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INFLUENCE OF THE ENVIRONMENT ON STRUCTURE AND VIBRATIONAL SPECTRA OF METHANOL CLUSTERS

The study investigates the influence of the environment on the geometric parameters and IR absorption spectra of small methanol clusters (monomer, dimer, and trimer) using quantum chemical calculations with the DFT method (B3LYP/cc-pVTZ). It is shown that argon atoms affect the structure of the methanol molecule more strongly than methanol molecules do. The main effect of the environment on the structure of methanol molecules consists in the elongation of the C–H and O–H bonds, which manifests itself in the IR spectra as a red shift of the corresponding absorption bands. A comparison of the modeling results for methanol clusters of different sizes demonstrated that the magnitude of the spectral shift decreases with an increasing number of molecules in the cluster. The comparison of the modeling results with experimental data led to the conclusion that this approach is suitable for interpreting the spectra of monohydric alcohols in matrix isolation.

Keywords: methanol, hydrogen bonding, IR spectra, cluster, argon.

1. Introduction

Methanol is the simplest representative of the homologous series of monohydric alcohols, whose molecules contain one hydroxyl group. Due to this feature, hydrogen bonds are formed between alcohol molecules in the condensed phase, leading to the formation of a cluster structure. The processes of cluster formation in alcohols are effectively studied by vibrational spectroscopy methods [1–5]. At the same time, traditional spectroscopic techniques provide only average information about the structure of a substance, without allowing one to obtain detailed data on the behavior of individual molecules or small clusters. To overcome this limitation, the matrix isolation technique is applied. Its essence lies in the rapid cooling of the studied molecules and their fixation in an inert gas environment (mainly argon) at a temperature of about 10 K. The resulting matrices are transparent to infrared radiation, which makes it possible to record IR absorption spectra of isolated molecules. Such spectra can be directly compared with the results of quantum-chemical calculations, since they reflect the vibrational spectra of individual molecules or small complexes, similar to those predicted by computational models.

One of the main advantages of the matrix isolation method is its high accuracy, caused by the minimal influence of the external environment on the studied molecules. However, in a number of experiments, a weak influence of the matrix has been detected, manifested as a slight (up to several percent) shift of spectral bands relative to their positions in the gas-phase spectra. This phenomenon, known as the matrix shift, arises due to structural changes in the isolated molecules under the influence of the surrounding matrix. For instance, in [6] it was shown that upon isolating methanol in a neon matrix, the O–H stretching bands shift toward the long-wavelength region,

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whereas in an argon matrix they shift toward the short-wavelength region relative to the corresponding gas-phase bands.

Small methanol clusters are the subject of active research, including by means of the matrix isolation technique [7–9]. In all cases, a matrix shift, i.e., a displacement of spectral bands relative to those recorded in the spectra of gaseous methanol, is observed. To assess the influence of the argon matrix on the structure of isolated molecules and clusters, a number of studies have employed quantum-chemical modeling. In particular, matrix shifts for water clusters of different sizes isolated in an argon matrix were analyzed in [10]. It was shown that all bands in the calculated IR absorption spectra of water clusters in the argon environment are shifted toward the long-wavelength region compared to the spectra in vacuum, in good agreement with experimental results. Later, IR spectroscopy and quantum-chemical modeling were used to study the influence of the argon matrix on other monohydric alcohols — propanol [11] and ethanol [12]. Similar studies of matrix effects on organic acid molecules were reported in [13, 14].

The aim of this work is to determine the influence of argon and methanol environments on the structure and vibrational spectra of the methanol monomer, dimer, and trimer by means of quantum-chemical modeling, as well as to compare the obtained results with experimentally recorded IR absorption spectra of methanol in the gas phase, in the liquid state, and under matrix isolation conditions, in order to evaluate the adequacy of the chosen approach.

2. Computational and Experimental Details

Quantum-chemical calculations of the equilibrium geometries and infrared absorption spectra of methanol were carried out using the Gaussian 09 program package [15]. The calculations were performed within the framework of density functional theory (DFT), employing the B3LYP functional in combination with the cc-pVTZ basis set. The computations were conducted for isolated methanol molecules (monomer), as well as for the dimer and trimer species.

The modeling was performed for three different environments: vacuum, methanol, and argon. In Gaussian, gas-phase calculations were performed by default, while solvent effects were taken into account by means of the polarizable continuum model (PCM). The corresponding solvent was defined using the standard Solvent option within the SCRF keyword.

Infrared absorption spectra of liquid and gaseous methanol were recorded using a VERTEX 70 (Bruker) spectrometer in the spectral range of 650–4000 cm^{-1} with a resolution of 1 cm^{-1} at room temperature. The IR spectrum of methanol isolated in an argon matrix was obtained using an IFS 113 (Bruker) spectrometer at 20 K in the spectral range of 500–4000 cm^{-1}, maintaining the same spectral resolution. The ratio of methanol to argon molecules during matrix preparation was $1:1000$.

3. Results and Discussion

Table 1 presents the calculated geometric parameters (bond lengths and bond angles) as well as the dipole moments of the methanol molecule in vacuum, in methanol, and in argon. As can be seen, the surrounding environment has no noticeable effect on the C–O bond length. This may be due to the fact that this bond is located “inside” the methanol molecule. The lengths of the “peripheral” O–H and C–H bonds are more sensitive to the influence of the environment: in both argon and methanol surroundings, they increase by several thousandths of an angstrom compared to the corresponding values in vacuum. The bond angles also change slightly: the C–O–H angle increases by 1°, while the O–C–H and H–C–H angles increase by about 0.1°. The dipole moment of the molecule in vacuum is 1.94 D, in methanol it decreases slightly to 1.91 D, and in argon it decreases to 1.69 D.

As is well known, bond lengths are directly related to the corresponding vibrational frequencies. Therefore, a change in bond length results in a shift

Table 1. **Calculated geometric parameters and dipole moments of the methanol molecule in vacuum, methanol, and argon**

Parameter	Vacuum	Methanol	Argon
C–O, Å	1.425	1.425	1.425
O–H, Å	0.962	0.965	0.965
C–H, Å	1.092	1.096	1.096
C–O–H, °	108.1	109.1	109.1
O–C–H, °	110.4	110.3	110.3
H–C–H, °	108.5	108.6	108.6
Dipole moment, D	1.94	1.91	1.69

Table 2. **Calculated frequencies and intensities of vibrational bands in the IR absorption spectra of the methanol molecule in vacuum, methanol, and argon**

Mode	Vacuum		Methanol		Argon		$\nu_{\rm met} - \nu_{\rm vac}$, cm^{-1}	$\nu_{\rm ar} - \nu_{\rm vac}$, cm^{-1}
	$\nu_{\rm vac}$, cm^{-1}	I, a.u.	$\nu_{\rm met}$, cm^{-1}	I, a.u.	$\nu_{\rm ar}$, cm^{-1}	I, a.u.		
1	310.2	154.4	362.5	155.3	378.1	122.1	52.3	67.9
2	1029.2	159.4	1033.1	148.1	1035.8	115.6	3.9	6.6
3	1081.2	5.6	1089.2	17.3	1089.3	14.5	8.0	8.1
4	1172.0	1.2	1182.4	1.3	1178.7	0.7	10.4	6.7
5	1375.2	38.7	1378.1	38.8	1380.3	31.1	3.0	5.1
6	1477.8	3.2	1482.7	3.4	1482.9	3.6	4.9	5.1
7	1484.6	3.8	1488.1	3.2	1495.2	2.2	3.5	10.6
8	1505.0	6.8	1508.2	6.7	1511.4	4.5	3.2	6.4
9	2995.9	72.8	2954.0	74.7	2953.8	66.2	–41.9	–42.1
10	3042.5	81.7	2999.1	83.1	2997.8	71.7	–43.4	–44.7
11	3099.6	46.4	3068.3	45.9	3070.8	33.6	–31.3	–28.8
12	3810.8	49.9	3775.5	49.3	3774.2	30.6	–35.3	–36.6

of the respective band in the IR absorption spectrum. At the same level of theory as that used for geometry optimization, the IR absorption spectra of the methanol molecule in vacuum, methanol, and argon were calculated. Table 2 presents the calculated vibrational frequencies and band intensities of the methanol molecule in vacuum, methanol, and argon. The last two columns show the shifts of each spectral band in argon and methanol, respectively, relative to the spectrum of the monomer in vacuum.

As can be seen from Table 2, the largest shift (52 cm^{-1} in methanol and 68 cm^{-1} in argon) is observed for the lowest-frequency band (mode 1), which corresponds to the torsional vibration of the methanol molecule and is associated with the variation of the C–O–H angle. Most of the bands are shifted toward higher frequencies (blue shift); however, the stretching vibrations of the C–H and O–H bonds (modes 9–12) are shifted toward lower frequencies (red shift), which is indicated in the table by the "–" sign preceding the corresponding values. This behavior can be explained by the fact that the C–H and O–H bond lengths increase in both methanol and argon environments compared to those in vacuum, leading to a decrease in the stretching vibration frequencies of these bonds.

The magnitude of the blue shifts for the stretching vibrations of C–H and O–H bonds (modes 9–12) amounts to 30–40 cm^{-1}, while the red shifts for the deformation vibrations (modes 2–7) do not exceed 10 cm^{-1}. This is due to the fact that, in the presence of the surrounding medium, the bond lengths of the methanol molecule undergo greater deformation than the corresponding bond angles. The calculation results also indicate that the spectral shifts in the argon environment are several wavenumbers larger than those in methanol, suggesting that the argon surroundings exert a stronger influence on the methanol molecular structure than the methanol medium itself.

At the same level of theory, quantum-chemical calculations of the equilibrium geometric structure and IR absorption spectra of the methanol dimer were performed in vacuum, methanol, and argon environments. Table 3 presents the calculated geometric parameters (bond lengths and bond angles) and dipole moments of the methanol dimer in vacuum, methanol, and argon.

As shown by the comparison of the calculated geometric parameters of the dimers in different environments, the argon surroundings lead to a slight increase in the C–O and O–H bond lengths in both molecules of the dimer compared to the corresponding bond lengths in vacuum. At the same time, the length of the hydrogen bond (O...H) decreases. Table 4 presents the calculated vibrational frequencies and the corresponding band intensities. The last two columns show the shifts of each spectral band in methanol and argon, respectively, relative to the spectrum in vacuum.

As shown in Table 4, the spectral bands of the methanol dimer in methanol and argon shift only slightly relative to the corresponding bands in vacuum, which is quite expected since the geometric parameters of the clusters remain practically unchanged under the influence of the surrounding medium (see Table 3). However, while in the methanol environment the positions of the spectral bands change only by tenths of a wavenumber, in argon these shifts reach several and even tens of wavenumbers. Thus, as in the case of the monomer, the argon environment has a stronger effect on the structure of the dimer than the methanol environment.

Table 5 presents the calculated geometric parameters and dipole moments of the methanol trimer in different environments, and Table 6 shows the calculated vibrational spectra and the corresponding spectral shifts.

Table 3. **Calculated geometric parameters and dipole moments of the methanol dimer in vacuum, methanol, and argon**

Parameter	Vacuum	Methanol	Argon
C_1–O_5, Å	1.4143	1.4143	1.4151
C_7–O_{11}, Å	1.4289	1.4289	1.4296
O_5–H_6, Å	0.9685	0.9685	0.9698
O_{11}–H_{12}, Å	0.9607	0.9607	0.9613
C_1–H_2, Å	1.0966	1.0966	1.0964
C_1–H_3, Å	1.0963	1.0963	1.0962
C_1–H_4, Å	1.0900	1.0900	1.0900
C_7–H_8, Å	1.0928	1.0928	1.0924
C_7–H_9, Å	1.0925	1.0925	1.0923
C_7–H_{10}, Å	1.0872	1.0872	1.0872
O_{11}...H_6, Å	1.8985	1.8985	1.8930
C_1–O_5–H_6, °	108.4761	108.4761	108.351
C_7–O_{11}–H_{12}, °	109.2733	109.2733	109.0631
O_5–C_1–H_2, °	112.5205	112.5205	112.5104
O_5–C_1–H_3, °	112.5515	112.5515	112.5189
O_5–C_1–H_4, °	107.5812	107.5812	107.6484
O_{11}–C_7–H_8, °	111.4226	111.4226	111.3437
O_{11}–C_7–H_9, °	111.8613	111.8613	111.8238
O_{11}–C_7–H_{10}, °	106.5433	106.5433	106.7075
H_2–C_1-H_3, °	108.1072	108.1072	108.0881
H_2–C_1–H_4, °	107.9035	107.9035	107.9292
H_3–C_1–H_4, °	107.9871	107.9871	107.9579
H_8–C_7–H_9, °	109.3895	109.3895	109.3977
H_8–C_7–H_{10}, °	109.0374	109.0374	108.8629
H_9–C_7–H_{10}, °	108.474	108.474	108.5959
H_6–O_{11}–C_7, °	108.5071	108.5071	111.5977
H_6–O_{11}–H_{12}, °	123.5494	123.5494	116.7594

As can be seen from the data presented in Tables 5 and 6, despite the fact that the calculated geometric parameters of the methanol trimer do not change with varying environment, vibrational band shifts are still observed. This can be explained by the fact that the variations in geometric parameters are very small – less than 0.001 Å. Accordingly, these changes are not reflected in Table 5, but they manifest themselves in the vibrational spectra as shifts of the absorption bands. In the IR spectrum of the methanol trimer in a methanolic environment, the positions of the vibrational bands practically do not change compared to the spectrum in vacuum (the difference does not exceed 0.1–0.2 cm^{-1}), whereas in the argon environment these shifts are somewhat larger – up to 10 cm^{-1}. Thus, as in the case of the monomer, the argon environment has a stronger effect on the trimer structure than the methanolic one. Moreover, the direction of the spectral band shifts is the same in all cases.

Quantum-chemical calculations of the optimized geometry and IR absorption spectra of methanol in three different environments have shown that the influence of the environment on the methanol molecular structure mainly consists in the elongation of the C–H and O–H bonds, which is manifested in the IR absorption spectra as a red shift of the corresponding vibrational bands. Comparison of the modeling results for methanol clusters of different sizes (monomer, dimer, and trimer) revealed that the magnitude of the spectral shift decreases with increasing cluster size, which may be associated with the higher symmetry of the cyclic trimer compared to the monomer.

The obtained data should be compared with experimental results on methanol isolated in low-temperature argon matrices. Therefore, below we present a comparison between the quantum-chemically simulated structures and IR absorption spectra of small methanol clusters containing one, two, and three molecules in three different environments – vacuum, methanol, and argon – and the available experimental data. The calculations in vacuum model the spectra of the corresponding clusters in the gas phase; therefore, it is reasonable to compare the simulated spectra of the methanol monomer in vacuum with the experimentally obtained spectra of gaseous methanol. The results of frequency calculations for methanol clusters

Table 4. **Calculated frequencies and intensities of vibrational bands in the IR absorption spectra of the methanol dimer in vacuum, methanol, and argon**

Mode	Vacuum		Methanol		Argon		$\nu_{\text{met}} - \nu_{\text{vac}}$, cm^{-1}	$\nu_{\text{ar}} - \nu_{\text{vac}}$, cm^{-1}
	ν_{vac}, cm^{-1}	I, a.u.	ν_{met}, cm^{-1}	I, a.u.	ν_{ar}, cm^{-1}	I, a.u.		
1	152.7	3.0	152.8	3.2	153.7	2.1	0.1	1
2	184.3	5.1	184.5	5.2	189.5	4.2	0.2	5.2
3	213.4	4.4	213.5	4.7	215.5	3.3	0.1	2.1
4	253.4	0.7	253.4	0.7	253.2	0.5	0.0	–0.2
5	278.9	11.5	279	11.6	282.7	7.4	0.1	3.8
6	290.8	27.1	291	27.2	295.1	24.7	0.2	4.3
7	690.2	165.6	690.8	164	708.6	124.3	0.6	18.4
8	742.8	204	743.1	203	752.5	170.8	0.3	9,7
9	888.4	81.9	888.5	80.8	892.1	51.1	0.1	3.7
10	907.1	107	907.3	106	912.4	83.2	0.2	5.3
11	1108.5	30.7	1108.5	29.6	1108.5	21.3	0.0	0.0
12	1126,3	44.1	1126.3	44.6	1129.3	34.4	0.0	3.0
13	1154.6	3.5	1154.5	2.6	1153	2.5	–0.1	–1.6
14	1170.5	0.5	1170.5	0.5	1170.7	0.4	0.0	0.2
15	1416.6	54.6	1416.7	54.2	1419.2	42.1	0.1	2.6
16	1426.6	40.1	1426.7	40.7	1430.2	29.3	0.1	3.6
17	1465.4	1.1	1465.5	0.9	1468.5	0.7	0.1	3.1
18	1481.8	8.4	1481.9	8.8	1485.5	8.4	0.1	3.7
19	1492.7	3.3	1492.9	3.3	1500.1	2.2	0.2	7.4
20	1510	1.5	1510.2	1.5	1518	0.8	0.2	8.0
21	1515.6	5.2	1515.8	5.3	1522	5.9	0.2	6.4
22	1516.6	6.3	1516.8	6.5	1525.3	2.1	0.2	8.7
23	2947.3	112	2947.3	112	2947.6	97.0	0.0	0.3
24	2966.5	66.1	2966.5	66.0	2967	58.2	0.0	0.5
25	2996	76.1	2996	76.0	2996.1	58.6	0.0	0.1
26	3047.9	29.3	3047.9	29.2	3049	21.0	0.0	1.1
27	3086.9	19.3	3087	19.7	3087.5	12.1	0.1	0.6
28	3088.3	10.4	3088.3	10.8	3088.5	14.2	0.0	0.2
29	3385.5	40.5	3385.5	40.9	3383.5	23.3	0.0	–2.0

Table 5. **Calculated geometric parameters and dipole moments of the methanol trimer in vacuum, methanol, and argon**

Parameter	Vacuum	Methanol	Argon
C–O, Å	1.4243	1.4243	1.4243
O–H, Å	0.979; 0.98; 0.98	0.979; 0.98; 0.98	0.979; 0.98; 0.98
C–H, Å	1.096; 1.096; 1.096	1.096; 1.096; 1.096	1.096; 1.096; 1.096
O...H, Å	1.876; 1.899; 1.872	1.876; 1.899; 1.872	1.876; 1.899; 1.872
C–O–H, °	110.3; 110.2; 109.9	110.3; 110.2; 109.9	110.3; 110.2; 109.9
O–C–H, °	110.2; 110.2; 110.1	110.2; 110.2; 110.1	110.2; 110.2; 110.1
H–C–H, °	108.7; 108.8; 108.7	108.7; 108.8; 108.7	108.7; 108.8; 108.7

in the methanolic environment should be compared with the IR absorption spectra of liquid methanol, where each cluster is surrounded by other methanol molecules. The spectra of methanol isolated in an argon matrix are compared with the calculated spectra of methanol clusters in the argon environment.

Table 6. **Calculated frequencies and intensities of vibrational bands in the IR absorption spectra of the methanol trimer in vacuum, methanol, and argon**

Mode	Vacuum		Methanol		Argon		$\nu_{\text{met}} - \nu_{\text{vac}}$, cm^{-1}	$\nu_{\text{ar}} - \nu_{\text{vac}}$, cm^{-1}
	ν_{vac}, cm^{-1}	I, a.u.	ν_{met}, cm^{-1}	I, a.u.	ν_{ar}, cm^{-1}	I, a.u.		
1	61.6	4.1	61.9	4.0	71.7	3.7	0.3	10.1
2	75.3	2.2	75.5	2.2	82.2	2.8	0.2	6,9
3	86.5	10.3	86.7	10.1	95.0	5.3	0.3	8,6
4	90.2	19.6	90.5	19.4	100.7	15.4	0.3	10.5
5	96.8	16.5	97.1	16.2	106.4	14.5	0.3	9.5
6	166.1	3.6	166.3	3.3	171.5	3.9	0.2	5.4
7	184.6	6.0	184.8	6.7	190.2	4.1	0.2	5.6
8	207.0	4.3	207.1	4.2	209.6	1.5	0.1	2.6
9	211.0	6.5	211.1	6.5	214.1	4.8	0.1	3.0
10	223.6	0.6	223.4	0.6	218.5	1,5	–0.2	–5.1
11	229.5	0.3	229.3	0.3	223.9	0.6	–0.2	–5.6
12	233.4	0.3	233.2	0.3	228.0	0.5	–0.2	–5.4
13	647.3	239	648.1	236	674.1	174	0.8	26.8
14	706.4	357	707.6	354	744.8	257	1.2	38.4
15	828.8	37.9	829.3	37.0	845.8	26.2	0.5	17.0
16	1037.6	293	1037.7	291	1040.8	224	0.1	3.2
17	1040.2	172	1040.3	171	1042.2	148	0.1	1.9
18	1054.1	23.2	1054.3	23.4	1057.9	17.1	0.1	3.7
19	1126.6	46.1	1126.7	46.3	1128.6	38.9	0.0	2.0
20	1130.6	64.0	1130.7	64.0	1135.7	48.4	0.2	5.1
21	1162.9	1.4	1163.0	1.4	1165.1	0.9	0.1	2.2
22	1186.5	0.5	1186.5	0.5	1184.0	0.6	–0.1	–2.5
23	1186.8	2.5	1186.7	2.6	1184.6	0.1	–0.1	–2.2
24	1187.5	2.5	1187.4	2.4	1184.7	2.7	–0.1	–2.8
25	1411.9	135	1412.1	133	1419.9	100	0.3	8.1
26	1415.2	135	1415.5	136	1427.3	122	0.3	12.1
27	1460.6	14.8	1460.9	134	1468.5	11.8	0.2	7.9
28	1482.7	2.6	1482.7	2.9	1482.9	3.0	0.0	0.2
29	1483.6	0.7	1483.6	0.8	1483.5	1.4	0.0	0.0
30	1487.3	1.5	1487.3	1.5	1488.1	1.4	0.0	0.8
31	1490.8	4.1	1491.0	4.7	1496.7	3.5	0.2	5.9
32	1492.1	4.1	1492.3	4.2	1498.2	3.8	0.2	6.1
33	1492.7	4.0	1492.9	4.3	1498.9	2.3	0.2	6,1
34	1508.0	4.4	1508.2	4.8	1513.6	5.9	0.2	5.5
35	1509.2	6.9	1509.3	6.5	1514.6	4.1	0.1	5.5
36	1509.5	8.7	1509.7	8.3	1515.1	1.2	0.1	5.5
37	2957.9	89.6	2957.9	88.3	2957.9	73	0.0	0.1
38	2959.3	171	2959.3	170	2959.9	143	0.0	0.5
39	2962.5	24.5	2962.5	25.4	2963.2	29.0	0.0	0.7
40	3005.4	77.4	3005.4	76.5	3005.4	58.2	0.0	0.0
41	3007.6	78.6	3007.5	77.4	3007.2	62.5	–0.1	–0.3
42	3010.2	74.3	3010.3	74.5	3010.7	61.4	0.1	0.5
43	3062.7	57.2	3062.7	57.7	3063.2	41.2	0.0	0,5
44	3064.9	62.8	3065.0	61.6	3065.5	41.7	0.1	0.6
45	3065.3	41.9	3065.3	42.7	3066.0	3.5	0.0	0.7
46	3463.4	56.1	3463.5	55.0	3465.9	36.3	0.1	2.5
47	3509.7	1074	3510.0	1070	3520.8	914	0.3	11.1
48	3522.6	987	3522.9	983	3533.3	845	0.3	10.6

Table 7 presents the calculated shifts of vibrational bands in the IR absorption spectra of methanol molecules and clusters in vacuum and in the argon environment under the influence of the surroundings, as well as the experimentally observed IR absorption bands of methanol in the gas phase [16] and in the argon matrix [17].

As can be seen, there is a fairly good correlation between the calculated and experimentally observed matrix shifts of the spectral bands. The direction of the shifts coincides for all bands, since both the calculations and the experiment show an increase in frequency by several wavenumbers. The magnitudes of the shifts are also of the same order, except for the C–H stretching vibrations, for which the calculated shifts are an order of magnitude smaller than the experimental ones. This discrepancy may be attributed to the anharmonicity of these vibrations, which was not taken into account in the calculations. For the same reason, the calculated and observed frequencies of the C–OH and H–CH deformation vibrations also differ.

Table 7. **Comparison of the calculated and experimentally observed frequency shifts of methanol spectral bands in the presence of argon**

Vibration	Simulation			Experiment		
	$\nu_{\rm vac}$, cm^{-1}	$\nu_{\rm Ar}$, cm^{-1}	$\Delta\nu$, cm^{-1}	$\nu_{\rm gas}$ [16], cm^{-1}	$\nu_{\rm matrix}$ [17], cm^{-1}	$\Delta\nu$, cm^{-1}
Str. C–O	1029.2	1035.8	6.6	1031.5	1033	1,5
Str. C–O trimer	1037.6	1040.8	3.2	1045	1052	7
	1040.2	1042.1	1.9	1065	1076	11
Def. COH	1411.9	1419.9	8.1	1321	1330	9
	1415.2	1427.3	12.1	1331	1337	6
	1460.6	1468.5	7.9	1346	1340	6
				1358	1366	8
				1371	1379	8
Def. HCH	1487.3	1488.1	0.8	1454	1466	12
	1490.8	1496.7	5.9	1471	1474	3
	1492.1	1498.2	6.1			
Str. C–H	2947.3	2947.6	0.3	2826	2832	6
	2966.5	2967.0	0.5	2844	2846	2
	2996.0	2996.1	0.1	2865		
	3047.9	3049.0	1.1	2922	2929	7
	3086.9	3087.5	0.6	2940	2955	15
	3088.3	3088.5	0.2	2972	2961	
					3005	
Str O–H monomer	3810.8	3774.2	–36.6	3681	3665	–16

The calculated values of the shifts of methanol bands in methanol relative to the corresponding bands of methanol in vacuum are presented in Table 8. These results are compared with the experimentally observed shifts of the absorption bands in the IR spectrum of liquid methanol relative to those of gaseous methanol, as reported in [16].

When comparing the calculated and experimentally observed frequency shifts for methanol molecules in a methanolic environment, it becomes evident that there is no correlation between them. For instance, the calculated shift for the C–O stretching vibration is toward higher frequencies by 3.9 cm^{-1}, whereas the experimental band of the C–O stretching vibration in liquid methanol is observed at 1022 cm^{-1}, which is 9.5 cm^{-1} lower than in the gas-phase spectrum. Thus, both the magnitude and direction of the shift differ.

The deformation band associated with the COH bending mode shows no change in position between the liquid and gas phases experimentally, while the calculation predicts a shift of 10.4 cm^{-1}. Similarly,

Table 8. **Comparison of the calculated and experimentally observed frequency shifts of methanol absorption bands in a methanolic environment**

Vibration	Simulation			Experiment		
	$\nu_{\rm vac}$, cm^{-1}	$\nu_{\rm met}$, cm^{-1}	$\Delta\nu$, cm^{-1}	$\nu_{\rm gas}$ [16], cm^{-1}	$\nu_{\rm liquid}$ [16], cm^{-1}	$\Delta\nu$, cm^{-1}
Str. C – O	1029,2	1033,1	3,9	1031,5	1022	– 9,5
Def. COH	1172,0	1182,4	10,4	1114	1114	0
Def. HCH	1477,8	1482,7	4,9	1454	1410	–34
	1484,6	1488,1	3,5	1471	1452	–19
Str. C–H	2947,3	2947,6	0,3	2826	2831	5
	2966,5	2967,0	0,5	2844		
	2996,0	2996,1	0,1	2865		
	3047,9	3049,0	1,1	2922	2933	11
	3086,9	3087,5	0,6	2940	2943	3
	3088,3	3088,5	0,2	2972	2981	
Str. O–H monomer	3810,8	3775,5	–35,3	3681	–	
Str. O–H trimer	3509,7	3510,0	0,3	3370	3315	–55

the shifts of the HCH bending vibrations do not match in either direction or magnitude. Agreement in the direction of the shift is observed only for the C–H stretching vibrations, although the calculated and experimental values differ by an order of magnitude.

The situation with the O–H stretching vibrations is more complex, as the frequency of this band strongly depends on the presence of hydrogen bonding between molecules. In gaseous methanol, a band corresponding to the free hydroxyl group is observed at 3370 cm^{-1}, while in the liquid phase it disappears because all molecules are involved in hydrogen-bonded cluster formation, causing the O–H stretching frequency to decrease to 3315 cm^{-1}. Since liquid methanol contains clusters of different sizes, each characterized by its own O–H stretching frequency [3, 8, 9, 16], it is therefore not entirely appropriate to compare these experimental results with modeling data obtained only for the trimer.

4. Conclusions

Comparison of the quantum-chemical calculation results of spectral shifts in the IR absorption spectra of methanol clusters under the influence of different environments with experimental data allows the following conclusions to be drawn. The shifts of methanol spectral bands in vacuum and in argon, calculated using the DFT method with the B3LYP/cc-pVTZ approximation, are in good agreement with the experimentally observed shifts of the corresponding bands in the spectra of methanol isolated in an argon matrix relative to those in the spectra of gaseous methanol. This correspondence indicates that this modeling approach can be effectively applied to interpret matrix shifts in the spectra of monoatomic alcohols under matrix isolation, as it adequately reproduces both the magnitude and direction of spectral band shifts induced by the argon environment.

In contrast, the shifts calculated by the same method for methanol in a methanolic environment do not agree with the experimentally observed shifts of the bands of liquid methanol relative to the gaseous phase. This suggests that such an approach fails to properly account for the influence of surrounding methanol molecules on the methanol molecule itself. Indeed, in the liquid state, as in other alcohols, hydrogen bonds are formed between methanol molecules, leading to the appearance of clusters consisting of different numbers of molecules. The formation of hydrogen bonds significantly affects the physical and chemical properties of the substance, including its spectral characteristics. Therefore, to analyze the differences in the vibrational spectra of methanol in various aggregation states, it is necessary to consider the presence of hydrogen bonding, rather than only the effect of the methanolic environment around the molecule.

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ВПЛИВ ОТОЧЕННЯ НА СТРУКТУРУ ТА КОЛИВАЛЬНІ СПЕКТРИ КЛАСТЕРІВ МЕТАНОЛУ

У роботі досліджено вплив оточення на геометричні параметри та спектри ІЧ поглинання малих кластерів метанолу (мономер, димер, тример) за допомогою квантово-хімічних розрахунків методом DFT (B3LYP/cc-pVTZ). Показано, що на структуру молекули метанолу сильніше впливає оточення атомами аргону, ніж оточення молекулами самого метанолу. Вплив оточення на структуру молекул метанолу головним чином полягає у збільшенні довжин зв'язків C–H та O–H, що проявляється у спектрах ІЧ поглинання у вигляді червоного зсуву відповідних спектральних смуг. Порівняння результатів моделювання для кластерів метанолу різних розмірів показало, що величина спектрального зсуву зменшується зі збільшенням числа молекул у кластері. Порівняння результатів моделювання з експериментальними даними дозволило зробити висновок про доцільність використання даного підходу для інтерпретації спектрів одноатомних спиртів у матричній ізоляції.

Ключові слова: метанол, водневий зв'язок, ІЧ спектри, кластер, аргон.