JOURNAL OF SPECTROSCOPY AND DYNAMICS

Quantum chemical simulation and low-temperature FTIR investigations of the structure and spectral characteristics of methanol monomer and dimer in an argon matrix

Pitsevich G.A.[a],*, Doroshenko I.Yu.[b], Pogorelov V.Ye.[b], Umrejko D.S.[a]

[a] Belarusian State University, Minsk, Belarus
[b] Kiev National Taras Shevchenko University, Kiev, Ukraine

**Author for correspondence: G. A. Pitsevich, email: pitsevich@bsu.by*

Received 10 Feb 2011; Accepted 30 May 2011; Available Online 15 Jun 2011

Abstract

Low-temperature FTIR spectra of methanol in an argon matrix are analyzed on the basis of B3LYP/cc-pVTZ and B3LYP/acc-pVQZ calculations of the geometry and IR spectra of methanol monomer and dimer. The adequacy of the scaled force fields is checked by the comparison of the calculated and experimental spectra of methanol isotopomers. Assignment of the absorption bands in the FTIR spectrum of methanol registered at 10 K to the monomer and dimer vibrations was made taking into account the torsion-vibration interaction. A series of the absorption bands caused by the formation of the intermediate cluster structures during the sample heating from 20 to 35 K was detected. Using the results of computer simulation of the methanol dimer interaction with Ar atoms, new possible mechanism of the broad absorption bands formation in the region of torsional, bending and stretching vibrations of a hydroxyl group of the dimer donor molecule appearing at the sample heating above 30 K was suggested.

Keywords: Methanol; FTIR spectra; Ab initio DFT calculations; Force fields

1. Introduction

Alcohol molecules attract the attention of investigators because of their ability to form various cluster structures due to the intermolecular hydrogen bonds formation. A study of such structures enables one to trace the transition from individual molecules in the gas phase to liquid media in more detail [1, 2]. For a more comprehensive analysis of the structure of molecular aggregates various experimental methods are used. It is worth to note the approaches involving ionization of the vapor formed above the surface of liquid alcohols with the subsequent division of the ionized molecules, their associations or fragments using mass-spectrographs [2-5]; Raman and IR spectral analysis [6-9]; investigations of torsional-rotational spectra in IR and microwave regions [10-12], x-ray, neutron, and NMR spectroscopy [13-15]; selective excitation of the individual clusters using IR/UV double resonance spectroscopy [16]; low-temperature spectral investigations of the clusters trapped into inert gas matrices [17-19]. It is notable that very often the results obtained by different methods do not agree with each other. For example, as it is mentioned in [3], detection of the dominating cluster structure in liquid tret-butyl alcohol by IR spectroscopy indicates the prevalence of cyclic aggregations, whereas x-ray diffraction reveals that the chain structures and a cyclic hexamer prevail. NMR investigations show the cyclic tetramer as a dominant cluster in the liquid phase. According to the data on neutron scattering, intermolecular interactions are essential but not as dominant as it is generally accepted. It is worth to note that the methods of neutron scattering in liquids are less informative than the vibrational spectroscopy as regards the molecular structure and intermolecular interactions. These results obviously reveal mobility of the cluster structures distribution and the influence exerted on it by the media and experimental methods. A large number of works are devoted to the calculations of the structure and spectra of alcohol clusters using non-empirical quantum-chemical methods and molecular dynamics [20-22].

A methanol molecule is the simplest representative of alcohols. In the literature there are a lot of experimental [23, 24] and theoretical [25] works devoted to investigations of alcohol associations. The investigations of methanol in matrix isolation [17] reveal the sensitivity of various associations to the matrix type, to the ratio between the numbers of the methanol and matrix molecules, to the sample temperature, etc. The influence of monochromatic laser radiation in the region of O-H bond vibrations of donor molecules [19] and even of polychromatic radiation of the IR spectrometer globars [23] on the ratio between different clusters in low-temperature matrices was observed. Because of this, each experiment is unique supplementing the general picture of various structure transformations of methanol clusters under the effect of different external factors.

In the present work we have focused our attention on the behavior of methanol monomer and dimer in an argon matrix during a sequential temperature variation from 10 to 50 K. The details of the experiment are recounted in [1, 2].

2. Methanol monomer and dimer structure

The equilibrium geometry of a methanol molecule was calculated by two approaches: (I) the approximation B3LYP/acc-pVQZ was used within the package FIREFLY [26], (II) the approximation B3LYP/cc-pVTZ within the package WinGAMESS [27]. In both cases the optimization was performed for a full set of the internal coordinates; the value of OPTTOL parameter was equal to 10^{-8}; a set of the spherical functions was used, and symmetry of the molecule was specified as C_S. Using approaches I and II, the equilibrium configurations of the methanol dimer were calculated. In both cases the full optimization of the dimer geometry was performed assuming the C_1 symmetry. In accordance with the both approaches, the geometric parameters of individual methanol molecules in the dimer are changed insignificantly as compared to the monomer. However, both approaches predicted decreasing of the C-O bond length in the donor molecule (~1.415 Å) and its increasing in the acceptor molecule (~1.429 Å) in comparison with that in the monomer (~1.421 Å) and this should naturally lead to variation of the corresponding force constants and to splitting of the frequencies of C-O stretching vibrations in donor and acceptor molecules of the dimer. And according to these data a red shift relative to the frequency of this vibration in the monomer should belong to the acceptor, and a blue shift – to the donor molecule. Comparing the geometric parameters of dimers which characterize a relative orientation of the monomer molecules, it can be affirmed that two different conformers of the methanol dimer were found.

3. Calculations of the force fields and IR spectra of methanol monomer and dimer

The optimized geometries of methanol monomer and dimers were used for the calculations of the force fields and IR spectra by the two approaches described above. The absence of imaginary frequencies indicates that both the calculated configurations correspond to minima of the potential surface. To improve the agreement between the calculated frequencies of the monomer in the region 1000 – 1500 cm^{-1} and the experimental ones, a factor for the Hessian scaling was selected. Its value in the first and in the second case was 0.988 and 0.987, respectively. The scaled Hessian was introduced into the input files for the IR spectra calculation using the quantum-chemical packets [26, 27]. Simultaneously, the elements of the force fields for an independent set of the internal coordinates were calculated. Their values were obtained in hartree/bohr^2, hartree/radian^2, and hartree/(bohr*radian) units, and then recalculated into cm^{-2}. The obtained field, together with the optimized molecular geometry, was used as source data for calculations of normal vibrations within the packet [28]. Divergence in the values of the frequencies calculated using [26-28] was below 0.1 cm^{-1}. Only those force constants which were determined by the derivatives of the energy with respect to the natural coordinates of the C-H and O-H bonds length change were subjected to further scaling. The values of the scaling factor in the first and in the second cases were 0.962 and 0.965, respectively. After two stages of the field scaling the final forms of normal vibrations were practically the same as the initial ones. The values of the calculated and experimental [29] vibrational frequencies of a methanol molecule are listed in Table 1. As the data on the spectra of the deuterated and other isotopomers of methanol are present in the literature, the calculations of the normal vibrations of these molecules were performed. The calculations for the cases I and II were performed using the program packet [28], where the twice scaled fields were used as input data, taking the masses H^2, C^{13} and O^{18} instead of the masses of hydrogen, carbon, and oxygen atoms. The calculated and experimentally registered frequencies [30-32] are given in Tables 2 and 3. When analyzing the data from Tables 1-3, note that both approaches are in a good agreement with each other and with the experimental data. It is especially so for the frequency interval 1000 – 1400 cm^{-1}. Just this interval will be of the greatest interest for us. Somewhat worse agreement is observed for the experimental data and for the calculated values of bending vibrations of C-H bonds (1400 - 1500 cm^{-1}). The largest disagreement between the calculated frequencies and the experimental data is observed for stretching C-H vibrations. As mentioned in [18, 33], a possible source of the problem in this spectral range (2800-3050 cm^{-1})

Table 1. The values of the calculated frequencies and intensities of the methanol molecule vibrations and the experimental ones.

Number of the vibration and the symmetry type	Approach I			Approach II			Experimental values*	
	Frequency (cm^{-1})		I, $D^2/(a.m.u.\cdot Å)^2$	Frequency, (cm^{-1})		I $D^2/(a.m.u.\cdot Å)^2$	Frequency, (cm^{-1})	I (rel.)
	Without scaling	After two scalings		Without scaling	After two scalings			
12/A"	287.63	286.76	2.504	264.34	262.46	2.619	-	-
8/A'	1038.69	1032.59	2.887	1040.97	1034.02	2.858	1033.5	1.09
7/A'	1077.22	1072.22	0.024	1079.85	1072.46	0.011	1074.5	0.01
11/A"	1169.57	1162.76	0.011	1171.03	1162.78	0.014	1145±4	0.002
6/A'	1367.21	1360.68	0.588	1370.61	1360.89	0.604	1339.5	0.02
5/A'	1477.18	1467.43	0.078	1480.86	1470.24	0.093	1454.5	0.004
10/A"	1496.87	1491.46	0.072	1494.17	1483.22	0.046	1465±3	0.07
4/A'	1505.79	1497.71	0.128	1509.27	1498.27	0.096	1479.5	0.07
3/A'	2998.04	2864.74	1.462	2981.82	2857.80	1.508	2844.2	0.12
9/A"	3045.62	2911.54	1.255	3024.01	2898.26	1.620	2970.6	0.16
2/A'	3090.40	2954.08	0.604	3099.61	2970.60	0.720	2999.0	0.15
1/A'	3860.82	3690.68	0.747	3824.25	3665.64	0.590	3681.5	0.25

*The information on the IR absorption bands of methanol in the gas phase and the numbering of the vibrations are taken from [30].

Table 2. The values of the calculated frequencies of the deuterated isotopomers of methanol molecule and the experimental ones.

CH_3OD			CD_3OH			CD_3OD		
I (cm^{-1})	II (cm^{-1})	Exp.,[*] (cm^{-1})	I (cm^{-1})	II (cm^{-1})	Exp.,[*] (cm^{-1})	I (cm^{-1})	II (cm^{-1})	Exp.,[*] (cm^{-1})
227.95	208.96	-	272.12	248.91	-	209.17	191.36	-
863.88	861.99	865	855.63	853.51	858	772.25	769.61	775
1038.78	1045.16	1041	896.28	897.61	890	896.25	897.60	888
1162.74	1162.77	1160	984.86	988.83	988	979.38	983.43	983
1241.49	1240.66	1210	1079.07	1075.47	1061	1053.18	1053.47	1029
1467.25	1470.16	1427	1081.57	1079.38	1081	1081.54	1075.43	1071
1491.43	1483.19	1458	1139.39	1141.04	1134	1087.09	1086.67	1083
1496.07	1496.30	1475	1300.13	1301.39	1297	1142.29	1146.08	1135
2690.10	2677.02	2720	2054.68	2053.64	2077	2054.67	2053.64	2080
2864.86	2857.85	2840	2164.19	2152.88	2235	2164.17	2152.87	2228
2911.53	2898.25	2965	2195.17	2203.75	2235	2194.49	2203.07	2228
2954.45	2971.05	2965	3690.56	3665.49	3690	2690.57	2672.74	2724

[*]According to [31].

Table 3. The values of the calculated frequencies of methanol isotopomers and experimentally registered ones.

Molecule	Vibration					
	Stretch C-O			Rocking CH_3		
	I (cm^{-1})	II (cm^{-1})	Exp. (cm^{-1})	I (cm^{-1})	II (cm^{-1})	Exp. (cm^{-1})
$C^{13}H_3OH$	1016.93	1020.21	1018.2[*]	1065.71	1064.03	1065[*]
CH_3O^{18} H	1006.53	1009.50	1007.49[**]	1070.07	1068.52	1073[**]
$C^{13}H_3O^{18}H$	989.21	993.05	991[*]	1064.98	1062.47	-

[*]According to [32], [**] according to [33]

may be the Fermi resonance between overtones and combined frequencies of bending C-H vibrations and some stretching vibrations of these bonds. Really, the overtones (2949 and 2931.4 cm^{-1}) and the combined frequency (2940.2 cm^{-1}) caused by the fundamental bending vibrations 1474.5 and 1465.7 cm^{-1} are located in the spectral interval 2965-2915 cm^{-1}, where the abundant number of the absorption bands are exhibited (2962; 2955.5; 2929.5 and 2920 cm^{-1}), which may be due to stretching C-H vibrations only. Analyzing the values of the calculated and experimental frequencies of methanol isotopomers (Tables 2 and 3), for the first approach one can observe a better agreement. For example, the mean deviation of the calculated frequencies from the experimental ones for stretching C-O vibration and rocking C-H vibration by the first approach was 1.34 and 2.02 cm^{-1} respectively, while by the second approach – 1.82 and 2.725 cm^{-1}. Because of this, in analysis of the monomer and dimer behavior based on low-temperature FTIR spectra in an argon matrix we have mainly relied on the results of the first approach. Computer simulation of the methanol dimer and Ar atoms interaction was performed only using the second approach since the increasing numbers of atoms lead to a dramatic increase in computation time.

At the next stage, using the equilibrium configurations of the methanol dimers obtained within the framework of approaches I and II, the IR spectra and force fields in the corresponding approximations were computed. The obtained Hessians were scaled with the factors 0.987 and 0.988, respectively, and the fields were recalculated for an independent set of natural coordinates. Then only the force constants associated with the changes of the C-H and O-H bonds lengths were scaled using the factors 0.965 and 0.962, respectively. Using the initial geometries and twice scaled force fields, IR spectra of the dimers were calculated within the packet [28]. The results of the calculations are given in Table 4, showing that stretching and bending C-H vibrations of the acceptor molecule are shifted to higher frequencies as compared to the corresponding frequency of the monomer, while for the donor molecule the shift to lower frequencies is observed. A value of the splitting of the localized C-H vibrations is unexpectedly high. The frequencies of the vibrations corresponding to the A'' type symmetry in the monomer for the donor and acceptor molecules are practically the same. Contrary to the described above, as it should be expected, all vibrations involving the hydroxyl group motions are blue-shifted in the donor molecule and red-shifted in the acceptor molecule with respect to those in the monomer. The vibrations under 300 cm^{-1} are due to joint motion of the atoms in the dimer donor and acceptor. As far as is known, the most intense is C-O stretching vibration in IR spectra of the methanol monomer that is in a full agreement with the results of quantum-chemical calculations. The calculations of normal vibrations of the dimer based on the data of the two approaches predict even greater localization of the C-O stretching modes in comparison with the monomer. Indeed, whereas for the monomer the contributions of $\nu_{C\text{-}O}$ in potential energy distribution (PED) of the vibrations 1032.59 and 1034.02 cm^{-1} calculated for cases I and II are 76 и 66%, respectively, in the case of the dimer for the donor and acceptor molecules at the frequencies 1054.82; 1059.91 and 1027.25; 1031.25 cm^{-1} for the cases I and II these contributions are 97; 98 and 95; 98% respectively. It means that the absorption bands assigned to these vibrations in the dimer should also have the highest intensity. So, high localization of stretching C-O vibration in the methanol dimer indicates that a difference in the frequencies of these vibrations for the donor and acceptor molecules (more than 20 cm^{-1}) is hardly caused by a change in the kinematic coefficients. Then, values of the force constants for these bonds should differ. Really, comparison of the scaled force fields for the monomer and the dimer shows that, whereas the force constants for C-O bond of the monomer in cases I and II were $k^{I}_{C\text{-}O}$=8.1675 cm^{-2} and $k^{II}_{C\text{-}O}$=8.2639 cm^{-2}, for the dimer the calculated values (in cases I and II) were as follows: $^{a}k^{I}_{C\text{-}O}$=7.9699 ; $^{d}k^{I}_{C\text{-}O}$=8.3886 cm^{-2} and $^{a}k^{II}_{C\text{-}O}$=8.038 ; $^{d}k^{II}_{C\text{-}O}$=8.4382 см$^{-2}$. It should be noted that the difference in the calculated force constants of the donor and acceptor hydroxyl groups ($^{a}k^{II}_{O\text{-}H}$=11.779 and $^{d}k^{II}_{O\text{-}H}$= 11.162 cm^{-2}) is insufficient to give the calculated value of splitting (150 cm^{-1}). The essential contribution here is made by the difference in kinematics of the hydroxyl group vibrations. According to the results of calculations, value of the force constant of the hydrogen bond is lower than the force constant for hydroxyl group almost by two orders of magnitude ($k^{II}_{O\text{- - -}H}$=0.271 cm^{-2}). Let us compare the force constants of the valence angle C-O-H ($k^{II}_{C\text{-}O\text{-}H}$=0.9756 cm^{-2}) and of the angle, in the vertex of which the hydrogen atom belonging to the hydroxyl group of the donor molecule is located ($k^{II}_{O\text{-}H\text{- - -}O}$ = 0.0534 cm^{-2}). These constants differ by a factor of 20.

4. Analysis of the experimental data and assignment of the absorption bands

The 1:1000 ratio of methanol molecules and argon atoms should lead to the monomer domination in the initial sample at 10 K. But at this temperature spectrum of methanol has a more complex structure than may be expected on the basis of the initial assumptions. There are two bands of comparable intensities (1033.25 and 1036.5 cm^{-1}) and two bands, the intensities of which are lower by an order (1052.5 and 1029.9 cm^{-1}) which may be assigned to stretching C-O vibrations only. The band caused by the free hydroxyl group vibration has complex structure. Here one can distinguish four maxima with the frequencies 3673.5; 3672.5; 3665.5 and 3660 cm^{-1}. There is also a weak doublet 3526 and 3522 cm^{-1} directly indicating a possibility for the existence of a methanol dimer in small amounts in the initial sample. The majority of the remaining bands also have a complex multiplet structure, some of them being represented by doublets. Supposing that most intense band in FTIR spectrum at 1033.25 cm^{-1} belongs to C-O stretching vibration in the monomer, it is important to understand nature of the band at 1036.25 cm^{-1}, the intensity of which is slightly less than first one. According to [19], in the low-temperature IR spectra of methanol trapped into nitrogen matrices the stretching C-O vibrations in the donor molecule are exhibited in the interval 1050 - 1051.4 cm^{-1}, and in the

Table 4. The values of the calculated vibrational frequencies for the methanol dimer.

Approach I			Approach II		
Without scaling	After two scalings	Potential energy distribution (PED)	Without scaling	After two scalings	Potential energy distribution (PED)
Frequency (cm^{-1})			Frequency (cm^{-1})		
3849.40	3679.73	$(100\%\ \nu_{O-H})_a$	3833.53	3674.56	$(99{,}9\%\ \nu_{O-H})_a$
3655.82	3494.82	$(101\%\ \nu_{O-H}-1\%\ \nu_{O.....H})_d$	3676.70	3524.31	$(99{,}9\%\ \nu_{O-H})_d$
3107.51	2970.12	$(90\%\ \nu_{C-H}+10\%\ \nu_{C-H})_a$	3120.56	2990.68	$(93{,}8\%\ \nu_{C-H}+9{,}1\%\ \nu_{C-H})_a$
3097.24	2960.00	$(94\%\ \nu_{C-H}+6\%\ \nu_{C-H})_d$	3081.34	2953.09	$(93{,}8\%\ \nu_{C-H}+6\%\ \nu_{C-H})_d$
3052.56	2917.76	$(54{,}1\%\ \nu_{C-H}+45{,}1\%\ \nu_{C-H})_a$	3059.93	2932.62	$(100\%\ \nu_{C-H})_a$
3017.26	2883.84	$(80{,}3\%\ \nu_{C-H}+20{,}7\%\ \nu_{C-H})_d$	3006.78	2881.76	$(85\%\ \nu_{C-H}+10\%\ \nu_{C-H})_d$
2997.54	2865.12	$(50{,}3\%\ \nu_{CH}+40{,}5\%\ \nu_{CH}+10\%\ \nu_{CH})_a$	3006.49	2881.48	$(94\%\ \nu_{C-H})$a
2967.42	2836.26	$(79\%\ \nu_{CH}+17\%\ \nu_{CH}+4\%\ \nu_{CH})_d$	2969.14	2845.63	$(94\%\ \nu_{C-H}+6\%\ \nu_{C-H})_d$
1509.84	1499.61	$(62\%\ \delta_{HCH}+6\%\ \delta_{OCH})_d+(22\%\ \delta_{HCH})_a$	1517.44	1506.45	$(54\%\delta_{O-C-H}+43\%\delta_{H-C-H})_a$
1508.41	1498.20	$(50\%\ \delta_{HCH}+22\%\ \delta_{OCH})_a+(29\%\ \delta_{HCH})_d$	1513.83	1502.76	$(81\%\ \delta_{H-C-H}+6\ \delta_{O-C-H})_d$
1499.41	1489.20	$(47\%\ \delta_{HCH}+47\%\ \delta_{HCH}+4\%\ \delta_{OCH})_a$	1499.54	1488.65	$(90\%\ \delta_{H-C-H}+6\%\ \delta_{O-C-H})_a$
1496.71	1486.44	$(95\%\ \delta_{HCH}+13\%\ \delta_{OCH})_d$	1498.47	1487.48	$(98\%\ \delta_{H-C-H})_d$
1480.08	1470.16	$(91\%\ \delta_{OCH})_d$	1481.83	1471.15	$(120\%\ \delta_{O-C-H})_a$
1477.60	1467.69	$(72\%\ \delta_{OCH}+12\%\ \delta_{HCH})_a$	1480.00	1469.40	$(58\%\ \delta_{O-C-H}+41\%\ \delta_{H-C-H})_d$
1421.47	1411.99	$(64\%\ \delta_{O-H}+11\%\ \delta_{HCH}+14\%\ \delta_{OCH})_d$	1435.88	1425.63	$(63\%\ \delta_{O-H}+37\%\ \delta_{O-C-H})_d$
1367.30	1358.25	$(64\%\ \delta_{O-H}+29\%\ \delta_{OCH}+8\%\ \delta_{HCH})_a$	1371.33	1361.55	$(65\%\ \delta_{O-H}+28\%\ \delta_{O-C-H}+8\%\ \delta_{H-C-H})_a$
1173.44	1165.75	$(53\%\ \delta_{O-C-H}+32\%\ \delta_{O-C-H})_a$	1175.66	1167.36	$(91\%\ \delta_{O-C-H}+5\%\ \delta_{H-C-H})_a$
1172.93	1165.23	$(43\%\ \delta_{O-C-H}+42\%\ \delta_{O-C-H})_d$	1173.55	1165.27	$(91\%\ \delta_{O-C-H}+5\%\ \delta_{H-C-H})_d$
1115.44	1108.19	$(30\%\ \delta_{OCH}+16\%\ \delta_{O-H}+39\%\ \delta_{OCH}+11\%\ \tau_{O......H})_d$	1119.34	1111.48	$(5\%\ \nu_{C-O}+71\%\ \delta_{O-C-H}+15\%\ \delta_{O-H})_d$
1079.31	1072.29	$(6\%\ \nu_{C-O}+35\%\ \delta_{O-H}+56\%\ \delta_{OCH})_a$	1080.50	1072.89	$(58\%\ \delta_{O-C-H}+35\%\ \delta_{O-H})_a$

1061.13	1054.82	$(97\%\ \nu_{C-O}+1\%\ \delta_{O-H})_d$	1066.85	1059.91	$(98{,}44\%\ \nu_{C-O})_d$
1033.39	1027.25	$(95\%\ \nu_{C-O}+3\%\ \delta_{O-H}+3\%\ \delta_{OCH})_a$	1037.96	1031.25	$(98{,}83\%\ \nu_{C-O})_a$
662.32	659.79	$(19\%\ \delta_{CO\ldots H}+15\%\ \tau_{C-O}+77\ \tau_{O\ldots\ldots H})_d$	678.04	673.45	$(57\%\ \delta_{O-H-O}+18\%\ \delta_{H\ldots O-C}+16\%\ \tau_{C-O}+33\%\ \tau_{H\ldots O})_d$
302.09	299.67	$(57\%\ \tau_{O-H}+80\%\ \tau_{C-O}-43\%\ \tau_{O\ldots\ldots H})_a$	335.17	332.76	$(80\%\ \tau_{C-O}+18\%\ \tau_{H\ldots O})_a$
170.01	165.67	$77\%\ \nu_{O\ldots H}+6\%\ \delta_{O-H\ldots\ldots O}+8\%\ \delta_{C-O\ldots\ldots H}+28\%\ \tau_{O-H}-23\%\ \tau_{O\ldots\ldots H}$	201.09	198.04	$34\%\ \nu_{O\ldots H}+49\%\ \tau_{C-O}+12\%\ \tau_{O-H}+7\%\ \delta_{O-H-O}+3\%\ \delta_{C-O\ldots H}$
114.90	114.05	$12\%\ \delta_{O-H\ldots\ldots O}+24\%\ \tau_{C-O}+98\%\ \tau_{O\ldots\ldots H}+24\%\ \tau_{C-O}-70\%\ \tau_{O\ldots\ldots H}$	190.40	185.48	$50\%\ \nu_{O\ldots H}+8\%\ \delta_{O-H-O}+5\%\ \delta_{C-O\ldots H}+35\%\ \tau_{C-O}-16\%\ \tau_{O-H}+17\%\ \tau_{O\ldots H}$
102.38	101.26	$13\%\ \nu_{O\ldots H}+18\%\ \delta_{O-H\ldots\ldots O}+11\%\ \delta_{C-O\ldots\ldots H}+46\%\ \tau_{C-O}+9\%\ \tau_{O-H}+10\%\ \tau_{O\ldots\ldots H}-9\%\ \tau_{O\ldots\ldots H}$	126.77	125.72	$5\%\ \nu_{O\ldots H}+123\%\ \tau_{O\ldots H}-30\%\ \tau_{O\ldots H}+18\%\ \tau_{C-O}$
62.62	61.14	$6\%\ \nu_{O\ldots H}+11\%\ \delta_{O-H\ldots\ldots O}+293\%\ \tau_{O-H}+342\%\ \tau_{O\ldots\ldots H}-560\%\ \tau_{O\ldots\ldots H}$	95.52	94.33	$160\%\ \tau_{O\ldots H}-72\%\ \tau_{O\ldots H}-15\%\ \tau_{O-H}+11\%\ \delta_{O-H}+8\%\ \nu_{O\ldots H}$
54.43	54.03	$28\%\ \delta_{O-H\ldots\ldots O}+56\%\ \delta_{C-O\ldots\ldots H}+39\%\ \tau_{O-H}+12\%\ \tau_{O\ldots\ldots H}-35\%\ \tau_{O\ldots\ldots H}$	68.78	68.32	$46\%\ \delta_{C-O\ldots H}+97\%\ \tau_{O-H}-34\%\ \tau_{O\ldots H}-18\%\ \tau_{O\ldots H}$
43.66	43.46	$407\%\ \tau_{O\ldots\ldots H}+310\%\ \tau_{O-H}$	55.03	54.64	$13\%\ \delta_{O-H-O}+25\%\ \delta_{C-O\ldots H}+31\%\ \tau_{O-H}+23\%\ \tau_{O\ldots H}$

$_a$ refers to the acceptor vibrations, $_d$ refers to the donor vibrations

acceptor molecule – in the interval 1028.3 – 1033.6 cm^{-1}. Similar data are presented in [17] for low-temperature spectra of methanol in helium and argon matrices. The frequency values were respectively 1024.7; 1050 cm^{-1} and 1025; 1050.1 cm^{-1}. Here most interesting is the last result. On the basis of these data we assign the band at 1029.9 cm^{-1} to the ν_{C-O} of the acceptor molecule, and the band at 1052.5 cm^{-1} to the corresponding vibration in the donor molecule. This is suggested by the fact that their intensities are close, and by correlation with [17]. This assignment agrees well with data of normal mode calculations, according to which the frequencies of C-O stretching vibrations in acceptor and donor molecules are 1027.27 and 1054.82 cm^{-1}. Since the bands in the interval 1025-1037 cm^{-1} are significantly overlapping, separation of the spectral contours was performed, using the Lorentz contour for each of these three bands. The result is demonstrated in Figure 1. The parameters of each individual contour were specified as follows: bands maxima 1029.9; 1033.25 and 1036.5 cm^{-1}, halfwidths – 3.8; 0.8 and 1.15 cm^{-1}, and intensity ratio 1: 6.5: 2.7. The band 1052.5 cm^{-1} is as wide as the band 1029.9 cm^{-1}, and this is another argument in favor of their common origin. The fact that halfwidths of the bands 1029.9 and 1052.5 cm^{-1} are almost 5 times larger than that of the band 1033.3 cm^{-1} probably indicates overlapping of several closely located absorption bands corresponding to different equilibrium conformers of the dimer. Besides the above mentioned doublet 3526 and 3522 cm^{-1}, in the region of the stretching O-H vibrations the presence of a dimer may be indicated by the band at 662.5 cм$^{-1}$, that cannot be assigned to the monomer. It may be supposed that the band 1036.5 cm^{-1} can be assigned to the vibrations of

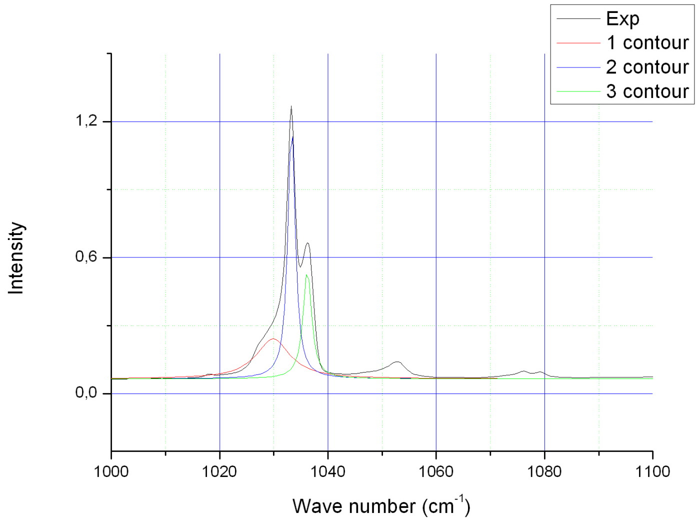

Figure 1. The separation of the band contours of the stretch C-O vibrations.

C-O bond in the methanol trimer since, according to [19], the band at 1036.4 cm^{-1} corresponds to stretching C-O vibration in one of the cyclic trimer conformers. However, in this case the trimer should be present in the initial sample in the amount comparable with that of the monomer but this contradicts the common sense and is not confirmed by the presence of the structured bands in the interval 3500 – 3400 cm^{-1} typical for the cyclic and chain trimers [19]. A similar multiplet nature of most absorption bands in FTIR spectra of the methanol trapped into neon matrices at the temperature 2.7 – 7 K was observed in [34]. In this work the idea was suggested that, though the influence of a neon matrix on the molecules rules out the overall rotation of methanol, torsional tunneling of CH_3 group is still possible. As a result, the ground vibrational state is split into the energy more preferable of A_1 type state and slightly higher located state E. The energy gap between these states in the gas phase is 9.12 cm^{-1} [34]. Due to the interaction with the matrix, height of the potential barrier increases, whereas the corresponding gap in the neon matrix decreases to 6.7±0.5 cm^{-1} [34]. The excited vibrational states of methanol are also split due to the torsion-vibration interaction. A value of the splitting changes at the transition from one fundamental vibration to another. The selection rules A_1 ⇛ A_2 and E ⇛ E, which are strict for the gas phase, are broken in matrix and the transitions A_1 ⇛ E and E ⇛A_1 are exhibited in spectrum too. The interaction of methanol with nitrogen matrix is more significant [35]. Due to increasing of the torsional barrier, splitting of the ground and excited vibrational states is close to zero, leading to the absence of the multiplet structure of absorption bands. It is noted that argon by its matrix properties is closer to neon [35]. The multiplet structure of the bands in argon matrix can be of the same nature as in neon matrix. A repeated value of the splitting of different bands should correspond to the splitting of the ground vibrational state. Analyzing the difference of the frequencies in the doublets 1033.25 and 1036.5 cm^{-1}, 1076.1 and 1079.2 cm^{-1}, 1179.5 and 1183.5 cm^{-1}, 1337 and 1341 cm^{-1}, 3522 and 3526 cm^{-1}, one can assume that a value of the ground state splitting lies in the interval 3.2 - 4 cm^{-1}. Then the intense doublet 1033.25 and 1036.5 cm^{-1} may be interpreted with the assumption that value of the splitting of the torsion-vibrational levels in the ground and excited states is almost the same in agreement with the data obtained in the gas phase and in the neon matrix [34]. The low-frequency component corresponds to the transition A_1 ⇛ A_1, the high-frequency one – to the transition A_1 ⇛ E, and the 'hot band' E ⇛ E coincides with the low-frequency component. A similar scheme of the transitions may be assumed for the doublets 1076.1 and 1079.2 cm^{-1}, 1179.5 and 1183.5 cm^{-1}, 3522 and 3526 cm^{-1} since their low intensity makes a thorough study of their structure impossible. However, in the absence of direct experimental data concerning reversible temperature changes in the intensity components of the multiplets, we cannot completely exclude other formation mechanisms of the multiplet band structure. Different multiplicity of IR bands, the absence of redistribution of the relative intensity components of the multiplets after the matrix annealing at 25, 20 and 35 K,

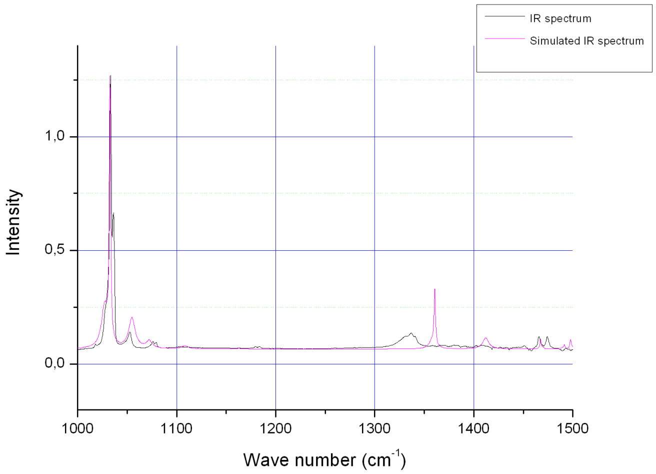

Figure 2. The calculated IR spectrum of the methanol monomer and dimer (pink line) and the experimental IR spectrum of methanol trapped in argon matrix at 10 K (black line).

and the lack of proportionality between the splitting of the fundamental vibrations and overtones on the one hand, and the vibrational quantum numbers, on the other hand are the arguments against the site effect. But we cannot exclude the appearance of the splitting due to the interaction of methanol with residual impurities in the sample of such molecules as nitrogen. Irrespective of a nature of the band multiplet structure, the initial IR spectrum registered at 10 K is mainly formed by monomers and some conformers of the dimer existing in a small amount. The resultant spectrum of the methanol monomer and dimer was simulated using the results of the calculation I. For all bands the Lorentz contour was used, the widths of the absorption bands for the monomer were equal to 0.8 cm^{-1}. The same bandwidth was chosen for those vibrations, the frequency of which is almost the same in the dimer donor and acceptor; as a rule they originate from the vibrations with A$''$ symmetry in monomer. For remaining bands the width value was equal to 3.8 cm^{-1}. The experimental and calculated spectra are shown in Figure 2. The bands assignment in the initial IR spectrum of methanol to the vibrations of monomer and dimer are given in Table 5.

5. Analysis of temperature changes in the spectra

To analyze the temperature influence on the ratio of different clusters of methanol trapped into argon matrix, lower temperature spectra were subtracted from high temperature spectra and superposed. It should be noted that at the sample heating up to 15 and 20 K the intensities of the monomer absorption bands slightly decrease, and the intensities of the dimer bands slightly increase. Further heating from 25 to 35 K, apart from continued decrease of the monomer and dimer band intensities leads to the absorption bands of new cluster structures which were absent at lower temperatures. Compared to the clusters formed at the temperatures 45 K and higher, they are distinguished by relatively small halfwidth of the bands, close to those for dimers and trimers, by fact that at 45 K these bands and hence the corresponding clusters totally disappear. In the region of stretching C-O vibrations the intensity of the bands in the interval 1037 – 1051 cm^{-1} begins to increase as well as the band intensity at 1032 cm^{-1} (Figure 3). In the interval 600 – 900 cm^{-1} the bands with the frequencies 651 and 720 cm^{-1} appear when the temperature approaches 25 K and the bands at 645 and 780 cm^{-1} appear when the temperature comes to 35 K. New bands at 1360, 1364 and 1370 cm^{-1} appear in the interval 1100-1500 cm^{-1}, moreover the intensity of the bands 1447 and 1450 cm^{-1} is increased (Figure 4). Additionally, at 35 K a triplet of the bands at 1118, 1123 and 1130 cm^{-1} is observed. The interval 2800 - 3050 cm^{-1} exhibits bands at 2832 and 2989 cm^{-1}, and the interval 3200 -3700 cm^{-1} reveals more broadened but still rather narrow bands with maxima near 3490 and 3378 cm^{-1}. When the temperature reaches 40 K, one can observe a complete disappearance of those clusters which were present at 10 K and a considerable intensity decrease of the new bands which have appeared at 25-35 K. At 45 K almost all narrow bands disappear from the spectrum. Simultaneously with the transformations of narrow bands beginning from 30 K, increasing of

Table 5. The assignment of the bands in the IR spectrum of methanol to the vibrations of the monomer and the dimer.

Experimental data		Monomer		Dimer	
				Donor	Acceptor
Frequency (cm^{-1})	I (rel.)	The calculated frequency (cm^{-1})	PED	The calculated frequency (cm^{-1})	The calculated frequency (cm^{-1})
3673.5	0.03	3690.68	100% ν_{O-H}		3679.73
3672.5	0.1				
3665.5	0.25				
3660	0.1				
3526	0.06			3494.82	
3522	0.05				
3005	0.15	2954.08	88% ν_{C-H}+12% ν_{C-H}		
2962	0.16	2911.54	51,1% ν_{C-H}+49,1% ν_{C-H}		
2955.5	0.18				
2929.5	0.1				
2920	0.05				
2916	0.05				
2910	0.04				
2847	0.12	2864.74	45,3% ν_{CH}+42,5% ν_{CH}+12% ν_{CH}		
1474.5	0.07	1497.71	70%δ_{HCH}+37% δ_{OCH} +1% δ_{O-H}	1498.20	1499.61
1465.7	0.07	1491.46	49% δ_{H-C-H}+46% δ_{H-C-H}		1489.20
1451	0.001	1467.43	82% δ_{O-C-H}+18% δ_{H-C-H}		1467.69
1408.5	0.002			1411.99	
1341	0.02	1360.68	62% δ_{O-H}+30% δ_{OCH}+6% δ_{HCH}		
1337	0.03				
1331	0.01				
1183	0.002	1162.76	47% δ_{O-C-H}+47% δ_{O-C-H}		
1180	0.002				
1079.5	0.01	1072.22	26% ν_{C-O}+37% δ_{O-C-H}+25% δ_{O-H}		1072.29
1076.1	0.015				
1052.5	0.1			1054.82	
1036.5	0.45	1032.59	76% ν_{C-O}+10% δ_{O-C-H}+12% δ_{O-H}		
1033.25	1.1				
1029.9	0.16				1027.25
662.5	0.1			659.79	

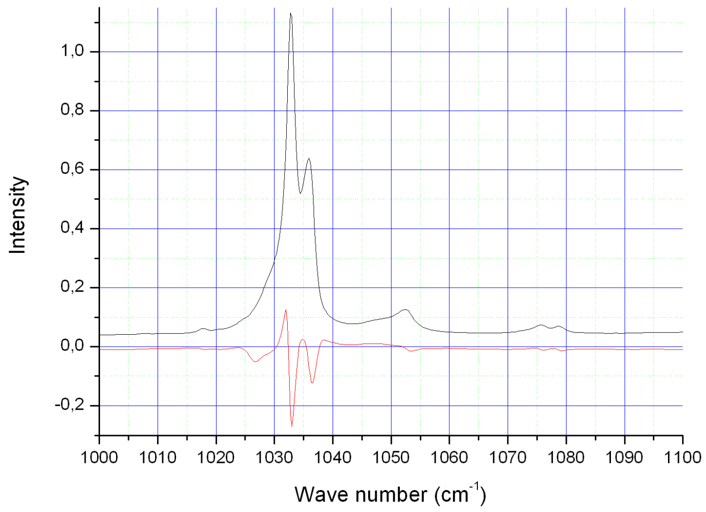

Figure 3. FTIR spectrum of methanol in an argon matrix at 25 K (top) and the difference spectrum for the temperatures 25 and 15 K (bottom).

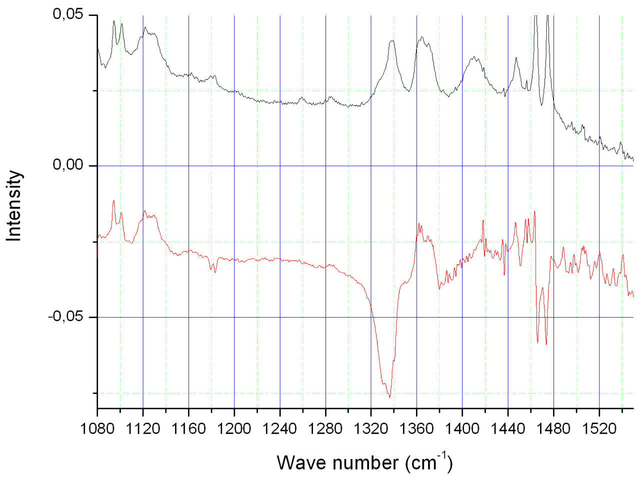

Figure 4. FTIR spectrum of methanol in an argon matrix at 35 K (top) and the difference spectrum for the temperatures 35 and 20 K (bottom).

the intensity of rather broad absorption bands is observed. In the interval 600 - 900 cm^{-1} the band appears the maximum of which shifts to the low-frequency region from 800 to 750 cm^{-1} with a temperature increase, and the halfwidth increases from 70 to 120 cm^{-1}. The interval 1300 -1550 cm^{-1} reveals another band with maximum near 1450 cm^{-1} and with a halfwidth about 60 cm^{-1}. The intensity of the bands in the region 3000 – 3700 cm^{-1} with the maximum shifted to the low-frequency region due to the temperature increase and a halfwidth above 200 cm^{-1} increases (Figure 5). These three broadened bands we attribute to the cluster size growth, increasing of their conformational variety, and reduction of their structural rigidity. Note also that the band caused by the stretching C-O vibration is no longer structured, its halfwidth at 50 K being 22 cm^{-1}. And if the nonstructural broad band with a maximum near 3200 cm^{-1} and a halfwidth exceeding 200 cm^{-1} is traditionally assigned to stretching vibrations of hydroxyl groups of the

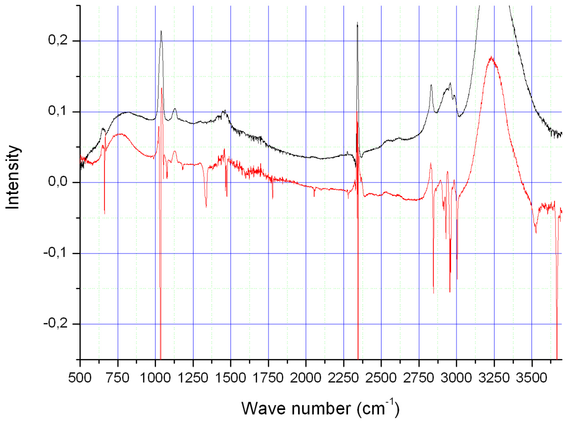

Figure 5. FTIR spectrum of methanol at 45 K (top) and the difference spectrum for the temperatures 45 and 15 K (bottom).

donor molecules, a wide band with maximum near 750 cm^{-1} should obviously be assigned to torsional vibrations, and a broadened band at 1450 cm^{-1} - to bending vibrations of hydroxyl groups of the donor molecules.

6. The influence of the clusters non-rigidity on the formation of the broadened bands in IR spectra

Let us discuss another possible mechanism of the band broadening by the example of methanol dimer. In comparison with the monomer, methanol dimers and other chain clusters as well as large cyclic and branched clusters are less rigid. They have greater ability to deform of the equilibrium geometry, compared to the monomer and, probably, cyclic trimers and tetramers. In the case of dimer one can establish three parameters the deformation of which requires lower forces: change of the O----H bond length, change of the O----H-O angle, change of the relative position of the molecules determined by rotation about the hydroxyl bond. The formal criterion for this may be the values of the force constants for these internal coordinates which, as it was mentioned earlier, are considerably less than those for the ordinary chemical bonds and valence angles. Changing of the non-rigid parameters should mainly affect the frequencies of the vibrations with involving the hydroxyl group of a donor molecule both due to change in some force constants and in kinematic parameters of these vibrations. To study these problems, the calculations were carried out using the second approach. The values of the three parameters which are especially interesting for us varied relative to their equilibrium values by step 0.01 Å, 1^0 and 5^0, respectively. During optimization of the dimer geometry the varied value of one of these parameters was fixed, minimization of the energy was performed for all other parameters. Then a IR spectrum was calculated for the optimized geometry.

Table 6 presents the calculated frequencies at slightly deformed dimer geometry. According to the simulation results, small changes in non-rigid parameters of the dimer structure lead to variation of the frequency of the hydroxyl group stretching vibration for the donor molecule by about 50 cm^{-1}, deformational vibration – by about 25 cm^{-1}, torsional vibration – by about 50 cm^{-1}. Similar variations in the frequency of the stretching C-O vibration never exceed 4 cm^{-1}. In other clusters the frequencies of torsional, bending and stretching vibrations of the hydroxyl group of donor molecules in the equilibrium configurations will differ from those of the dimer. Varying of the frequencies of these vibrations for each such cluster is possible due to small deformations of the equilibrium parameters. This may be responsible for the experimentally observed broadening of the bands in the corresponding spectral regions. In order that this effect was really exhibited in the spectra a mechanism of the deformed clusters stabilization is needed. The steric factors and van der Waals interactions of the clusters with the matrix atoms may represent such a mechanism. According to [36], where in the approximation MP2/acc-pVTZ the potential surface of the methanol molecule interaction with an argon atom was calculated, on the potential surface there are minima determining the equilibrium distances between Ar and methanol atoms. The

Table 6. The values of the frequencies of torsion, deformation and stretch vibrations of the hydroxyl group of the donor molecule of methanol dimer with small deformations of its equilibrium geometry.

The deviation from the equilibrium geometrical parameters	The values of the vibrational frequencies (cm^{-1})			
	Torsion vibration of O-H bond (cm^{-1})	Deformational vibration of O-H bond (cm^{-1})	Stretch vibration of O-H bond (cm^{-1})	Stretch vibration of C-O bond in donor/acceptor (cm^{-1})
The length of the hydrogen bond				
$\Delta l_{O—H}= -0.05$ (Å)	708.03	1440.00	3649.35	1068.29/1037.51
$\Delta l_{O—H}= +0.05$ (Å)	654.48	1432.80	3697.92	1065.36/1038.83
The value of the angle O----H-O				
$\Delta\varphi_{O\text{-}H—O}= +5^0$	678.74	1438.33	3675.53	1067.73/1038.19
$\Delta\varphi_{O\text{-}H—O}= -5^0$	675.62	1426.45	3686.50	1066.19/1036.58
Rotation around the bond O-----H				
$\Delta\tau_{O—H}= +10^0$	681.98	1429.37	3673.86	1067.19/1038.52
$\Delta\tau_{O—H}= -10^0$	681.37	1440.56	3678.21	1067.40/1038.29

stabilization energy of a methanol – argon system comes to 0.72 kcal/mol. This means that in a frozen matrix the interaction forces between argon atoms and atoms of the methanol clusters can deform the equilibrium configuration of the latter. The influence of the matrix on the value of the potential barriers of internal rotation in a methanol molecule is confirmed experimentally [34, 35]. Possible deviations from the equilibrium cluster configuration depend on the ratio between maximal gradients at the potential surface of argon atoms and atoms of the methanol cluster and at the potential surface of the methanol cluster itself as a function of the above described - non-rigid internal coordinates. A growth of the cluster internal energy should be compensated by a decreasing energy of the system “cluster plus argon atoms” as a whole.

7. Computer simulation of the interaction between methanol dimer and argon atoms.

Computer simulation of the interaction between argon atoms and methanol dimer in some situations was performed. Firstly, two argon atoms were positioned along the axes of O-C bonds from the side of carbon atoms and then the geometry of the system was optimized

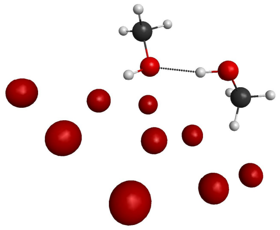

Figure 6. The initial positions of the argon atoms and the methanol dimer in the third computer experiment.

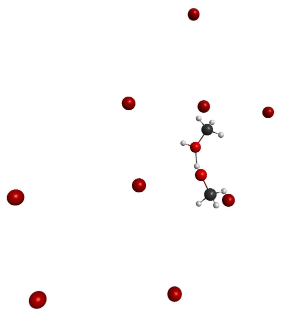

Figure 7. The final positions of the argon atoms and the methanol dimer in the third computer experiment.

for all the parameters. Secondly, two argon atoms were added to the methanol dimer with the deformed O-H----O angle similarly to the first case and the system was optimized for all the parameters at the fixed O-H---O angle. After optimization, the space positions of argon atoms were fixed and the system was optimized again for the remaining parameters. Thirdly, the interaction of the methanol dimer with the surface of the argon matrix was simulated. At one surface 9 argon atoms were positioned, while the methanol dimer being positioned at some distance from this surface. Then the positions of argon atoms at the initial surface were fixed with the possibility of their motion along the surface, and optimization of the system geometry was performed for all the remaining parameters. The atomic configurations before and after the optimization are shown in Figures. 6 and 7. In the letter case the dimer geometry deformed due to a relative rotation about the hydrogen bond was stabilized by two argon atoms. IR spectra for the optimized systems were calculated. The absolute values of deviations of

Table 7. The values of the frequencies of torsion, deformation and stretch vibrations of the hydroxyl group of the donor molecule taking into account the interaction with argon atoms.

		Vibrational frequencies (cm^{-1})			
	Deformations of the dimer geometry parameters	Torsion vibration of O-H bond (cm^{-1})	Deformation vibration of O-H bond (cm^{-1})	Stretch vibration of O-H bond (cm^{-1})	Stretch C-O vibration in donor/acceptor (cm^{-1})
I	$\Delta l_{O—H}$= 0.003 (Å)	688.78	1436.26	3676.76	1034.97/1067.88
	$\Delta\varphi_{O\text{-}H—O}$= 0.31^0				
	$\Delta\tau_{O—H}$= 3.2^0				
II	$\Delta l_{O—H}$= 0.006 (Å)	676.84	1434.1	3658.0	1035.4/1067.3
	$\Delta\varphi_{O\text{-}H—O}$= 0.28^0				
	$\Delta\tau_{O—H}$= 4.5^0				
III	$\Delta l_{O—H}$= 0.003 (Å)	675.41	1431.04	3677.44	1032.74/1067.21
	$\Delta\varphi_{O\text{-}H—O}$= 2.7^0				
	$\Delta\tau_{O—H}$= 4.1^0				
IV	$\Delta l_{O—H}$=0.004 (Å)	692.31	1432.44	3674.95	1032.89/1067.67
	$\Delta\varphi_{O\text{-}H—O}$= -1.237^0				
	$\Delta\tau_{O—H}$= -8.211^0				

the non-rigid dimer parameters from the equilibrium values and the frequencies of stretching, bending and torsional vibrations of the hydroxyl group of a donor molecule as well as stretching C-O vibrations are listed in Table 7. As seen from Table 7 computer simulation of the dimer interaction with argon atoms enables us to demonstrate variation of the frequency values for stretching vibrations for donor hydroxyl group almost by 20 cm^{-1}, of torsional vibrations by 17 cm^{-1}, and of bending vibrations by 5 cm^{-1}. The frequency of the stretch C-O vibration is varied by 2.5 cm^{-1} in the acceptor molecule. A variety of relative positions of the methanol dimer and argon atoms should lead to the appearance of the dimer distorted structures, with the hydroxyl group vibrations filling the determined intervals of the frequency variations. Such a situation should also be the case for larger clusters of methanol. This should lead to the appearance of broad absorption bands in the regions of stretching, bending and torsional vibrations of the hydroxyl group of the donor molecules formed due to superposition of large number of the narrow bands corresponding to each individual cluster.

8. Conclusions

A complex analysis of the temperature changes in FTIR spectra of methanol trapped into the argon matrix, the results of ab initio calculations of IR spectra for the alcohol monomer and dimer, and the literature data have enable us to determine that at 10 K a FTIR spectrum is formed by the absorption bands of the monomer and some conformers of the methanol dimer. The assignment of the absorption bands at this temperature was performed taking into account the possibility of torsion-vibration interaction. It was shown that when the sample was heated from 20 to 35 K the intensity of the absorption bands assigned to vibrations of the methanol monomer and dimer was reduced and simultaneously the new structured absorption bands assigned to the formation of new small clusters have appeared. All these bands disappear at 40 K. But at 30 K and especially at temperatures up to 40 K and higher the intensity of broad absorption bands increases in the regions of torsional, bending and stretching vibrations of the donor molecule hydroxyl group. A possible mechanism for the formation of these band contours was suggested as the result of the appearance of the ensemble of the deformed structures for clusters of different sizes stabilized by the steric and van der Waals interactions with the matrix atoms. Variations of the geometrical parameters determining relative position of the individual molecules in the clusters change the frequency values of the vibrations associated with the donor molecule hydroxyl group. This approach was supported by computer simulation effect exerted by Ar atoms on the configuration and frequencies of the corresponding methanol dimer vibrations.

Acknowledgement

This work was supported by Belarusian Republican Foundation for Fundamental Research (Grant №Ф11K – 032). We gratefully acknowledge the hospitality of Professor Valdas Sablinskas and his colleagues from Vilnius University where the experimental FTIR spectra discussed in this article were registered.

References

1. V.Pogorelov, I.Doroshenko, P.Uvdal, V.Balevicius, V.Sablinskas, Mol. Phys. 108 (2010) 2165.
2. I.Doroshenko, V.Pogorelov, V.Sablinskas, V.Balevicius, J. Mol. Liq. 157 (2010) 142.
3. G.S.Fanourgakis, Y.J.Shi, S.Consia, R.H.Lipson, J. Chem. Phys. 119 (2003) 6597.
4. Y.J.Hu, H.B.Fu, E.R.,Berstein, J. Chem. Phys. 125 (2006) 154306.
5. A.W.Garrett, D.L.Severance, T.S.Zwier, J. Chem. Phys. 96 (1992) 7245.
6. P.Lalanne, J.M.Andanson, J.C.Soetens, T.Tassaing, Y.Danten, M.Besnard, J. Phys. Chem. A 108 (2004) 3902.
7. T.Troxler, P.G.Smith, J.R.Stratton, M.R.Topp, J. Chem. Phys. 100 (1994) 797.
8. D.S.Venables, A.Chiu, C.A.Schmuttenmaer, J. Chem. Phys. 113 (2000) 3243.
9. P.J.Krueger, H.D.Mettee, J. Mol. Spectrosc. 18 (1965) 131.
10. L.H.Xu, J.T.Hougen, J.M.Fisher, R.M.Lees, J. Mol. Spectrosc. 260 (2010) 88.
11. E.A.Cohen, B.J.Drouin, E.A.Valenzuela, R.C.Woods, W.Caminati, A.Maris, S.Melandri, J. Mol. Spectrosc. 260 (2010) 773.
12. D.Lauvergnat, L.H.Coudert, S.Klee, M.Smirnov, J. Mol. Spectrosc. 256 (2009) 204.
13. A.H.Narten, A.Habenschuss, J. Chem. Phys. 99 (1979) 2069.
14. F.Aliotta, M.C.Bellissent-Funel, D.I.Donato, P.Migliardo, C.Vasi, Physica B: Condensed Matter 180-181 (1992) 861.
15. J.A.Ripmeester, R.E.Hawkins, D.W.Davidson, J. Chem. Phys. 71 (1979) 1889.
16. K.L.Bardu-Debus, N.Seure, F.Lahmani, A.Zehnacker-Rentien, PCCP 4 (2002) 4866.

17. U.Buck, F.Huisken, Chem. Rev. 100 (2000) 3863.
18. N.Bakkas, Y.Bouteiller, A.Loutellier, J.P.Perchard, S.Racine, Chem. Phys. Lett. 232 (1995) 90.
19. S.Coussan, A. Loutellier, J.P.Perchard, S.Racine, A.Peremans, A.Tadjeddine, W.Q.Zheng, J. Chem. Phys. 107 (1997) 6526.
20. P.G.Jasien, W.J.Stevens, J. Chem. Phys. 84 (1986) 3271.
21. A.Chung-Phillips, K.A.Jebber, J. Chem. Phys. 102 (1995) 7080.
22. L.Zoranic, F.Sokolic, A.Perera, J. Chem. Phys. 127 (2007) 4502.
23. S.Coussan, N.Bakkas, A.Loutellier, J.P.Perchard, S.Racine, Chem. Phys. Lett. 217 (1994) 123.
24. M.Suhm, Adv. Chem. Phys. 142 (2009) 1.
25. F.C.Hagemeister, C.J.Gruenloh, T.S.Zwier, J. Phys. Chem. 102 (1998) 82.
26. Alex A. Granovsky, Firefly version 7.1.G, http:// www.classic.chem.msu.su/gran/firefly/index.html.
27. http://www.msg.ameslab.gov/GAMESS/GAMESS.html.
28. Sivchik, V. V., Grushetskii, K. M., J. Appl. Spectrosc. 19 (1975) 1062.
29. A. Serrallach, R. Meyer, Hs. H. Günthard., J. Mol. Spectrosc. 52 (1972) 94.
30. Sverdlov, L. M., Kovner, M. A., Krainov, E. P., Vibrational Spectra of Polyatomic Molecules [in Russian], Nauka, Moscow (1970).
31. I.Mukhopadhyay, R.M.Lees, W.Lawis-Bevan, J.W.C.Johns, J. Chem. Phys. 102 (1995) 6444.
32. R.M. Lees, Reba-Jean Murphy, Giovanni Moruzzi, Adriana Predoi-Cross, Li-Hong Xu, D.R.T. Appadoo, B. Billinghurst, R.R.J. Goulding, Saibei Zhao, J. Mol. Spectrosc. 256 (2009) 91.
33. Babich I.L., Kondilenko I.I., Korotkov P.A., Pogorelov V.E., Opt. Spectrosc. 29 (1970) 1011.
34. J.P.Perchard, J. Chem. Phys. 332 (2007) 86.
35. Perchard J.P., Romain F., Bouteiller Y., Chem. Phys. 343 (2008) 35.
36. U. Tasic , Y. Alexeev, G. Vayner, T. D. Crawford, T. L. Windusb, W. L. Hase, PCCP 8 (2006) 4678.

Cite this article as:

G. A. Pitsevich *et al.*: **Quantum chemical simulation and low-temperature FTIR investigations of the structure and spectral characteristics of methanol monomer and dimer in an argon matrix.**
J. Spectrosc. Dyn. 2011, **1**: 9