Raman spectra of complexes of HCl with DMF with a strong quasisymmetric H-bond in solutions

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Raman spectra of complexes of HCl with DMF with a strong quasisymmetric H-bond in solutions were obtained. The formation of these complexes is accompanied by significant changes in almost all the vibration frequencies and line intensities, the changes in Raman and IR spectra being similar in many features. A weak background scattering was found in the Raman spectra, which coincides in shape with the continuous absorption in IR spectra.

Key words: H-bond; Raman spectra; DMF, HCl, complexes.

Ions and complexes formed by a strong symmetric H-bond that play an important role in acidic catalysis have a number of specific features. Multiple attenuated total reflection (MATR) IR spectroscopy is the main method for detection of these species. In particular, the investigations of aqueous solutions of strong acids were useful in rationalizing the mechanism of their electrolytic dissociation.[1] The formation of species with strong symmetric H-bonds drastically changes the overall spectrum of the base molecules involved, which has been proven experimentally and grounded theoretically.[2] One can expect that the features observed in the IR spectra that accompanied the formation of strong symmetric H-bonds in ions and in uncharged complexes will also appear in the Raman spectra. A detailed study of Raman spectra of these ions and complexes has not been described yet.

In the present work we obtained and analyzed Raman spectra of the complexes that were formed in solutions of HCl in DMF. This system is a convenient model from the following considerations. First, the features of IR spectra of the H-complexes under study are similar to those observed in other acid-base systems, in particular, in aqueous solutions of strong acids.[2–4] Second, the vibration spectrum of DMF has a variety of lines, and this gives us the opportunity to follow the effect of the formation of a complex with a strong quasisymmetric H-bond on various vibrations of the DMF molecule.[2] The IR spectral data on the ion-molecular composition of the HCl—DMF system and on the structure of the species formed[5] served as the basis for the analysis of the Raman spectra.

Experimental

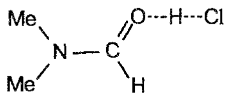
The procedure for purification of reagents and preparation of solutions has been described earlier.[5]

Raman spectra of solutions of HCl in DMF were recorded on a DFS-24 spectrophotometer with a double monochromator and an improved registration system. We used the 488 nm line of an LG-106M argon ion laser as the source of excitation; other lines of the laser were suppressed by an interference filter. The spectral slitwidth was 2—6 cm^{-1} at the registration of the overall spectrum and 15 cm^{-1} at the registration of the background scattering.

Raman spectra were recorded of pure DMF, of 33.3 % solution of HCl in DMF of stoichiometric composition 1 : 1 ($C^0_{HCl} = C^0_{DMF}$ = 10.5 mol L^{-1}), and of 43.3 % solution of HCl, in which the concentrations of 1 : 1 and 2 : 1 complexes are approximately equal.

Results and Discussion

In the studies of ion-molecular interactions in an HCl—DMF system by IR spectroscopy we found that complexes of different compositions were formed (1 : 1 and 2 : 1) depending on the component ratio in the solution. Concentrations of these complexes were measured and their structures were suggested.[5] The structure of a quasi-ionic pair was assigned to the complex of composition 1 : 1, in which a strong quasisymmetric H-bond was realized. The proton is not bound completely with the DMF molecule and the DMF structure changes more significantly than in the formation of an ordinary molecular complex.



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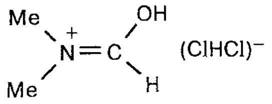
When complexes of composition 2 : 1 are formed, the protonation of the DMF molecule occurs and an ionic pair is formed.



Continuous background absorption, which is different for complexes of the compositions 1 : 1 and 2 : 1, was observed in the IR spectra of solutions of HCl in DMF.

Table 1 lists the line frequencies in the Raman spectra of solutions under study, and the assignment of the DMF frequencies is given according to the literature data.[6,7] Experimentally, relative intensities of the sets of the lines of the 1 : 1 and 2 : 1 complexes were obtained. The Raman spectrum of an equimolecular mixture of HCl and DMF, which predominantly consists of the 1 : 1 complex (no less than 10 mol L^{-1} of the 1 : 1 complex and no more than 0.5 mol L^{-1} of the 2 : 1 complex) displays separate well-resolved lines. On going from pure DMF (C^0_{DMF} = 13 mol L^{-1}) to the 1 : 1 complex, the frequencies of the majority of lines of DMF change significantly, the intensity coefficient of many lines decreases, some lines disappear (ν/cm^{-1}: 323, 1407, 1538, 2772, 2861, 2883), and new lines appear (ν/cm^{-1}: 278, 963, 1228, 1313, 1483, 3016); see Table 1. These changes in the spectrum indicate that in the 1 : 1 complex strong interaction of the HCl and DMF molecules occurs. This results in new vibrations characteristic for the formation of a new separate particle.

The principal difference of Raman spectra of the 1 : 1 complex from its IR spectra is the absence of strong background absorption in the region 900—1600 cm^{-1}, which results in a diffusive character of some bands, therefore, it is difficult to measure them.

The 43.3 % solution of HCl in DMF comprises 4.2 mol L^{-1} of the 1 : 1 complex and 4.8 mol L^{-1} of the 2 : 1 complex. On going from the 1 : 1 complex to the 2 : 1 complex the Raman spectrum changes far less than on going from DMF to the 1 : 1 complex. First, the line at 1726 cm^{-1} appears (Fig. 1), which corresponds to vibration of C=N double bond, which indicates the protonation of the DMF molecule during the formation of the 2 : 1 complex (see Ref. 5). Moreover, the lines at 963 and 1018 cm^{-1} disappear, and the new lines at 888, 1161, and 1390 cm^{-1} appear. The position of the majority of the lines does not change, but the

Table 1. Frequencies (ν) and relative intensities (*I*) of the lines in the Raman spectra of DMF and of solutions of HCl in DMF. The intensity coefficients (*k*) for the lines of the 1 : 1 and 2 : 1 complexes of HCl with DMF

DMF			33.3 % HCl (1:1),		43.3 % HCl			
ν/cm^{-1}	(*I*)	Vibration type	ν	(*I*)	ν	(*I*)	$k_{1:1}$	$k_{2:1}$
—			278	(0.1)	285	(0.2)	0.01	0.04
323	(1)	γ(Me—N—Me)	—		—		—	—
410	(4)	δ(Me—N—Me)	414	(3)	412	(3.5)	0.3	0.4
660	(8)	δ(O=C—N)	639	(3)	638	(4.5)	0.3	0.7
866	(10)	ν_s(N—Me)	849	(2.5)	848	(3.5)	0.25	0.5
—			—		888	(0.1)	—	0.02
—			963	(0.1)	—		—	—
1011	(0.6)	$\delta(C—H)_\perp$	—		—		—	—
1094	(3)	$\gamma(CH_3)N$	1128	(2.5)	1130	(3)	0.25	0.4
—			—		1161	(0.1)	—	0.02
—			1228	(0.2)	1226	(0.2)	0.02	0.03
—			1313	(0.4)	1308	(0.7)	0.04	0.14
—			—		1390	(0.1)	—	0.02
1407	(8)	$\delta_s(CH_3)N$	—		—		—	—
1440	(7)	ν(C—N)	1430	(6)	1429	(7)	0.6	1
—			1483	(0.2)	1481	(0.2)	0.02	0.03
1538	(0.2)		—		—		—	—
1659	(3)	ν(C=O)	1691	(1)	1692	(1)	0.1	0.15
—			—		1726	(1)	—	0.2
2772	(0.15)		—		—		—	—
2810	(1)		2821	(1)	2820	(1)	0.1	0.15
2861	(2)	γ(C—H)	—		—		—	—
2883	(0.3)		—		—		—	—
2930	(10)	$\nu_s(CH_3)N$	2944	(10)	2945	(14)	1	2
2995	(1.4)	$\nu_{as}(CH_3)N$	2990	(1.5)	2996	(3.5)	0.15	0.7
—			3016	(0.4)	3020	(0.7)	0.04	0.14

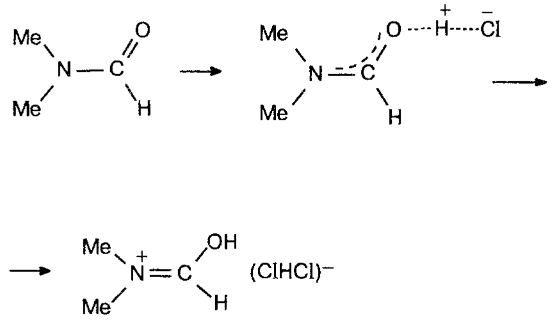
Note: Here $k_{1:1}$ and $k_{2:1}$ are the intensity coefficients for the lines of the 1 : 1 and 2 : 1 complexes, respectively.

intensity coefficients of almost all of the lines strongly increases (see Table 1). This indicates that the structure of DMF in quasi-ionic pair (1 : 1 complex) is close to that of protonated DMF. However, the positive charge transfer to the nitrogen atom and the formation of a double bond do not occur in the 1 : 1 complex.

In the spectra of the 1 : 1 and 2 : 1 complexes we detected weak background scattering in region of 1700—2700 cm^{-1} (see Fig. 1), which coincided in shape with continuous absorption in their IR spectra. The intensity of this absorption in the IR spectrum is only twice as low as the intensity of the most intense bands and is comparable with the observed intensity for the other bands in the spectrum. The relative intensities of the background scattering in the Raman spectra are substantially lower and are 20 and 10 % of intensities of the majority of the lines in the spectra of the 1 : 1 and 2 : 1 complexes, respectively.

The characteristic feature of an 1 : 1 uncharged complex, in which a strong quasisymmetric H-bond in the bridge O...H...Cl is realized, is the intense continuous absorption in the region 1500—1650 cm^{-1} between vibration bands of C—N and C=O bonds. Weak background scattering in this region was also observed in the Raman spectrum of the 1 : 1 complex. The ratio of line intensities at 1560 and 1692 cm^{-1} is 0.3. In the IR spectrum the ratio of the corresponding optical densities is 0.7. In the Raman spectrum of the 2 : 1 complex the scattering in this frequency region is absent.

Thus, the changes in the Raman spectra are in good agreement with the conclusions drawn from the analysis of IR spectra,[5] and are consistent with the changes in DMF structure when 1 : 1 and 2 : 1 complexes are formed.



The analysis of the Raman spectra shows (see Table 1) that the formation of the species with a strong quasisymmetric H-bond is accompanied by substantial changes in almost all of the frequencies and intensities of vibrations of the molecules involved in the H-complex and similarities with charecteristic features of IR spectra of these systems are observed.

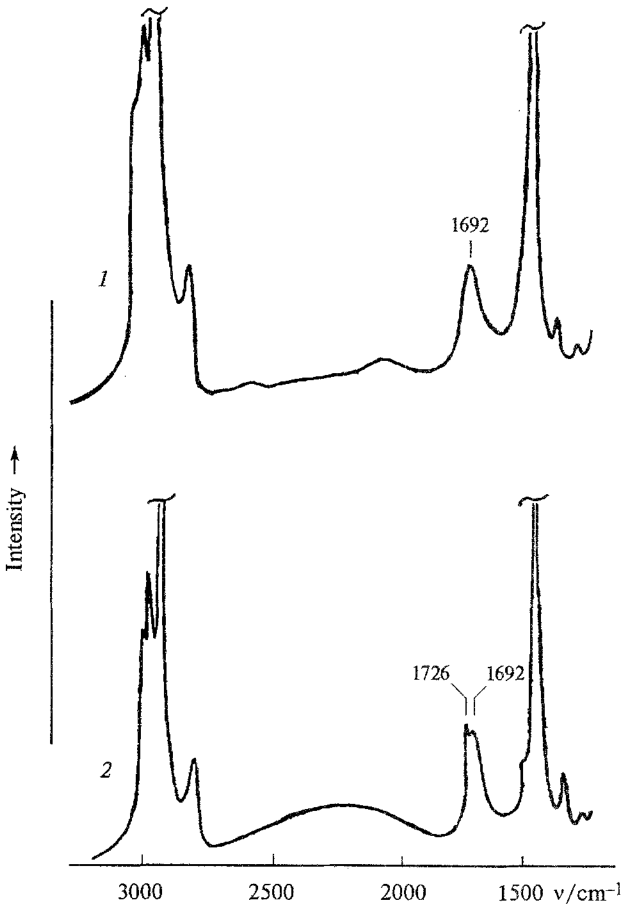


Fig. 1. Raman spectra of solutions of HCl in DMF: (*1*) 33.3 % solution of HCl (1 : 1); (*2*) 43.3 % solution of HCl.

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