Hydrogen bond CH...O in a methanolic solution of hydrogen chloride

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The existence of a hydrogen bond in which a methyl group of the $(MeOH)_2H^+$ ion acts as a proton donor is examined. The fundamental vibration frequencies of this ion were calculated for different numbers and strengths of CH...O bonds. The atomic charges in neutral ($(MeOH)_n$, n = 1—4) and protonated ($(MeOH)_mH^+$, m = 2—6) associates of methanol molecules were also calculated. The experimentally observed decrease in the ν(CH) vibration frequencies of the $(MeOH)_2H^+$ ion to 2890 cm^{-1} and 2760 cm^{-1} is attributable to the fact that each methyl group of the ion is involved in formation of two CH...O bonds with strength of ~12.5 kJ mol^{-1}. The proton-donating ability of the CH bond depends on the charge on its H atom; however, it does not correlate with the dipole moment of this bond.

Key words: hydrogen bond, methanol, methyl group, proton bisolvate, stretching vibration frequencies.

In the investigations of neutral and charged molecular complexes, considerable attention has been given to the properties of intermolecular bonds,[1—11] in particular, much consideration has been centered on the elucidation of the nature of functional groups involved in formation of intermolecular bonds and conditions necessary for the realization of these bonds. In this connection, the possibility of the involvement of methyl groups possessing small dipole moments in hydrogen bonding is of interest. Only in the case of molecules in which the C atom is directly bonded to a strong electron-donating substituent (for example, Cl_3CH and NCH) was the ability of CH groups to form intermolecular bonds observed. In recent years, experimental data have been reported, which allowed conclusions about the appearance of H_2CH...O bonds in some complex polyatomic systems[12,13] as well as in a number of solutions of halogen-substituted saturated hydrocarbons.[14] This gave grounds to suggest that hydrogen bonds can be formed also by H atoms of methyl groups in liquid methanol.

To test this suggestion, changes in the stretching vibration frequencies of the methyl group in methanol in going from the gaseous state to the liquid phase were analyzed.[15] It was found that directed interactions between molecules evidently exist in liquid methanol, which is manifested not only in formation of OH...O bonds but also in formation of substantially weaker CH...O bonds. This means that the CH bond of the methyl group exhibits moderate proton-donating ability.

In this work, by a hydrogen bond we mean a directed intermolecular interaction whose spectral manifestation is identical to that of the XH...Y complexes. Apparently, the energy of interaction cannot serve as an indicator of hydrogen bonding because (according to the data reported previously[8,9]) the H...Y bond can be very weak. The experimental[10] and theoretical[11] studies demonstrated that the spectral manifestations of strong and weak intermolecular interactions are qualitatively identical. Thus, the frequency, the integrated intensity, the half-width, and the shape of the contour of the ν(XH) band change monotonically as the strength of the H...Y bond in XH...Y complexes increases.[10] The profile of the density of forces that affect the nuclei of the H and Y atoms from different regions of the electron cloud of the complex changes analogously.[11]

The appearance of additional positive charges on the hydrogen atoms of the Me group should lead to an increase in its proton-donating ability and hence, to the strengthening of the CH...O bond. Spectral manifestations of this effect may be reasonably diversified. However, in any case the center of gravity of CH stretching vibration frequencies should be substantially red-shifted. Therefore, studies of the vibrational spectrum of the molecular system whose methyl group exhibits higher proton-donating ability would allow one not only to test the conclusion made previously[15] but also to elucidate the effect of an additional positive charge carried by the atoms of the Me group on the strength of H bonds formed by this group. Besides, it was of interest to estimate the changes in the atomic charges of the methyl group due to the enhancement of its proton-donat-

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ing ability and to reveal the relative contribution of the solvation effect to these changes.

We chose a methanolic solution of hydrogen chloride as an object of studies. Stable charged proton bisolvates $Me\overset{H}{O}...H^+...\overset{H}{O}Me$ contain methyl groups in which the hydrogen atoms carry higher positive charges than those located on the atoms of the Me groups in nonprotonated molecules of liquid methanol. The ν(CH) vibration frequencies of the $(MeOH)_2H^+$ ion were estimated with a relatively high accuracy[16,17] because its vibrational spectrum is specially extracted "in the pure form" from the spectrum of a solution. The equilibrium composition of the system (6.4 mol L^{-1} of HCl and 9.1 mol L^{-1} of nonprotonated MeOH) allows, in principle, each methyl group of the proton bisolvate to be involved in 2.7 CH...O(Cl) bonds.

This estimation was made on the assumption that in a solution of this composition HCl molecules completely dissociate and each Cl^- ion adopts a coordination number of 4. (Interactions between the chlorine ion and four OH groups of methanol molecules located at distances of ~3 Å from this ion are most probable. This conclusion follows from the data on the structures of the ClO_4^- ion and of the $FClO_3$ and Cl_2O_7 molecules[18] as well as of a large number of chlorine oxyfluorides in which the coordination numbers are even higher[19] due to stereochemical activity of lone electron pairs of the chlorine atom.) In this case, all OH groups are involved in formation of OH...O(Cl) bridges, while the formation of CH...O(Cl) bridges is restricted to Me groups of proton bisolvates. Methyl groups of nonprotonated molecules do not form hydrogen bonds due to their lower proton-donating ability and a deficit of proton-accepting centers in the solution under study. Assuming that Me groups of nonprotonated molecules form one CH...O(Cl) bond each, as in the case of liquid methanol,[15] each Me group of protonated molecules can form two hydrogen bonds.

The IR spectrum of the solution under study has a broad region (~3500—1000 cm^{-1}) of continuous absorption typical for systems containing ions with strong symmetrical hydrogen bonds.[17,20] Due to the great intensity of this absorption, the positions of the maxima can be determined only crudely even for the strongest bands. To obtain more accurate values of ν(CH) vibration frequencies, the spectrum of the $(MeOH)_2H^+$ ion "in the pure form" was repeatedly extracted.

We measured the spectrum of a highly concentrated HCl solution in methanol whose equilibrium composition (5.4 mol L^{-1} of HCl and 11.9 mol L^{-1} of nonprotonated MeOH) differs from the composition of the solution used previously.[16] The conditions of measurement of the spectrum (by the method of multiple attenuated total reflection) and the procedure for its resolution were identical to those reported previously.[16] The spectrum of the $(MeOH)_2H^+$ ion coincides (to within the accuracy of measurements and calculations) with that reported previously.[16]

The error of the determination of $\nu_{as}(CH)$ and $\nu_s(CH)$ in the spectrum extracted is rather high (±20 and ±15 cm^{-1}, respectively) due to which it is impossible to reliably estimate the difference in the spectra of the $(MeOH)_2H^+$ ion obtained by subtracting the spectra of MeOH molecules in the liquid phase and in the free state, respectively, from the spectrum of the solution. Therefore, the conclusion about the number of hydrogen bonds formed by the Me group of the protonated methanol molecule cannot be made based only on the spectral data.

The frequencies of three maxima, which are observed in the spectrum of the $(MeOH)_2H^+$ ion and which are assigned[16] to stretching vibrations of the OH and Me groups, are given in Table 1. The frequencies of the corresponding vibrations of the methanol molecule in the gaseous[21] and liquid[22] phases are given in Table 1 for comparison. The calculation of anharmonic vibrations[17] of the $(MeOH)_2H^+$ ion confirmed the validity of the assignment.[16] Therefore, in this work we used the above-mentioned values of the stretching vibration frequencies of the OH and CH bonds in solving inverse spectral problems.

The results of calculations[17] also imply that changes in the stretching vibration frequencies of the OH and Me groups due to the presence of an inversion center in the proton bisolvate are no more than 10 cm^{-1}. This value is smaller than the error in the determination of the positions of the maxima of the absorption bands in the spectrum of the $(MeOH)_2H^+$ ion, which was obtained experimentally "in the pure form". Consequently, when considering spectral effects, which are substantially higher than 10 cm^{-1}, the anharmonicity of vibrations can be ignored and all calculations can be performed in the harmonic approximation. In this case, the resonance splitting of frequencies due to the symmetry of the ion decreases to ~3 cm^{-1}.

Vibration frequencies ν(CH) of the $(MeOH)_2H^+$ solvated ion

The vibrations of the $(MeOH)_2H^+$ ion, which forms OH...O(Cl) and CH...O(Cl) bonds with the surrounding methanol molecules in a solution, were calculated according to the FG-matrix method with the use of spec-

Table 1. Stretching vibration frequencies (ν/cm^{-1}) of the OH and Me groups of the methanol molecule and the $(MeOH)_2H^+$ ion

Assignment of vibrations	MeOH gas[21]	MeOH liquid[22]	$(MeOH)_2H^+$ liquid[16]
ν(OH) (A′)	3681.5	3329	3100±20
ν_{as}(Me) (A′)	2999.0		
ν_{as}(Me) (A″)	2970±4	2945	2890±20
ν_s(Me) (A′)	2844.2	2832	2760±15

troscopic masses of the atoms. The force field of MeOH molecules involved in the ionic complex under consideration was taken equal to that of the molecule of liquid methanol (see Ref. 15, where it was demonstrated that in the liquid phase its methyl group has the symmetry C_{3v}). The possibility of the involvement of one, two, or three CH bonds in hydrogen bonding was modeled by decreasing the force constants (F_{CH}) of the corresponding bonds of the Me group. This approach assumes that $\Delta F_{CH} \sim \Delta H_{CH...O}$.[23] When the $\overset{H}{\mathrm{MeO}}\ldots\ldots\mathrm{H}^+\ldots\overset{H}{\mathrm{O}}\mathrm{Me}$ ion forms several CH...O(Cl) bridges, their strengths were assumed to be equal because the absorption bands observed in the experimental spectrum under consideration are not split, which is possible only if $\Delta H_{CH...O}$ and $\Delta H_{CH...Cl}$ have similar values. Hereinafter, we consider only CH...O bonds.

The CH stretching vibration frequencies as a function of the number and strength of hydrogen bonds formed by the Me group of the $(MeOH)_2H^+$ ion are shown in Fig. 1. The vertical bars indicate the frequency ranges corresponding to the errors in the determination of ν(CH) due to the lack of knowledge of the precise geometry of the methyl group in the system under consideration. The boundary values of these bars correspond to a change in the H—C—O angles of the isolated methanol molecule by ±2°, which agrees with the results of quantum-chemical calculations (MINDO/3).

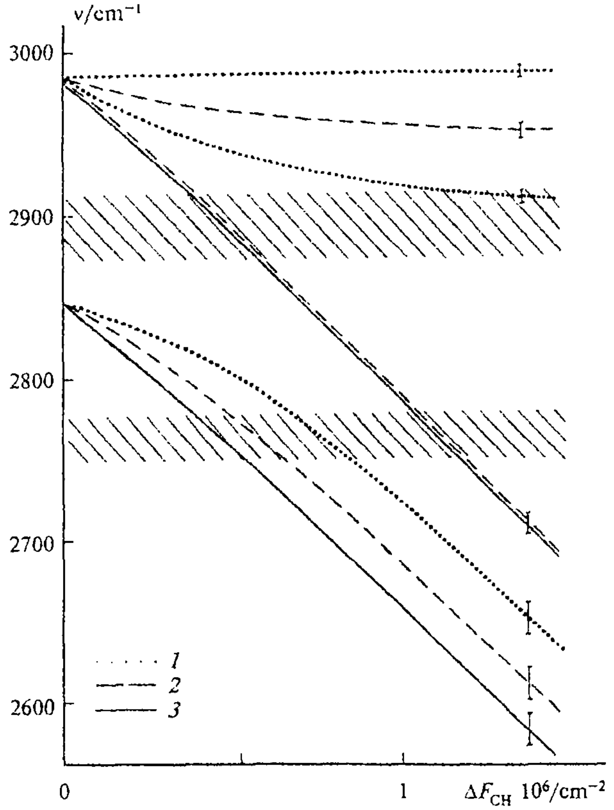

Fig. 1. Stretching vibration frequencies of the Me group of the $(MeOH)_2H^+$ ion as a function of the strength and the number of CH...O bonds formed: *1*, for one bond; *2*, for two bonds; *3*, for three bonds. The changes in the frequency as the H—C—H angle changes by ±2° are indicated by vertical bars. The frequency regions in which the maxima of the ν_{as}(CH) and ν_s(CH) absorption bands are located (see Ref. 16) are indicated by dashed lines.

Any change in the H—C—O angles leads to oppositely directed shifts of the frequencies of symmetric and antisymmetric CH stretching vibrations. Thus, an increase in the H—C—O angle by 2° causes a decrease in the frequencies of both ν_{as}(Me) vibrations by 4 cm^{-1} with a simultaneous increase in the ν_s(Me) frequency by 10 cm^{-1}. The experimental data shown in Fig. 1 are represented as corridors of values whose widths (30—40 cm^{-1}) correspond to the accuracy with which the maxima of the absorption bands in the spectrum of the $(MeOH)_2H^+$ ion can be determined from the optical-density curve (see Table 1).

The results of calculations for the model, in which one methyl group of the proton bisolvate forms one CH...O bridge (see Fig. 1), demonstrated that the frequency of its vibration such that two free CH bonds vibrate in antiphase (ν_{as}(CH)(A'')) is independent of the strength of the hydrogen bond and remains equal to the frequency of the degenerate vibration of the free methyl group (2985 cm^{-1}). The frequency of the second vibration of the Me group such that free CH bonds vibrate in phase (ν_{as}(CH)(A')) decreases monotonically as the strength of the H bond increases. The frequency of the totally symmetric vibration ν_s(CH)(A'), which gives rise to the most pronounced shift of the hydrogen atom of the CH...O bridge, also decreases monotonically. A comparison of these results with the experimental data shows that the observed absorption bands cannot be attributed to vibrations of the Me group of the $(MeOH)_2H^+$ ion that forms one CH...O bond whatever the value of its strength (ΔF_{CH}).

When Me groups of the proton bisolvate form two hydrogen bonds (see Fig. 1), the frequency of the antisymmetric vibration ν_{as}(CH)(A') decreases rapidly and virtually linearly as the value of ΔF_{CH} decreases. The frequency of this vibration nearly coincides with the frequency of the degenerate vibration of the Me group that forms three hydrogen bonds. For the formation of two and three H bonds, the results of calculations agree well with the experimental data[16] when $\Delta F_{CH} \cong 0.5 \cdot 10^6$ cm^{-2}. This change in the force constant of the CH bond is 7.4 times smaller than the change in the force constant of the OH bond ($3.7 \cdot 10^6$ cm^{-2}) estimated by solving the inverse spectral problem for the $(MeOH)_2H^+$ ion. Consequently, the energy of formation of the CH...O bridge should be 7—8 times smaller than the value of $\Delta H_{OH...O}$ (see Ref. 23). The enthalpy of addition of another methanol molecule to the $(MeOH)_2H^+$ ion is 89 kJ mol^{-1} (see the experimental data[24]). Therefore, the energy of formation of the CH...O bond can be as high as 12.5 kJ mol^{-1}.

This value of $\Delta H_{CH...O}$ is the lower limit. The value

$\Delta F_{CH} = 0.5 \cdot 10^6$ cm^{-2} was obtained on the assumption that the force constants of the methyl groups of the $(MeOH)_2H^+$ ion are equal to those of the nonprotonated methanol molecule. According to the results of quantum-chemical calculations, this assumption is true only within ±6%. From abundant experimental data (see, for example, Refs. 3—7) it follows that the formation of a hydrogen bond leads to changes in the force constants in a relatively long chain of bonds adjacent to this H bond. In this case, the force constants of the bonds nearest to the hydrogen bond (we called them the first bonds) and of all the bonds with odd numbers decrease, while the force constants of the bonds with even numbers increase. The larger the strength of the hydrogen bond under consideration the larger the value of this change.[5,6]

The strong (134 kJ mol^{-1}) O...H$^+$ bond formed through the interaction of the lone electron pair of the oxygen atom with the central proton has the most substantial effect on the force constants of the Me group of the $H_3C\overset{H}{O}......H^+...\overset{H}{O}CH_3$ ion. Because of this, the force constants of the CH bonds and, consequently, the frequencies of their stretching vibrations ν(CH) should (according to the "evenness" rule) slightly increase.

Therefore, the absorption bands at 2890 and 2760 cm^{-1}, which are observed in the spectrum of the $(MeOH)_2H^+$ ion extracted from the spectrum of the solution, can be assigned to vibrations of the Me groups that form two or three CH...O(Cl) hydrogen bridges.

Atomic charges in free and solvated MeOH molecules

To explain why the CH...O bond formed between the Me group of the proton bisolvate and the methanol molecule is stronger than the CH...O bond between two MeOH molecules, we analyzed the charge distribution over the atoms of neutral and protonated associates of methanol molecules. The atomic charges were calculated by the semiempirical MINDO/3 method using the LEV program whose algorithms have been reported previously.[25–27] This program allows one to calculate molecular complexes containing up to 35 atoms. We adopted the definition "the dipole moment of the bond" of the charged particle and used the procedure for its calculation reported previously.[28]

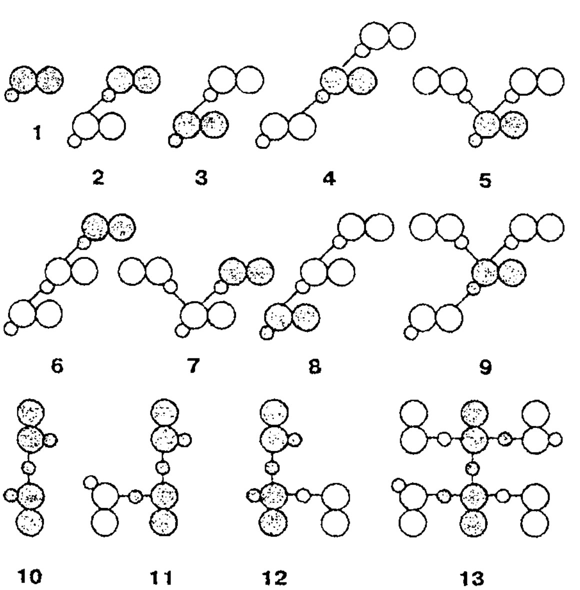

Fig. 2. Associates of methanol molecules **1—13** with different configurations. In **1—9**, molecules whose atomic charges are given in Table 2 are shaded; in **10—13**, the $(MeOH)_2H^+$ ions are shaded.

Table 2. Changes in the atomic charges (Q) in the methanol molecule (**1—9**) in relation to the number and positions of molecules of solvation

Atom	$Q_{\rm mon}$,	$(Q_i - Q_{\rm mon}) \cdot 10^{-3}$/au							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
H°	246	22	4	26	8	27	19	5	30
O	−469	−22	−8	−30	−15	−23	−20	−10	−37
C	382	6	−2	4	−3	7	5	−3	3
H"	−25	−9	6	−3	12	−11	−7	6	3
H	−67	−1	7	−3	10	−10	−8	6	9
H	−67	−7	4	5	10	−3	−1	6	3
ΣH	−159	−17	17	−1	32	−24	−16	18	15

Note. H° is the atom of the OH group, H" is the atom of the Me group located in the H°OC plane, and ΣH is the sum of the charges on the hydrogen atoms of the Me group.

The results obtained for neutral associates (Fig. 2, **1—9**) are given in Table 2. The formation of the OH...O bond between two methanol molecules leads to the transfer of a portion (0.011 au) of the electron density from the proton-acceptor molecule to the proton-donor molecule. In this case, interacting molecules are substantially polarized as a result of which each hydrogen atom of the Me group of the proton-donor molecule or of the proton-acceptor molecule is 0.006 au more negatively or positively charged, respectively. When MeOH molecules in liquid methanol are linked in chains (see Table 2, **4**), only one hydrogen atom of the Me group is positively charged. This result agrees with the conclusion that the Me group of the molecule of liquid methanol forms only one hydrogen bond. This conclusion follows from the analysis of ν(CH) vibration frequencies.[15]

As can be seen from the results of calculations of associates of methanol molecules with different configurations (see Table 2, **4—8**), the mutual effect of the molecules appears to be additive. This is reflected both in the total charge of the methanol molecule ($Q^{\rm tot}_{\rm mol}$) and in the charges on the hydrogen atoms of the Me groups ($Q^{\rm H}_{\rm Me}$). Actually, when the central molecule of the trimer acts simultaneously as a proton donor and proton acceptor (see Table 2, **4**), the effect of the terminal molecules on its total charge and the effect on the overall charge of the hydrogen atoms of its Me group compensate each other. When the molecule acts as a double proton acceptor (see Table 2, **5**), the changes in the values of $Q^{tot}{}_{met}$ and $Q^{H}{}_{Me}$ are twice as large as those observed in the proton-acceptor molecule of the methanol dimer (see Table 2, **3**). In the branched tetramer of methanol (see Table 2, **9**) in which the central molecule acts once as a proton donor and twice as a proton acceptor, both the above-mentioned charges have values identical to those in the proton-acceptor molecule in the $(MeOH)_2$ dimer.

The effect of the molecules of the second coordination sphere on the atomic charges of the methanol molecule (see Table 2) is substantially smaller than the above-considered effect of the molecules of the first coordination sphere. Thus, the charges $Q^{tot}{}_{met}$ and $Q^{H}{}_{Me}$ of the MeOH molecule remain virtually unchanged no matter whether the molecule acts as a proton donor with respect to the monomer, to the proton-donor molecule of the dimer, or to the proton-acceptor molecule of the dimer (see Table 2, **2**, **6**, and **7**). The charges remain unchanged also when the methanol molecule acts as a proton acceptor (see Table 2, **3** and **8**).

Atomic charges in free and solvated $(MeOH)_2H^+$ ions

In a HCl solution in methanol, $(MeOH)_2H^+$ ions can form OH...O and OH...Cl⁻ bridges. Neutral and protonated MeOH molecules can act as molecules solvating these ions. The calculation was carried out for the solvation of the ion by neutral methanol molecules.

The calculated values of the atomic charges and the dipole moments of the bonds of protonated associates of methanol molecules (see Fig. 2; **10**—**13**) are given in Table 3. A comparison of these results with the data in Table 2 demonstrates that the charge distribution over the atoms of the $(MeOH)_2H^+$ ion differs substantially from that in the MeOH molecule. The total charge of each molecule that solvates the central proton changes by 0.313 au. Nearly two-thirds of this value (0.206 au) is accounted for by the change in the charge on the hydrogen atoms of the Me group. The positive charge on the H atom of the hydroxyl group increases by 0.070 au.

The changes in the atomic charges in the $(MeOH)_2H^+$

Table 3. Atomic charges (Q) and dipole moments of the bonds (μ) of the $(MeOH)_2H^+$ ion in relation to the number and positions of methanol molecules of solvation

Atom	$Q\cdot10^{-3}$/au				Bond	μ/D			
	10	**11**	**12**	**13**		**10**	**11**	**12**	**13**
H^o	316	314	318	335	OH	1.099	1.201	1.218	1.194
O	−386	−390	−386	−411	CO	0.528	1.139	1.194	0.526
C	337	340	336	344	CH″	−0.283	−0.177	−0.160	−0.326
H''	23	19	22	13	CH	−0.243	−0.137	−0.107	−0.231
H	31	27	32	31	CH	−0.440	−0.321	−0.308	−0.458
H	−7	−8	−6	−12	O...H	0.855	0.086	−0.005	0.853
H^*	16	13	16	11	CH*	−0.322	−0.212	−0.140	−0.338
H^{cent}	372	369	370	362					
H^o	316	335	316	335	OH	1.099	−0.045	1.211	1.194
O	−386	−403	−390	−411	CO	0.528	1.121	1.238	0.526
C	337	344	335	344	CH″	−0.283	−0.205	−0.133	−0.326
H''	23	14	27	13	CH	−0.243	−0.119	−0.093	−0.231
H	31	30	35	31	CH	−0.440	−0.347	−0.309	−0.458
H	−7	−13	−6	−12	O...H	0.855	1.743	1.841	0.853
H^*	16	10	19	11	CH*	−0.322	−0.224	−0.178	−0.338
H^o	246^f	266	213	**	OH	1.130^f	0.981	2.206	**
O	-469^f	−511	−459	**	CO	-1.528^f	−0.395	−0.216	**
C	382^f	378	377	**	CH	-0.131^f	−0.350	−0.206	**
H''	-25^f	−14	14	**	CH	-0.352^f	−0.696	−0.729	**
H	-67^f	−80	−86	**	CH	-0.352^f	−0.362	−0.607	**
H	-67^f	−16	−63	**	O...H		2.628	−2.876	**
H^*	-53^f	−37	−45	**	CH*	-0.278^f	−0.469	−0.514	**

Note. H^o is the atom of the OH group, H'' is the atom of the Me group located in the H^oOC plane, H^{cent} is the central H atom of the $(MeOH)_2H^+$ ion, and f are the parameters of the free MeOH molecule.

* The average value of the charge on the H (the CH bond dipole moment) atoms of the Me group. ** The charges and the dipole moments of the proton-donor and proton-acceptor molecules that solvate the ion remain unchanged to within ±0.005 regardless of the number of molecules of solvation.

ion upon solvation by the proton-donor molecule or by the proton-acceptor molecule are an order of magnitude smaller than the changes in the charges that occur when the MeOH molecule enters into the composition of the proton bisolvate (see Table 3, **11** and **12**). The changes in the atomic charges in the molecules that solvate the ion are somewhat larger. However, these changes result primarily from polarization of the molecule by the ion rather than from redistribution of the electron density between the solvation molecule and the ion. Thus, the proton-donor molecule that solvates the ion acquires a charge of −0.004 au, while the proton-acceptor molecule acquires a charge of +0.023 au.

Knowing the values of these charges and assuming that the charge of the molecule that solvates the ion is the sum of additive contributions resulting from the formation of a hydrogen bond and from the charge transfer from the ion, the value of each contribution can be determined. The contribution of the formation of an H bond is +0.013 or −0.013 au depending on whether the molecule acts as a proton donor or proton acceptor. The contribution of the charge transfer from the ion is 0.010 au. The estimated value of the change in the charge of the molecule caused by the formation of a hydrogen bond agrees well with the analogous value (±0.011 au) calculated for the methanol dimer (see Table 2).

The charge distribution over the atoms of the proton bisolvate in the solution under study can be estimated by considering its structural fragment, namely, the $(MeOH)_2H^+$ ion, in which both hydroxyl groups form two OH...O bonds each with MeOH molecules (see Table 3, **13**). It is impossible to carry out direct calculations of this large associate. Therefore, the charges on the given atoms were calculated as additive sums of the changes in the charges caused by interactions of two proton-donor and two proton-acceptor molecules.

A comparison of the charges on the hydrogen atoms in the structural fragments in the solution and in liquid methanol (see Table 2, **4**) demonstrates that the average charge on the H atoms of the Me groups changes by 0.064 au and changes sign upon protonation of the MeOH molecule. The increase in the charge on the H atom (0.063 au) of the hydroxyl group is virtually identical to the above-mentioned change. The dipole moments of the CH bonds directed away from the H atom increase by 0.06 D, while the dipole moments of the OH bonds directed toward the hydrogen atom decrease by only 0.006 D. From these results it follows that the substantial low-frequency shifts of the stretching vibration bands of the methyl and hydroxyl groups that occur upon protonation of the methanol molecule (see Table 1) are apparently due to the appearance of additional positive charges on the hydrogen atoms of the CH and OH bonds rather than due to changes in the dipole moments.

The number of hydrogen atoms in the Me groups, which carry positive charges, increases from one to two in going from liquid methanol to the solution. Consequently, Me groups of free molecules and ions in the solution form most likely one and two CH...O bonds, respectively.

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The estimates of the force constants of the $(MeOH)_2H^+$ ion using the quantum-chemical calculations and the "evenness rule" imply that the low-frequency shifts of the ν(CH) bands observed in the experimental spectrum can occur only due to the formation of CH...O bonds between this ion and the surrounding molecules of the solvent.

The results of calculations of the atomic charges in neutral ($(MeOH)_n$, n = 1—4) and protonated ($(MeOH)_mH^+$, m = 2—6) associates of methanol molecules suggest that a) the proton-donating ability of the CH bond increases as the positive charge on the hydrogen atom increases; however, it does not correlate with the dipole moment; b) the proton-donating ability of the CH bonds in the $(MeOH)_2H^+$ ion increases due to the effect of the central proton, which is 1.5—2 orders of magnitude larger than the contribution of the effect of solvation of the ion by surrounding molecules; c) substantial redistribution of the electron density that occurs upon solvation of the proton is realized almost completely (by 94%) *via* molecules of its first coordination sphere. Apparently, this is the reason that the $(MeOH)_2H^+$ ion acts as a single particle in a solution.

The results of calculations of the vibrational spectrum of the solvated ion $(MeOH)_2H^+$, the data on its atomic charges, and the data on the equilibrium composition of the solution under study count in favor of the fact that each Me group of the ion forms two CH...O bonds with a strength of ~12.5 kJ mol^{-1}.

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