K. ∘ ∘ ∘ – Voigt contour, which is the convolution of Lorentzian and Gaussian curves with half-widths of 1.5 cm$^{-1}$ and 0.8 cm$^{-1}$, respectively
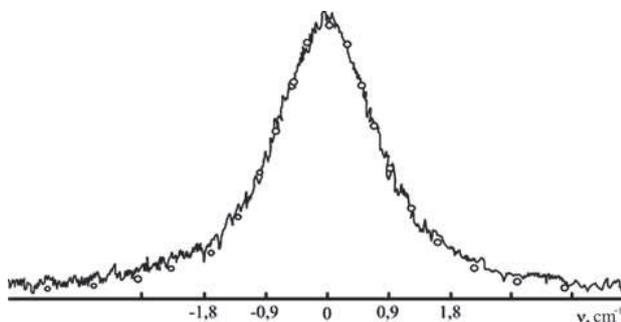


**Fig. 3.** Registered contour of the $\nu_1$ band of $CH_4$ at $T = 200$ K: *1* – $\rho = 74$ Amagat units, *2* – $\rho = 120$ Amagat units
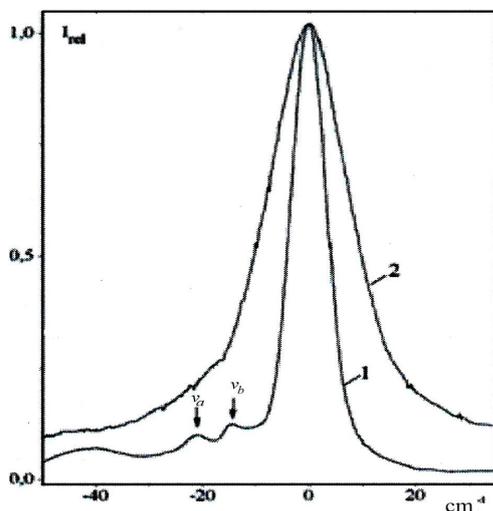


**Fig. 4.** Spectrum of of $CD_4$ in the region of $\nu_1$ at 295 K (*1* – pure $CD_4$ at 4 Amagat units, *2* – $CD_4$ + Ar at 144 Amagat units). $\nu_a$ and $\nu_b$ – the bands of impurities – deuteroethhanes ($C_2HD_5$ and $C_2D_6$)

energy, and it was shown that they can be effective in broadening of the studied bands.

The rotational and vibrational movements in a molecule are not independent. At molecular vibrations, there is a change in molecule's moments of inertia. Therefore, the rotational energy levels of the vibrating molecules differ from the corresponding levels of the "rigid" molecules – molecules with fixed nuclei.

In the degenerate vibrational state, the vibrational-rotational interaction leads to stronger effects. This is due to the presence of the vibrational angular momentum in the degenerate vibrational state. Since the vibrational transitions occur at higher vibrational energies than rotational (the former are associated with a significantly higher energy than the latter) vibrational transition is likely to be accompanied by rotational transitions. This fact has a great influence on the shape of the spectrum and is found in the spectra obtained in the gas phase at low pressures as the rotational fine structure superimposed on the vibrational spectrum. In the liquid phase, the rotational levels are outraged molecular interactions and collisions. So, instead of a fine structure detected in the gas phase, only the broadening of the vibrational bands is observed in the liquid phase. Often, the envelope shape is similar to the band broadened rotational fine structure observed in the gas phase. In other cases, the liquid phase arising in the interaction can completely change the form of a strip. In the crystalline solid phase at low temperatures, the molecular rotation cannot be implemented, the fine structure disappears completely, and the vibrational bands are very sharp.

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КОЛИВАЛЬНО-ОБЕРТАЛЬНА ВЗАЄМОДІЯ
В МОЛЕКУЛАХ ТИПУ СФЕРИЧНОЇ ДЗИҐИ

Р е з ю м е

У роботі встановлено, що в спектрах комбінаційного розсіювання світла при наднизькій густині газу $Q$-гілка коливальної смуги $\nu_1$ метану і дейтерометану має асиметричний контур. Зі збільшенням густини газового середовища зазначена смуга стає більш симетричною і уширюється. Форма контуру смуги описується згорткою Фойхта. Проаналізовано можливі механізми коливального уширення смуги $\nu_1$, такі як дефазування і міжмодовий обмін коливальною енергією. Доведено, що обидва механізми можуть бути ефективними в уширенні смуги, що спостерігається.