ASSOCIATES OF METHANOL MOLECULES: QUANTUM-CHEMICAL CALCULATIONS OF STRUCTURE AND VIBRATIONAL SPECTRA

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The character of molecular associations in liquid methanol is studied by quantum chemistry methods. The approximation of density-functional theory with the hybrid exchange-correlation potential B3LYP and atomic basis 6-31G (*d*,*p*) is used. The energy of formation and optimal spatial structure for an isolated molecule and associations of two, three, and four molecules of methanol are calculated. It is found that the sole stable form of a cluster in methanol is the cyclic one. The frequencies and intensities of vibrational Raman spectra are calculated in the harmonic approximation. They are in good agreement with experimental data.

Introduction

The topicality of studies of methanol is conditioned by both the fundamental science's high interest in it and the wide use of this substance in industry. Methanol is of interest for science because it is the simplest alcohol, the nearest analog to water. The presence of a hydroxyl group causes the formation of a hydrogen bond, which mainly determines the structure of methanol and the course of kinetic processes in it [1]. Methanol was studied for a long time in different phases and by different methods. But the investigations of it don't stop and new waves of interest in this object appear regularly. As a rule, they are concerned with new methods of investigation or with the rise of new abilities of old methods. Quite recently, the results of new experiments on the diffraction of neutrons in methanol were published [2, 3], and the new experimental data on the kinetics of relaxation processes of O—H vibrations were obtained by ultrafast infrared spectroscopy [4]. The numerical calculations of the spatial structure of one molecule and different models of methanol associations were carried out as well [5—8].

The key role among other methods belongs to the investigation of vibrational spectra — infrared absorption and Raman scattering. This method is a fine tool for the investigation of microscopic states of substances. Vibrational spectra are especially sensitive to the forming of hydrogen bonds between molecules. The largest changes occur in the spectrum of vibrations of those groups of atoms, which directly form H-bonds. In methanol, this role is played by vibrations of hydroxyl groups. In gas, the frequency of stretch O—H vibrations is 3670 cm^{-1}, whereas there are no bands in liquid methanol near a frequency of 3670 cm^{-1}. The spectral band corresponding to these vibrations is shifted very much, $\omega_{\mathrm{OH}} \approx 3400\ \mathrm{cm}^{-1}$, and its width is more than 300 cm^{-1}.

To clear up the mechanisms of formation of wide bands of proton vibrations in H-bonded systems, a number of theories was offered, in which the effect was considered as a result of fluctuations [9], the presence of a double-minimum potential [10, 11], and the strong anharmonicity of vibrations [12, 13]. Large progress was reached due to the theory of the anharmonic connection of O—H vibrations with low-frequency modes of the complex [14] and the molecular environment [15]. In last years, a large width of the bands of H-bonded vibrations is thought to be connected with the fast migration of protons along H-bonds [4]. The mentioned theories were suggested for the case where the molecules forming an H-bonded pair are different. In a pure liquid, the self-association of molecules takes place, which leads to a change of vibrational frequencies and to the appearance of new bands.

The very wide band of O—H vibrations at 3400 cm^{-1} is complicated. It consists of a number of bands with different frequencies which correspond to proton vibrations in different associations. Every partial band in itself is rather wide due to the factors mentioned above. The structurization of the O—H band can be observed only in solutions of methanol at low temperatures [16—19].

The band at 3400 cm^{-1} rightly attracts the largest interest of investigators. But other vibrational bands of methanol are interesting as well. They are also influenced by hydrogen bonds (though indirectly), and their widths are by far larger than bandwidths observed in simple liquids. It is expected that these bands are also complicated.

According to the said above, the problem of formation of vibrational bands may be divided into two parts: the dynamic problem and the kinetic one. The first part includes determining the frequencies and intensities of partial bands composing broad bands. The object of the second one is a mechanism of broadening of partial bands.

In our previous work [20], the Raman spectra of methanol in the wide temperature range (150—338 K) were experimentally investigated. This range includes both the solid phase of methanol (the melting temperature is 175 K) and the liquid state up to the boiling point (338 K). We found the principal peculiarity of vibrational bands of methanol: their shapes do not depend on temperature. This work continues our investigations of methanol and is devoted to the first of the stated problems. In this case, the character of self-association in liquid methanol and the electro-optical and spectral properties of associates are studied by methods of quantum chemistry.

1. Quantum Chemistry Simulation

In order to determine the role of self-associates in the formation of the vibrational spectrum of methanol, quantum chemical calculations were carried out. The numerical simulation was used to calculate the formation energy, optimal geometry (equilibrium spatial structure), and values of the dipole moments of a monomer molecule and self-associations of two, three, and four molecules. After the optimization of clusters, the calculations of frequencies (in the harmonic approximation) and intensities for the corresponding bands in Raman spectra were carried out. In calculations, the density-functional theory in the approximation of bi-exponential atomic basis 6-31G(d,p), the hybrid exchange three-parameter Becke potential [21], and the exchange-correlation Lee—Yang—Parr potential [22] (B3LYP) was used. The calculations were made with the program Gaussian 98 [23].

The results of the first stage of calculations, namely, a spatial structure and values of the formation energy of methanol associations and their dipole moments, are shown in Table 1.

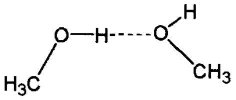
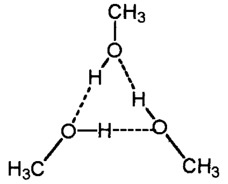
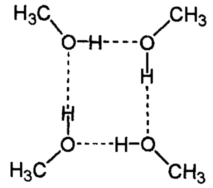
The obtained results allow making the conclusions about the structure of liquid methanol:

1. Methanol molecules form hydrogen bonds of middle power (this fact in itself is well known [1]). Such a bonding energy allows the creating of stable associations. Note that, among the considered clusters, a tetramer has the largest formation energy (and therefore the largest stability).

2. It turns out that only cyclic associations are stable. Even if the initial geometry assumed to be linear, the final result of the optimization was a cycle. This result is thought to be very important. Note that it is not generally accepted [8].

3. It is known that the polarity of the environment is a very important factor for the stability of associates

Table 1. Spatial structure, formation energy, and dipole moments of methanol associations (in parentheses, the mean formation energies per one hydrogen bond are given)

	Form of association	Energy, kcal/mol	Dipole moment, D
1.	H_3C——OH	—	1.93
2.		−4.8 (−4.8)	2.91
3.		−14.6 (−4.9)	0.90
4.		−26.9 (−6.7)	0.003

in condensed phase. It is seen from Table 1 that the presented associations substantially differ in dipole moments. That is why the polarity of associates can also affect the structure of liquid methanol. In solutions, the relative quantity of different associates will depend on the polarity of the solvent: polar solvents will stabilize complexes with large dipole moments, and, in weakly polar systems, the stability of associations with small dipole moments increases. One must take into account this circumstance in comparing the experimental data for determining the structure of methanol associations in different solvents.

After the optimization of the associates' geometry, the vibrational frequencies and intensities of Raman bands for these objects were calculated. The data not on all possible vibrations for the calculated systems (their number exceeds 150), but only on those registered in Raman spectra [20] are presented below. They are six bands corresponding to: O—H vibrations (3400 cm^{-1}), stretch C—H vibrations (2989 cm^{-1}, 2945 cm^{-1} and 2835 cm^{-1}), and another two bands 1115 cm^{-1} and 1033 cm^{-1} which develop complex vibrations (bending hydrogen vibrations in group CH_3 with participation of atoms C and O). The data on the registered Raman bands [20] and the results of calculations of the frequencies and intensities (in arbitrary units) of corresponding vibrations are presented in Table 2.

Let us compare experimental and theoretical results. At first, let us consider O—H vibrations. Here, one can discover such peculiarities:

1. The band with a frequency of 3670 cm^{-1} which corresponds to free vibrations of hydroxyl and is inherent in a monomer and a dimer, is not observed in the spectrum of liquid methanol (it is present only in the spectra of gas and diluted solutions). So we can make the conclusion about the absence of such molecules in liquid methanol. Note that the vibration of free hydroxyl is possible in multimolecular associations if they have a linear form. But the fact that there is no band at 3670 cm^{-1} in the vibrational spectrum of methanol indicates the absence of such structures. This fact experimentally confirms the theoretically obtained result about the cyclic form of stable associations.

2. Calculated Raman intensities of bonded hydroxyl groups in associations greatly exceed the intensities obtained for free hydroxyls. This is a known effect which is typical of H-bonds.

3. The frequencies of bonded O—H vibrations in associates are greatly shifted with respect to the frequency of a free hydroxyl. It is seen that, on the whole, they lie within the experimentally observed 3400 cm^{-1} band. It means that this broad band consists of partial bands of O—H vibrations of different associations. Comparing theoretical data with experimental spectra, one needs to account the fact that the given intensities are integral ones, but real partial bands are very wide because of fast relaxation processes connected with proton exchange [7]. This means that a band with large intensity really may have low maximum.

The discrepancy in the obtained results is also needed to be pointed out. In the calculated spectrum of a tetramer, there is a vibration with a frequency of 3207 cm^{-1} and an intensity of 437. The band of such an intensity should be seen in experiments very well at the wing of the 3400 cm^{-1} band. But it is not observed.

Below the stretch O—H vibrations of methanol on the frequency scale, there are stretch C—H vibrations. It is seen from the results shown in Table 2 that a number of calculated vibrations falls into the region of the registered bands at 2989 and 2945 cm^{-1}. In this case, trimers and tetramers give the largest contribution to the intensity. So, the regarded bands are also complicated. But, as in case of O—H vibrations, there is some discrepancy between theoretical and experimental data. In the calculated spectrum, all objects have vibrations near a frequency of $\sim$ 3050 cm^{-1} with rather high intensity. But this band does not develop experimentally.

The important result of the calculations is the increasing intensity of stretch C—H vibration bands in H-bonded associations. This intensity increases with the number of molecules in a cluster. Note also a small increase in the frequencies of these vibrations comparing with a monomer.

The next fact at issue is the total absence of vibrations in the region of the observed band at 2835 cm^{-1} in the theoretical spectrum. On the high-frequency side, the nearest vibration is situated at a distance of about 100 cm^{-1} (see Table 2), and, on the low-frequency side of the spectrum, vibrations appear only at a frequency of $\sim$ 1500 cm^{-1} (bending C—H vibrations).

In the literature (see, e.g., [24]), the nature of the pair of bands at 2945 and 2835 cm^{-1} is related to the Fermi resonance which appears between first tones of stretch C—H vibrations and overtones of bending vibrations of the same group. Really, according to calculations, the frequencies of these vibrations differ not more than by 20 cm^{-1}. It is clear from this point of view why there are no vibrations near a frequency of 2835 cm^{-1} among theoretically obtained data. The Fermi resonance is an

Table 2. Registered Raman bands and corresponding theoretically calculated ones (ω and γ — frequencies and widths of the bands, respectively, I — intensity of the registered bands, F — calculated intensity of the bands)

Registered bands		Theoretically calculated bands							
		monomer		dimer		trimer		tetramer	
ω, cm^{-1}; I; vibration	γ , cm^{-1}	ω, cm^{-1}	F, a.u.	ω, cm^{-1}	F, a.u.	ω, cm^{-1}	F, a.u.	ω, cm^{-1}	F, a.u.
3400; weak; $q(\mathrm{O-H})$	325	3669	72	3671	62	3454	73	3335	199
				3525	197	3443	93	3298	21
						3387	320	3297	21
								3207	437
—	—	3060	73	3078	57	3055	82	3052	145
				3041	96	3054	83	3051	46
						3052	84	3051	47
								3051	102
2989; middle; $q(\mathrm{C-H})$	50	2980	83	3017	79	2995	30	2998	96
						2990	120	2998	165
						2989	51	2998	16
								2998	40
2945; strong; $q^{-}_{\mathrm{CH_3}}(\mathrm{C-H})$	70	2934	134	2959	128	2944	254	2947	500
				2958	128	2940	138	2945	2
				2918	132	2938	6	2945	2
								2944	9
1115; weak; $\beta^{-}_{\mathrm{CH_3}}(\mathrm{COH})$	70	1148	4	1150	4	1154	6	1154	4
				1149	3	1153	2	1150	7
				1143	2	1152	1	1118	2
				1098	2	1143	2	1118	2
				1096	3	1107	1	1117	3
						1098	2		
1033; middle; $Q(\mathrm{C-O})$	30	1051	8	1047	3	1053	22	1053	2
		1026	2	1037	8	1038	4	1041	4
						1037	3	1041	4
								1035	1

essentially anharmonic (intermode) effect, and our calculations were carried out in the harmonic approximation.

But there is a disagreement between the obtained results and the Fermi-resonance-based consideration. Due to this effect, vibrational levels should be situated symmetrically with respect to the central position which is equal to half the sum of their energies. The difference between the frequencies of the observed bands is 110 cm^{-1}. If the bands at 2945 and 2835 cm^{-1} are moved apart by the Fermi resonance, then the unperturbed harmonic vibrations corresponding to them should have the frequencies of order of 2890 ± 10 cm^{-1}. But our calculated frequencies get rather well into the band at 2945 cm^{-1} (see Table 2).

Farther down the frequency scale, there is the region of bending C—H vibrations which lies within the limits 1514—1452 cm^{-1} (these vibrations are not presented in the table). These are the limits obtained for a tetramer. The frequencies of these vibrations for other associations and for a monomer are inside of this interval. According to the calculations, the intensities of these vibrations are small and they are not really observed in the experiment [20].

The bands at 1115 and 1033 cm^{-1} have the lowest frequency in the registered spectrum. As is seen from Table 2, the accordance of the calculated spectrum to the experimental data can be regarded as satisfactory. These bands correspond to the complex vibrations which include bending C—H and O—H vibrations and the vibrations of atoms C and O. Owing to such a complexity, we think that they are not so interesting for the analysis.

Conclusion

In the present paper, the results of quantum-chemical calculations of spatial structures and vibrational spectra of a monomer and different associations of methanol molecules are presented. The comparison with the Raman spectra experimentally obtained in the previous work [20] is also made.

The main results of our work are as follows:

1. In methanol, there are practically no monomers and dimers, and its structure is formed by self-associations of higher order.

2. The equilibrium structure of methanol associations is a cycle. A linear form is unstable.

3. The very wide band at 3400 cm^{-1} consists of partial bands of O—H vibrations of different associates.

4. In H-bonded clusters, the intensity of stretch vibrational bands not only of O—H, but also of C—H groups increases.

Of course, the real structure of methanol is much more complicated than the set of simple clusters. It must look like a certain spatial lattice of H-bonded molecules. Furthermore, this structure is changeable in time. But, as the calculations have shown, the model chosen in the work gives satisfactory results. In the subsequent works, we will complicate the model.

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АСОЦІАТИ МОЛЕКУЛ МЕТАНОЛУ: КВАНТОВО-ХІМІЧНІ РОЗРАХУНКИ СТРУКТУРИ ТА КОЛИВАЛЬНИХ СПЕКТРІВ

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Резюме

Методами квантової хімії досліджено характер асоціювання молекул в рідкому метанолі. У наближенні теорії функціоналу густини з використанням гібридного обмінно-кореляційного потенціалу B3LYP і атомного базису 6-31G(d,p) розраховано енергії утворення і оптимальну просторову будову ізольованої молекули метанолу та молекулярних асоціатів з двох, трьох і чотирьох молекул метанолу. Виявлено, що в метанолі стійкими є тільки циклічні асоціати. В гармонічному наближенні розраховано частоти та інтенсивності коливальних спектрів комбінаційного розсіяння, які задовільно узгоджуються з експериментальними даними.