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MANIFESTATION OF INTERMOLECULAR INTERACTIONS IN RAMAN SPECTRA AND *AB INITIO* CALCULATIONS OF MOLECULAR AGGREGATION IN LIQUID ETHYLENE GLYCOL

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We present the results of a study of intermolecular interactions in ethylene glycol by Raman spectra. For a more reasonable assumptions about the possibility of the existence of aggregated intermolecular complexes and monomeric molecules of ethylene glycol in the liquid, as well as manifestations of these formations in spectra, we carried out ab initio calculations of the normal vibration frequencies, depolarization ratios of bands, formation energy, and other physical and optical characteristics for aggregated complexes of molecules. Calculations were carried out in the framework of a self-consistent field (RHF) using the basis 6-31G++(d, p) with full optimization of the geometry of molecules. Calculations showed a possibility of the formation of an intermolecular H-bond between the H atom of the O–H group of one molecule and the O atom of another molecule. For a dimeric aggregate, the intermolecular H-bond length is 1.986 Å. In molecules of the dimer, there is a slight change of bonds' lengths, but also there is a significant change of the charge distribution between atoms. The energy of dimer formation is 4.6 kcal/mole, the dipole moment of an aggregate is 6.35 D (in the monomeric molecule, the dipole moment is 2.73 D). In Raman spectra, there are some features of the manifestation of the H-bonding between molecules: asymmetry of bands and splitting of bands that are the features that accompany the H-bond formation.

Keywords: liquids, Raman spectra, molecular aggregation, ethylene glycol.

1. Introduction

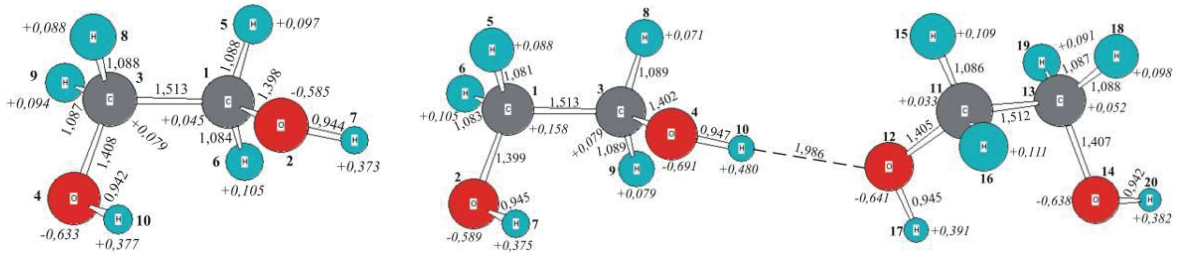
In the ethylene glycol molecule, there are two CH_2OH groups of atoms combined by a simple bond with each other through the carbon atoms. Therefore, these groups can rotate with respect to each other, or there is a possibility for different configurational isomers [1]. In this regard, although CH_2OH groups are identical, the relative position of O–H bonds is such that these CH_2OH groups of a monomer must be slightly different with respect to the charges of atoms and the bond lengths between atoms (see Fig. 1, *a*). Anyway, the hydrogen atoms of O–H groups can form a hydrogen bond. There are two such groups. Therefore, we have made calculations for the dimer formation in a case where one of the O–H groups is involved.

There is an interest in the structure of an aggregate of molecules formed by H-bonding. In Raman spectra, we studied a fragment of the spectrum, which contains, in our opinion, some features of the formation of a simple H-bond.

2. Experimental Technique and Method of Quantum-Chemical Calculations

Raman spectra were recorded with the help of an automated spectrometer DFS-52, which is a double monochromator with two gratings 1200 lines/mm. The excitation source was an Ar^+ ion laser LGN-503 with a wavelength of 488 nm and an output power of 1 W. All measurements were performed at the transverse (90°) scattering geometry with polarized exciting light. The measurements were made at a temperature of 20 °C. In the experiment, we used a chemically pure substance, which was subjected to additional distillation under vacuum. Errors in the determination of a bandwidth and a relative position of the bands were ± 0.3 cm^{-1}.

Quantum-chemical calculations were carried out in the B3LYP (DFT) approximation with a set of



a *b*

Fig. 1. Calculated structure of the monomer *a*) and the dimer *b*) of ethylene glycol (charges are in the units of electron charge, the distance is in Å)

the Gauss functions 6-31G++(d, p) [1] for isolated monomer molecules of ethylene glycol and for the dimeric ethylene glycol aggregate [2].

3. Results and Discussion

3.1. Quantum-chemical calculations

Calculation results for a monomeric molecule and an isolated dimer are presented in Fig. 1, *a* and *b*, correspondingly. It is seen that CH_2OH groups of an ethylene glycol molecule are different in some cases with respect to bond lengths and, especially, atomic charges in the molecule. This result indicates that CH_2OH groups are turned with respect to each other. Such rotation is connected with a barrier caused by the interaction of O-H bonds on the molecular edges. Moreover, there is a strong interaction of H atoms of CH_2OH groups with O atoms (H^8 and H^5 atoms with O^4 and O^2 atoms, consequently). Distances between H^8 and O^4–2.061 Å, H^5 and O^2–2.053 Å that is close to the average length of an H-bond.

This is something similar to a strong intramolecular interaction, intramolecular H-bond.

The calculations showed that the molecules of ethylene glycol can form intermolecular hydrogen bonds to form dimeric units. One hydrogen atom of the O–H group of one molecule and an oxygen atom of another molecule take part in the bonding. According to the calculations, the dimer formation energy is 4.6 kcal/mol.

Thus, the results of calculations show that the molecules of ethylene glycol are really aggregated through hydrogen bonds to form dimers. The study of the interaction of molecules and its manifestation in the Raman spectra is of a certain interest.

In principle, the molecules of ethylene glycol can form two hydrogen bonds for each CH_2OH group, and

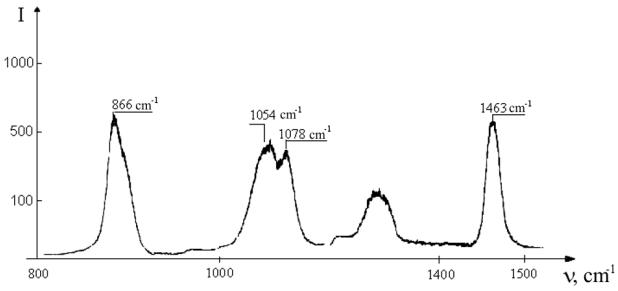


Fig. 2. Fragment of the Raman spectrum of ethylene glycol in the region of intermolecular and H-bond vibrations

chain-like formations are possible. The dimer formation carries a redistribution of charges and a change (small) in the bond lengths, and this happens differently for molecules of a proton donor and a proton acceptor. To find out the charge distribution and the distribution of bond lengths, we can be on the base of the structure of a dimer (Fig. 1, *b*). For the calculated structure of a monomer, the dipole moment of the molecule is 2.73 D, while it is 6.35 D for the dimer. The length of the hydrogen bond is 1.986 Å.

3.2. Raman spectra

The formation of an H-bond in the dimer leads to the manifestation of several bands associated with mutual vibrations and the vibration of the molecules along the hydrogen bond in the IR and Raman spectra. These bands are located in the range from 10 to 100 cm^{-1} [3]. Their intensity in the Raman spectra is low, and they scarcely can be registered against the Rayleigh wing (with a length up to 200 cm^{-1}). In the IR spectra, some of these bands are quite intense, and they can be registered.

We now turn to intramolecular vibrations and their manifestation in Raman spectra. Figure 2 shows a

small section of the experimentally recorded Raman spectrum of ethylene glycol. As can be seen from the figure, the band is quite complex. The band at 866 cm^{-1} is asymmetric in the high-frequency side, two bands at 1060 cm^{-1} are overlapped (1054 and 1078 cm^{-1}), and the band at 1463 cm^{-1} has the shape of a narrow line. Obviously, the formation of intermolecular hydrogen bonds must somehow influence the shape of bands.

The calculated values of the band frequencies are as follows: for the band at 866 cm^{-1}, the calculation gives the dimer bands at 950.9 and 954.2 cm^{-1}, the difference is $\sim$4 cm^{-1}. It is possible that the asymmetry of the band at 866 cm^{-1} is associated with this complexity. The doublet structure was predicted by calculations for the band at 1054–1078 cm^{-1}: the calculated values are 1159.2 and 1171.8 cm^{-1} with the frequency difference $\sim$21 cm^{-1} (in the experiment, we have $\sim$21 cm^{-1}). Note that the calculated and experimental frequencies differ by 10–15% [4]. The matching can be achieved by a correction factor. For a monomer and a dimer, this correction factor is 0.92. When considering the calculated data and their comparison with experiment, one should keep in mind the fact that the calculations are approximate, and the experimental data are obtained with some errors. Therefore, it is difficult to expect the full coincidence of the calculated and experimental data. However, the tendencies for the calculated data and experimental results are the same.

4. Conclusions

In this paper, we present the results of a study of intermolecular interactions in ethylene glycol by Raman spectra and *ab initio* calculations of normal vibration frequencies, depolarization ratios of bands, the formation energy, and other physical and optical characteristics for the aggregated complexes of molecules. The calculations were carried out in the framework of a self-consistent field (RHF) using the basis 6-31G++(d, p) with the full optimization of the geometry of molecules. The calculations showed a possibility of the formation of an intermolecular H-bond between an H atom of the O–H group of one molecule and an O atom of another molecule. For the dimeric aggregate, the intermolecular H-bond length is 1.986 Å. In molecules of the dimer, there is a slight change of bonds' lengths, but also there is a significant change of the charge distribution between atoms. The dimer formation energy is 4.6 kcal/mole, the dipole moment of the aggregate is 6.35 D (in a monomeric molecule, the dipole moment is 2.73 D). In Raman spectra, some features of the H-bonding between molecules such as the asymmetry and the splitting of bands, the features that accompany the H-bond formation, are found.

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ПРОЯВ МІЖМОЛЕКУЛЯРНОЇ ВЗАЄМОДІЇ У СПЕКТРАХ КОМБІНАЦІЙНОГО РОЗСІЮВАННЯ ТА КВАНТОВО-ХІМІЧНІ РОЗРАХУНКИ АГРЕГАЦІЇ МОЛЕКУЛ У РІДКОМУ СТАНІ ЕТИЛЕНГЛІКОЛЮ

Р е з ю м е

Представлено результати дослідження міжмолекулярної взаємодії в етиленгліколі методом спектроскопії комбінаційного розсіювання світла (КРС). Проведено квантово-хімічні розрахунки енергії утворення агрегатів, нормальних коливань, ступеня деполяризації відповідних смуг спектра КРС, та інших фізичних та оптичних характеристик молекулярних агрегатів та мономерних молекул етиленгліколю. Розрахунки проведено методом *ab initio* у наближенні самоузгодженого поля (RHF) із застосуванням базисних функцій 6-31G++(d, p) з повною оптимізацією геометрії молекул. Розрахунки підтвердили можливість утворення міжмолекулярного водневого зв'язку між атомом водню групи O–H однієї молекули та атомом кисню іншої молекули. Довжина міжмолекулярного водневого зв'язку у димерному агрегаті становить 1,986 Å. Виявлено деяку зміну довжини молекулярних зв'язків у димері, а також значний перерозподіл електронної густини між атомами. Енергія утворення димеру становить 4,6 ккал/моль, його дипольний момент дорівнює 6,35 Д (для порівняння дипольний момент мономерної молекули становить 2,73 Д). Відповідні зміни, що спостерігаються у спектрах КРС, такі як асиметрія та розщеплення деяких спектральних смуг, є характерними для утворення міжмолекулярного водневого зв'язку.

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ПРОЯВЛЕНИЕ МЕЖМОЛЕКУЛЯРНОГО ВЗАИМОДЕЙСТВИЯ В СПЕКТРЕ КОМБИНАЦИОННОГО РАССЕЯНИЯ И КВАНТОВО-ХИМИЧЕСКИЕ РАСЧЕТЫ АГРЕГАЦИИ МОЛЕКУЛ В ЖИДКОМ СОСТОЯНИИ ЭТИЛЕНГЛИКОЛЯ

Р е з ю м е

Представлены результаты исследования межмолекулярного взаимодействия в этиленгликоле методом спектроскопии комбинационного рассеяния света (КРС). Проведены квантово-химические расчеты энергии образования агрегатов, нормальных колебаний, степени деполяризации соответствующих полос спектра КРС, и других физических и оптических характеристик молекулярных агрегатов и мономерных молекул этиленгликоля. Расчеты проведены методом *ab initio* в приближении самосогласованного поля (RHF) с применением базисных функций 6-31G++(d, p) с полной оптимизацией геометрии молекул. Расчеты подтвердили возможность образования межмолекулярной водородной связи между атомом водорода группы O–H одной молекулы и атомом кислорода другой молекулы. Длина межмолекулярной водородной связи в димерном агрегате составляет 1,986 Å. Обнаружено некоторое изменение длины молекулярных связей в диммерах, а также значительное перераспределение электронной плотности между атомами. Энергия образования димера составляет 4,6 ккал/моль, его дипольный момент равен 6,35 Д (для сравнения дипольный момент мономерной молекулы составляет 2,73 Д). Соответствующие изменения, наблюдаемые в спектрах КРС, такие как асимметрия и расщепление некоторых спектральных полос, являются характерными для образования межмолекулярной водородной связи.