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RAMAN SCATTERING SPECTRA OF LIQUID BROMOFORM AND ITS SOLUTIONS

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In the Raman spectra, the vibration bands of bromoform in solutions of proton-donor solvents at 537 and 3020 cm⁻¹ undergo significant changes, which are associated with the aggregation of molecules of bromoform with solvent molecules (pyridine, nitrobenzene, nitromethane). There is a high frequency shift of the band of C–H vibrations of bromoform in such solvents. However, even at the maximum frequency shift, the frequency of C–H vibrations is less than the frequency of the vibration in the gas phase. In a neutral solvent (heptane), the width of the band of C–H vibrations decreases with a small high-frequency shift (~2 cm⁻¹). Changes of the parameters of C–Br vibrations in the Raman spectra show that these vibrations are subjected to the indirect influence of the formation of hydrogen bonds between CHBr₃ molecules and the molecules of proton-donor solvents.

Keywords: hydrogen bond, molecule, vibration, frequency, Raman spectra, hydrogen bond length, intermolecular hydrogen bond.

1. Introduction

Proton-donor ability of bromoform should be much less pronounced as compared with chloroform. Meanwhile, even for chloroform, not all spectroscopic data on the ability to form intermolecular hydrogen bonds are understood [1–10]. There is the evidence that the intermolecular hydrogen bonds exist in pure chloroform [6]. Due to the smaller proton-donor ability, the intermolecular interactions of bromoform CHBr₃ with a proton acceptor should be seen in the spectra less clearly than in the case of chloroform. In this work, we present the results of a study of intermolecular interactions in solutions of bromoform by Raman scattering (RS). We study the scattering spectra of CHBr₃, as well as its solutions in heptane, pyridine, nitrobenzene, and nitromethane. For the study, we selected strongly polarized lines at 3022 cm⁻¹ and 537 cm⁻¹ corresponding, respectively, to C–H and C–Br vibrations of molecules [11]. In the case of solutions with pyridine, we also investigated the line at 992 cm⁻¹ of pyridine, which is known to be very sensitive to

the formation of intermolecular associates including chloroform [10].

The hydrogen atom of a C–H bond of molecules is usually not active in the formation of an intermolecular hydrogen bond. However, in case of chloroform, bromoform, formic acid, and some other cases because of the presence of a highly electronegative environment of atoms, the hydrogen atom of a C–H bond is under particular conditions. The distribution of the electron cloud in the bond is such that hydrogen can participate in the formation of an intermolecular hydrogen bond. In the literature [1–9], there is no clarity on this issue.

The Raman spectra were measured on an automated spectrometer DFS-52 with the use of diffraction gratings 1800 lines/mm. Light scattering was excited by an argon laser LGN-503 with $\lambda = 4880 \text{ \AA}$ at in 90° geometry. The polarized components of lines were selected by a polarizer and a depolarizing wedge, the last was set after the exit slit of a spectrometer. The apparatus function was accounted by the method from [12].

We used chemically pure reagents with further purification. All measurements were carried out at a temperature of 20 °C.

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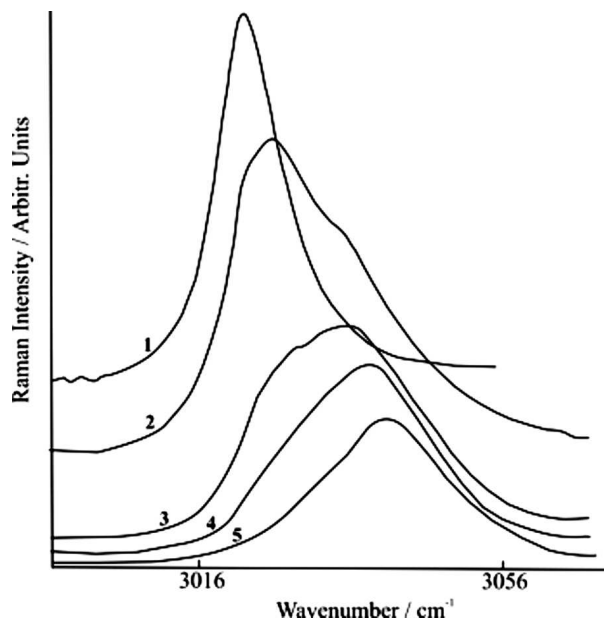


Fig. 1. Shape of the contour of the line of C–H vibrations of bromoform in pure liquid (1) and in solutions with nitromethane (respectively, the contents of CH_3NO_2 are 0.5, 0.7, 0.8, and 0.9 m.f. The intensities are not reduced to a single scale

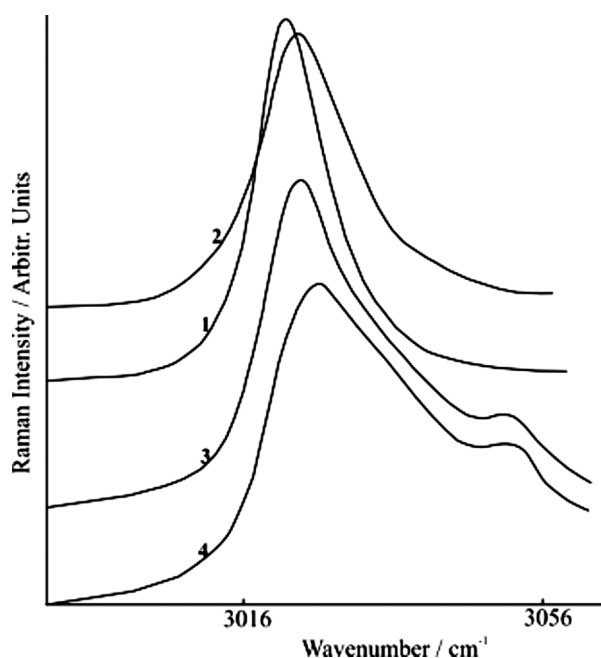


Fig. 2. Shape of the contour of the line of C–H vibrations of bromoform in a solution with nitrobenzene: pure bromoform (respectively, the isotropic and anisotropic components) 1 and 2; solutions in nitrobenzene (contents are, respectively, 0.3 and 0.5 m.f.) 3, 4

2. Experimental Results and Discussion

Qw now briefly discuss the shape and width of the lines in pure bromoform. Both lines are highly polarized with the depolarization ratio $\rho = 0.03$ for 537 cm^{-1} and $\rho = 0.10$ for the line 3022 cm^{-1} . We should note that, for the line 3022 cm^{-1} , the frequency of the maximum of the perpendicular polarized component is shifted as compared with the maximum of the parallel component by 1.5 cm^{-1} in the direction of higher frequencies, as there is for chloroform [13–14]. This shift has been previously observed for other compounds [15–16]. Separating the lines into the isotropic and anisotropic components [17] gives, respectively, the value of 10.3 cm^{-1} and 12.7 cm^{-1} for the half-widths. Taking these values of the half-widths, we calculate the vibrational and orientational relaxation times, by assuming the absence of interaction of molecular vibrations with their reorientations, to be, respectively, $\tau = 1.0$ and $\tau = 4.4$ ps. Similar calculations for the line 537 cm^{-1} give for these values, respectively, $\tau = 3.7$ and $\tau = 1.8$ ps. We note that the values obtained times for the relaxation of the orientational correlations are close to those of the anisotropy relaxation time determined from the Rayleigh line [18].

Let us turn to the study of the Raman line 3022 cm^{-1} in solutions of bromoform. The results could only be obtained for solutions with nitromethane, nitrobenzene and heptane. The most favorable conditions, when CHBr_3 is diluted in proton-acceptor solvents, are in the case of nitromethane (Fig. 1). It should be noted that similar results were obtained for solutions CHBr_3 – nitrobenzene (line 3051 cm^{-1} of nitrobenzene is somewhat complicated for the experiment) (see Fig. 2). Unlike many other proton-acceptor solvents, there is the high-frequency shift of C–H vibrations of bromoform in nitromethane and nitrobenzene. The maximum of the band shifts upon the dilution of CHBr_3 in nitromethane to 0.1 m.f. to 3041 cm^{-1} . The change of the shape of the band is original. At a low dilution of CHBr_3 in nitromethane, the band is asymmetric in the high-frequency side; at a chloroform concentration of 0.4 m.f., the band is more or less symmetric, but broadened. At still higher dilution, the asymmetry is shifted to lower frequencies.

Considering the data for a chloroform-nitrobenzene solution [19–20], the concentration change in the band

at 3022 cm^{-1} in a CHBr_3 – nitromethane solution can be explained by complexity of the band, the presence of a doublet structure, components of which corresponds to the monomers (low-frequency component) and associated molecules of bromoform (high-frequency component). Due to the increase of the high-frequency component intensity with the dilution of bromoform, the total band is shifted toward higher frequencies. Note that the forms of various polarized components of the band (for example, for an equimolar mixture) are different. In addition, the frequency dependence of the depolarization ratio within the band is asymmetric relative to the maximum of the band. This means that the depolarization ratios of the constituting lines are different.

The fact that the band shifts to higher frequencies cannot cause confusion. In fact, the position of the line of C–H vibrations of methane in the gas phase is generally higher than in the liquid state. Therefore, although there is a high frequency shift of C–H vibrations (for example, a solution of chloroform-nitrobenzene [19]), however, the frequency of vibrations is less than for the gas. Somewhat unexpected is the fact that the frequency of C–H vibrations in associates is higher than the frequency of vibrations of the monomers. According to [6], the high-frequency shift of C–H vibrations of chloroform was also observed in solvents such as acetone and water; and, for bromoform, in cyclohexane and CCl_4 [20]. Here are details on the half-widths of C–H vibrations of monomers and associated molecules. By assuming that we have only monomeric molecules in pure bromoform and only associated molecules in a solution with nitromethane at a high dilution (0.1 m.f.), the values of frequency and half-width (without polarization decomposition) are 3022.7 cm^{-1} and $\Delta\nu = 10.3\text{ cm}^{-1}$ for monomers and 3041 cm^{-1} and $\Delta\nu = 18.3\text{ cm}^{-1}$ for associates. As one can see, the half-widths are too large, and it is impossible to resolve clearly the structure of the band.

The concentration dependence of the 537-cm^{-1} line half-width for bromoform in a solution with nitromethane is shown in Fig. 3. For this line, as well as for the line at 3022 cm^{-1} , we observe the high-frequency shift (3.5 cm^{-1}) in the solution. It is worth note changes of the line width: with the dilution of bromoform, the line width first increases, then passes through a maximum; with a further dilution, there is a decrease of the line width. The picture is very simi-

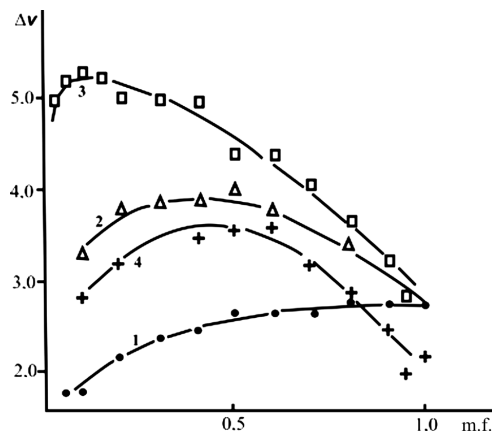


Fig. 3. Dependence of the width of the Raman lines on the concentration of a mixture: the line at 541 cm^{-1} of bromoform in, respectively, heptane, nitromethane, and pyridine 1, 2, 3, the line at 992 cm^{-1} in pyridine 4

lar to that observed for the line at 667 cm^{-1} of chloroform in solutions with proton-acceptor solvents [6]. In CHCl_3 solutions with pyridine, the doublet character of this line was shown. Vibrations with a frequency of 537 cm^{-1} of bromoform are similar to vibrations at 667 cm^{-1} of CHCl_3 [11]. Therefore, there is the reason to suggest that the shape of changes of the line half-width at 537 cm^{-1} with varying the concentration is associated with the presence of the overlapped lines of monomers (low-frequency component) and associates (high-frequency component) of molecules and a change in the ratio of intensities of the corresponding lines with varying the concentration.

It is clear that Br atoms in bromoform and in solutions with nitromethane do not participate in the formation of H-bonds. The splitting of the line at 537 cm^{-1} is a result of the indirect participation of the hydrogen of a C–H group in the formation of the intermolecular hydrogen bond. In the neutral solvent (heptane), the line width at 537 cm^{-1} behaves in the usual way with increase in the dilution – the dilution of bromoform reduces the line width (Fig. 3) with a small high-frequency shift ($\sim 2\text{ cm}^{-1}$), i.e. the behavior is similar to that expected for the behavior of the line at a dilution of the substance in a neutral solvent.

Finally, we discuss the behavior of the line at 537 cm^{-1} in the other proton-acceptor solvent – pyridine. There also was a slight high-frequency shift (1.5 cm^{-1} at the concentration of 0.05 m.f.) of the line. But, as in the case of solutions with nitromethane, the line width at 537 cm^{-1} passes through a

maximum, which is at a concentration of 0.1 m.f. of bromoform. The explanation is similar to that for the bromoform-nitromethane solution: the band is a result of the overlapping of lines of monomer bromoform molecules and bromoform-pyridine associates. The difference in the frequencies of the lines in comparison with those for chloroform-pyridine solutions is small ($\sim 1.5 \text{ cm}^{-1}$). In view of the line widths of 2.85 cm^{-1} for monomeric molecules and 5 cm^{-1} for associates, it is impossible to resolve them. The formation of associates in the system is manifested in the study of the line at 992 cm^{-1} of pyridine (Fig. 2). For chloroform solutions in pyridine, a split of the line ($\sim 2.5 \text{ cm}^{-1}$) into the lines of monomers of pyridine and associates is clearly observed [10].

In the case of bromoform-pyridine solutions, a clear split of lines of monomers and associates is not observed under any conditions. However, the behavior of the concentration dependence of the line width at 992 cm^{-1} and its high-frequency shift suggest the complexity of the band: the presence of the lines of monomers and associates of pyridine.

3. Conclusions

The above data indicate that there are many spectroscopic evidences that bromoform can form the hydrogen bond with proton-acceptor molecules, but this proton-donor ability is expressed much lower than that of chloroform. Just as for chloroform, the formation of intermolecular associates of bromoform in the case of certain proton acceptors may increase the frequency of C-H vibrations, which is due, in our opinion, to the peculiarities of the charge distribution in the interacting molecules.

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СПЕКТРИ КОМБІНАЦІЙНОГО РОЗСІЮВАННЯ РІДКОГО БРОМОФОРМУ І ЙОГО РОЗЧИНІВ

Резюме

В спектрах комбінаційного розсіювання смуги коливання бромоформу 537 та 3020 cm^{-1} в розчинах з протон-акцепторними розчинниками зазнають істотних змін, що зв'язується з агрегацій молекул бромоформу з молекулами розчинника (піридин, нітробензол, нітрометан). Має місце високочастотний зсув смуги C–H коливань бромоформу в таких розчинниках. Однак, навіть при максимальному частотному зсуві частота C–H коливань виявляється менше, ніж частота цього коливання в газовій фазі. У нейтральному розчиннику (гептан) смуга C–H коливань зменшує свою ширину при невеликому високочастотному зсуві ($\sim 2 \text{ cm}^{-1}$). Зміна параметрів C–Br коливань в спектрах КР показує, що ці коливання зазнають опосередкованого впливу виникнен-

ня водневого зв'язку між молекулами CHBr_3 і молекулами протонодонорних розчинників.

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СПЕКТРЫ КОМБИНАЦИОННОГО
РАСSEЯНИЯ ЖИДКОГО БРОМОФОРМА
И ЕГО РАСТВОРОВ

Резюме

В спектрах комбинационного рассеяния полосы колебаний бромформа при 537 и 3020 см^{-1} в растворах с протоноакцепторными растворителями претерпевают существен-

ные изменения, что связывается с агрегацией молекул бромформа с молекулами растворителя (пиридин, нитробензол, нитрометан). Имеет место высокочастотный сдвиг полосы C-H колебаний бромформа в таких растворителях. Однако, даже при максимальном частотном сдвиге частота C-H колебаний оказывается меньше, чем частота этого колебания в газовой фазе. В нейтральном растворителе (гептан) полоса C-H колебаний уменьшает свою ширину при небольшом высокочастотном сдвиге ($\sim 2 \text{ см}^{-1}$). Изменение параметров C-Br колебаний в спектрах КР показывает, что эти колебания испытывают опосредственное влияние образования водородной связи между молекулами CHBr_3 и молекулами протонодонорными растворителями.