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## MOLECULAR AGGREGATION IN LIQUID DIMETHYLFORMAMIDE AND ITS SOLUTIONS: *AB INITIO* CALCULATIONS AND RAMAN SPECTRA

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On the basis of *ab initio* calculations carried out with the help of the computer program Gaussian 98W in the framework of the Hartree–Fock self-consistent field (HFSCF) approach and making use of the 6-31G(d) basis set of the Gaussian functions, an opportunity of forming isolated dimers from two dimethylformamide (DMFA) molecules and from one DMFA and one dimethylsulfoxide (DMSO) molecules has been revealed. The DMFA intermolecular complex represents a closed dimer, whose formation is governed by two weak intermolecular hydrogen bonds and the interaction of molecular charges. The dimerization energy is about 8 kcal/mole, and the dipole moment of the aggregate equals zero. When the intermolecular complex is being formed, the change of bond lengths in the molecules and the charge redistribution between the atoms take place. An approximate account of the interaction with the nearest environment has been carried out for DMFA monomers and dimers in the framework of the Onsager model. In the Raman spectra for the C=O bond vibrations in dimers in liquids, the band shift towards lower frequencies and the variation of the band depolarization factor, in comparison with those of monomer molecules, have been established. The availability of both monomer and dimer molecules, which are in a certain balance in the liquid, must lead to the presence of both the bands of monomers and aggregates in the spectra. At a lower frequency difference of the C=O bond vibrations in those formations, the positions of the bands, the difference of their depolarization factor, and the different compositions of the parallel and perpendicular components of the scattered light have to result in the non-coincidence of the frequencies of the resulting band maxima for these two polarizations, which is really observed in experiment.

When experimentally studying the Raman spectra of DMFA and its solutions in various solvents, the frequency non-coincidence between the positions of the maxima of the C=O vibration bands in the parallel and normally polarized components of the scattering spectrum was revealed [1]. The frequency difference was equal to 14.5 cm<sup>-1</sup> for the pure liquid ( $\nu_{\perp}^{\max} = 1673.0$  cm<sup>-1</sup> and  $\nu_{\parallel}^{\max} = 1658.5$  cm<sup>-1</sup>). In solutions, this distinction disappeared under a

strong dilution. When diluting DMFA in CCl<sub>4</sub>, the bands corresponding to both polarizations were displaced insignificantly towards higher frequencies, with the parallel component of the band being shifted faster as the DMFA concentration diminished. As a result, when the mole fraction of DMFA was equal to 0.1, the frequency difference amounted to 3.3 cm<sup>-1</sup>. When diluting in DMSO, the band of parallel polarization was displaced towards higher frequencies, while the band of perpendicular polarization had insignificant shift towards lower frequencies. At the DMFA mole fraction of 0.2, the frequency difference amounted to 3.0 cm<sup>-1</sup> [1]. The observed phenomenon was accounted for by the aggregation of DMFA molecules. Note that such a non-coincidence of the frequencies of the band maxima is attributed in the literature to the resonance transfer of the vibration energy between interacting molecules [2–5]. In [6], a similar hypothesis was put forward. The influence of the resonant dipole-dipole interaction on the formation of the IR band structure was discussed in [7].

In the present work, *ab initio* calculations were carried out in order to consider an opportunity for the formation of aggregated intermolecular complexes in a liquid in more detail. To confirm the assumptions made earlier [1], concerning the spectral manifestations of the existence of monomers (separate molecules) and intermolecular complexes (dimers for a pure liquid and two-molecule complexes DMFA–DMSO for the DMFA solution in DMSO) in the liquid, *ab initio* quantum-chemical calculations of the spectra of normal vibrations, the band depolarization factors, and the Raman activity were fulfilled.

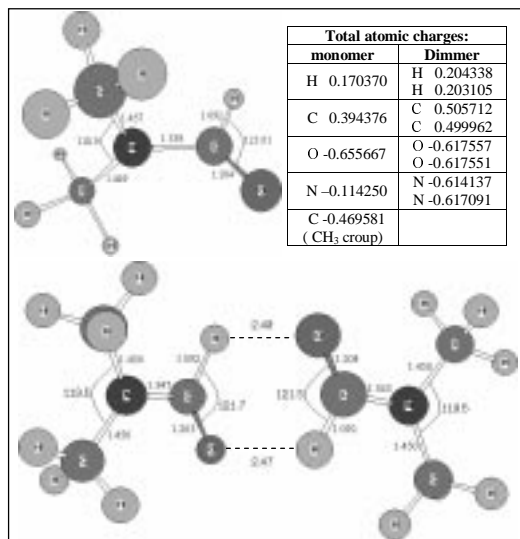


Fig. 1. Structural parameters of the dimethylformamide (DMFA) monomer and dimer in solvation shells consisting of DMFA molecules (pure liquid)

### *Ab Initio* Calculations for DMFA Monomers and DMFA Intermolecular Complexes

The calculations of the optimized structures of a DMFA monomer (a single DMFA molecule), a DMFA–DMFA dimer (two aggregated DMFA molecules), and a DMFA–DMSO dimer were carried out with the help of a computer program Gaussian 98W in the framework of the HFSCF approximation and making use of the 6-31G(*d*) basis set of the Gaussian functions [8]. For a formamide dimer, similar calculations were carried out in [9]. The optimization of energy was fulfilled for all internal coordinates of the researched objects. The normal-vibration frequencies were obtained with the help of analytical calculations of the second derivatives of the total energy with respect to coordinates. In Figs. 1 and 2, the structural parameters, the values of the bond lengths, the point charges at the molecule atoms, and the mutual orientation of molecules in dimers are presented.

The account of the molecule environment in the liquid state of the substance deserves the following remark. According to spectroscopic researches, the transition from the isolated state of a molecule or an intermolecular complex into the liquid state usually results in displacements of the observed bands towards lower frequencies and variations of some band parameters. For modeling the states of separate molecules and dimers in liquids, the account of the nearest environment of the examined molecular

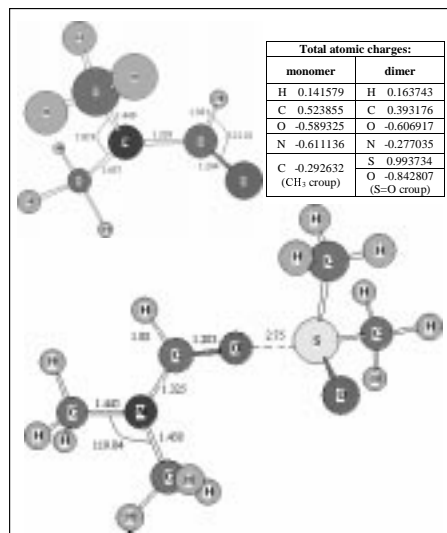


Fig. 2. Structural parameters of a DMFA monomer and the intermolecular complex DMFA–dimethylsulfoxide (DMSO) in solvation shells consisting of DMSO molecules

formations is carried out in the Onsager approximation [10]. Note that this approximation does not take into account every nuance of the interaction between molecules and the environment but makes the basic tendencies in the modification of structural parameters more clear.

The intermolecular complex is a closed dimer. The formation of such an aggregate is connected, first, to the availability of two weak intermolecular hydrogen bonds and, second, with the interaction of residual charges (see Fig. 1). Each  $\text{H} \cdots \text{O}=\text{C}$  distance is equal to about 2.5 Å. The C–H bonds of methyl groups, as is corroborated by calculations, do not participate in the formation of the aggregated complex. The total energy of dimerization is about 8 kcal/mol. When the intermolecular complex is formed, a charge redistribution in the fragment N–COH takes place.

The values of the frequencies of valent C=O vibrations for aggregates and monomers, in an isolated state and in the Onsager approximation (in a solvation shell), are given in the Table. Since the purpose of our research is to compare the spectra of an isolated molecule and the aggregated complex of two molecules and to reveal the spectrum features of the aggregated states in liquids, here we present the results of *ab initio* calculations. The comparison of the calculated values with experimental ones should be carried out taking into account the scaling factors, because the calculated values of normal vibration

frequencies are regularly overestimated in the applied HFSCF approximation by 10–15% for valence bond vibrations and by about 30% for deformation ones [11]. For obtaining the values of vibration frequencies comparable to experimental ones, a special procedure of the scaled quantum-mechanical force field (SQMFF) was applied earlier. It was proposed in [12] and allowed the authors to obtain *ab initio* vibration spectra with the values of frequencies comparable to those measured in experimental researches. According to this method, the spectra of normal vibrations for probe molecules coordinated on the surface of aluminosilicate catalysts were calculated [13]. The matter concerning the relation of the molecular vibration frequencies, calculated with the help of a Gaussian 98W program making use of the 6-31G(*d*) basis set and taking into account the results of [11], was also considered in [14–16].

The vibration frequencies of the C=O bonds of the aggregated complex are shifted towards lower frequencies by about 55 and 26  $\text{cm}^{-1}$  relative to the monomer frequency (the calculated frequencies of the C=O valence bond vibrations are equal to 1966  $\text{cm}^{-1}$  for a monomer and 1911 and 1940  $\text{cm}^{-1}$  for a dimer, with the latter vibration, as is seen from the Table, being scarcely active in Raman spectra. The comparison of the calculated vibration frequencies with experimental ones allows us to obtain the value of the scaling factor  $Sf_{\text{C=O}} = \frac{1665}{1966} = 0.847$  with respect to the frequency  $\nu_{\text{C=O}}$  without scaling the strength factors. Taking this value into account, the frequencies of the C=O vibrations in the dimer intermolecular complex should be expected to be about 1620 and 1643  $\text{cm}^{-1}$ .

The results of calculations can be summarized as follows:

– The interaction of two DMFA molecules may result in the formation of rather stable dimer aggregates with the formation energy of about 8 kcal/mol. The relative orientation of the two molecules in the dimer is such that the resulting dipole moment of the aggregate has an almost zero value. The tendency to dimerization is also preserved in the liquid state of the substance. The energy of the thermal motion of molecules in the liquid is comparable by the order of magnitude with the energy of dimerization; therefore, at a given temperature, we must have an equilibrium mixture of the monomer and aggregated molecules in the liquid. The temperature rise in the substance will lead to a displacement of the balance towards increasing the relative content of monomer molecules. A similar effect should be produced as well by diluting the substance in an inert solvent.

– The aggregation of molecules is such that the variation of the polarizability tensor  $\alpha_{ik}$  of the C=O bond takes place. In this connection, the derivatives  $\frac{\partial \alpha_{ik}}{\partial q_i}$  and, consequently, the depolarization factors of the corresponding bands change. The calculations show that the depolarization factors of the C=O vibration band of dimers is smaller than that of monomer molecules.

– The vibration frequency of the C=O bond in the aggregated molecules must be lower than that in the monomer ones. Taking into account the values of the Raman activity (see the Table), a single band of the C=O vibrations in dimers should actually be observable in the Raman spectra. If there were an equilibrium mixture of aggregates and monomer molecules in the liquid, two bands should be visible in the spectrum: the monomer and dimer ones, whose frequencies differ insignificantly. The high-frequency band has to correspond to the monomer molecules, and

#### Total energy of formation, dipole moment, frequencies of C=O and C–H (CHO grope) vibrations for monomer and dimer of dimethylformamide

Value	Isolated		In a solvation shell				
	Monomer	Dimer	Pure liquid		Solution in CCl <sub>4</sub>	Solution in DMSO*	
			Monomer	Dimer	Monomer	Monomer	Dimer
Total energy (Hartri)	-246.98794	-493.9889	-246.98774	-493.9882	-246.877868	-246.877665	-798.33331
Dipole moment(D)	4.18	0.166	5.1	0.28	4.2	4.3	6.0
C=O bond vibrations							
C=O vibrations frequencies ( $\text{cm}^{-1}$ )	1966.4	1911.8; 1940.2	1935.6	1906.0; 1911.9	1953.4	1935.3	1824.1
Depolarization ratio	0.41	0.39; 0.68	0.43	0.56; 0.37	0.41	0.42	0.33
Raman-activity( $\text{Å}^4/\text{AMU}$ )	12.6	37.9; 0.07	12.04	0.35; 187.9	12.38	12.03	24.6
C–H bond vibrations							
C–H vibrations frequencies ( $\text{cm}^{-1}$ )	3193.5	3282.8; 3278.9	3197.3	3255.6; 3280.1	3195.3	3197.4	3293
Depolarization ratio	0.75	0.15; 0.13	0.69	0.13; 0.05	0.7	0.6	0.14
Raman-activity ( $\text{Å}^4/\text{AMU}$ )	43.4	79.9; 30.8	48.3	378.4; 405.3	45.2	48.4	101.9

Note. In the cases of DMFA solutions in CCl<sub>4</sub> and DMSO, it was supposed that the solvation shell is made up of solvent molecules. This corresponds to the infinitesimally small concentration of DMFA molecules in the solution.

the low-frequency one to the aggregated formations. The small frequency difference and the large half-widths of the bands may lead to the situation where those bands will not be resolved by the device.

The results of calculations show that the environment of the monomer molecules weakly affects their parameters: for the solvation shells comprising the DMFA,  $\text{CCl}_4$ , or DMSO molecules, the parameters, although being different from one another, have no radical changes. The same result may also be expected for the parameters of dimer molecules. However, the formation of dimers brings about the modification of the charge distribution in the fragment N–COH, in comparison with the same fragment in a monomer. We should emphasize a strong influence of the molecule environment on the Raman activity of the dimer bands. Some features in the behavior of the dimer band and, correspondingly, the relation of the monomer and dimer band intensities can occur due to the variation of the Raman activity of the bands.

Provided that DMFA is strongly diluted in DMSO, the formation of complexes made up of two different molecules is possible. The two-molecule aggregates DMFA–DMSO substantially differ from the DMFA–DMFA dimers. For the DMFA molecule in the DMFA–DMSO complex, significant changes of the bond lengths of the N–COH fragment and the essential redistribution of charges between the fragment atoms in comparison with those in the monomer are observed. In this complex, the C=O bond is directed towards the S atom (see Fig. 2), with the distance between the S and O atoms being about 2.7 Å, the angle S...O=C close to 180°, and the energy gain of molecules about 1 kcal/mol. The frequency of the C=O bond vibrations in the DMFA–DMSO dimer is shifted towards lower frequencies, as it is in the DMFA–DMFA dimer, and has the depolarization factor equal to 0.33, the dipole moment of the dimer being equal to 6 D. According to calculations, the C–H bond in the COH group becomes stronger and the hydrogen does not participate in the formation of the H-bond. The charges of C, O, and N atoms of this group change substantially. The anisotropy of the molecule polarizability also varies and, hence, the anisotropy of the C=O bond polarizability has to change too.

### Comparison of Calculations and Experimental Data

Let us compare the results of calculations presented above with those observed in experiment [1]. The measured band of the C=O bond vibrations has different

views for the parallel,  $I_{\parallel}(\nu)$ , and perpendicular,  $I_{\perp}(\nu)$ , components of the Raman spectrum, in particular, the frequencies of the maxima of the  $I_{\parallel}(\nu)$  and  $I_{\perp}(\nu)$  bands do not coincide. At the selected geometry of light scattering,  $I_{\parallel}(\nu) = I_{\text{iso}}(\nu) + \frac{4}{7}I_{\text{an}}(\nu)$  and  $I_{\perp}(\nu) = \frac{3}{7}I_{\text{an}}(\nu)$ , where  $I_{\text{iso}}(\nu)$  and  $I_{\text{an}}(\nu)$  are the total intensities of the isotropic and anisotropic light scattering, respectively. The behavior of the depolarization factor is asymmetric with respect to the maxima of the dependences  $I_{\parallel}(\nu)$  and  $I_{\perp}(\nu)$ . Moreover, the frequency, where the value of the depolarization factor is minimal, is close to the frequency of the  $I_{\parallel}(\nu)$  maximum. This means that the isotropic contribution  $I_{\text{iso}}(\nu)$  into the  $I_{\parallel}(\nu)$  band is large and governs the position of the  $I_{\parallel}(\nu)$  maximum. Those features of the observed band of the C=O bond vibrations in DMFA are easy to be explained if one assumes that this band consists of at least two bands, i.e. the monomer and dimer ones, possessing different values of the depolarization factor. The value of the depolarization factor for the low-frequency band (experiment [1] and the above calculation show that it is a dimer band) is smaller, i.e. the relative contribution of the intensity of the isotropic scattering  $I'_{\text{iso}}(\nu)$  into the total intensity of the parallel component of the dimer band  $I'_{\parallel}(\nu)$  is larger than the relevant value for the high-frequency band of monomers. At room temperature, the intensity in the maximum of the low-frequency band  $I'_{\text{iso}}(\nu)$  is greater than the intensity of the high-frequency band  $I''_{\text{iso}}(\nu)$ . In Fig. 3, the parallel and perpendicular components of the C=O bond vibration band in DMFA, the depolarization factor  $\rho$  of this band, and the decomposition of the  $I_{\text{iso}}(\nu)$  contribution into components are shown. The intensity in the maximum of the resulting band  $I_{\parallel}(\nu)$  is determined by the intensity of the maximum of  $I'_{\text{iso}}(\nu)$ . Under the same conditions,  $\frac{4}{7}$  times the intensity in the maximum of the low-frequency band  $I'_{\text{an}}(\nu)$  is lower than  $\frac{4}{7}$  times the intensity in the maximum of the high-frequency band  $I''_{\text{an}}(\nu)$ . Therefore, the intensity in the maximum in the resulting band  $I_{\perp}(\nu)$  is determined by  $\frac{4}{7}$  times the intensity in the maximum of  $I''_{\text{an}}(\nu)$ . Due to the imposing of the  $I'_{\text{iso}}(\nu) + I''_{\text{iso}}(\nu)$  and  $\frac{4}{7}[I'_{\text{an}}(\nu) + I''_{\text{an}}(\nu)]$  contributions, the position of the maximum of the  $I_{\parallel}(\nu)$  band may deviate from the position of the minimum of the depolarization factor, being mainly determined by the intensity ratio of the isotropic components of the bands, provided that the depolarization factor should be not more than 0.4. Concerning the  $I_{\perp}(\nu)$  component, the position of its maximum will be determined by the intensity ratio of the anisotropic components of the overlapping bands. As a result, if the values of the depolarization factor of

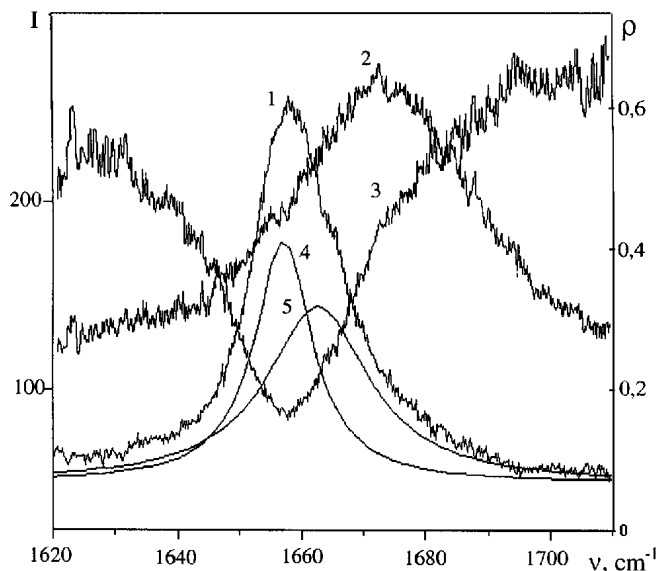


Fig. 3. Parallel (1) and perpendicular (2) components, and the depolarization factor  $\rho$  (3) of the C=O bond vibrations band in DMFA; the intensity dependences are not reduced to the same scale. Curves 4 and 5 represent the decomposition of the  $I_{\text{iso}}(\nu)$  contribution into components

the overlapping bands are different, the maxima of  $I_{\parallel}(\nu)$  and  $I_{\perp}(\nu)$  do not have to coincide.

What can stimulate the appearance of overlapping bands in the apparent contour of the C=O bond vibration spectrum for DMFA? Similar cases of band splitting for one or another kind of vibrations of atoms in a molecule have already been known for a long time in the case of the intermolecular hydrogen bond [17]. The intermolecular hydrogen bond is possible in the DMFA case, although, most likely, it has to be weak. Taking into account the data of calculations, according to which the resulting dipole moments of the DMFA aggregates are almost absent, one may suppose that the interaction of molecular charges should play an important role. Thus, in liquid DMFA, there are monomer molecules and dimer aggregates responsible for the neighbor bands of C=O bond vibrations with different values of the depolarization factor, which results in the complicated structure of the bands  $I_{\parallel}(\nu)$  and  $I_{\perp}(\nu)$  with non-coincident frequencies of their maxima.

The change of the liquid temperature or its dilution in any solvent, owing to the variation of the ratio between the monomer and dimer numbers, should result in a growth of the relative intensity of either of two bands and, at a strong temperature variation or strong dilution, to the reduction or even to the disappearance

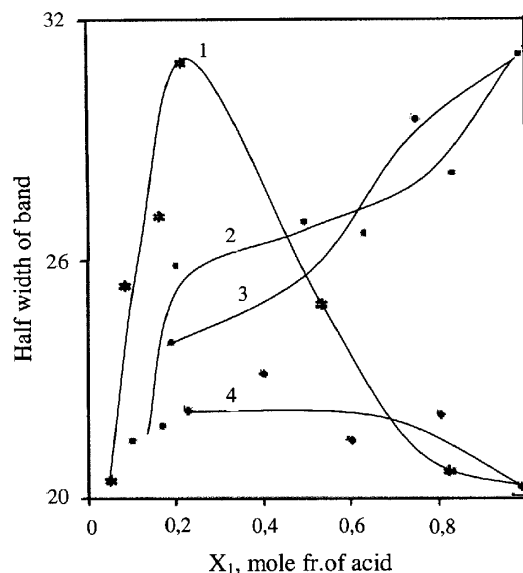


Fig. 4. Dependence of the band width of C=O bond vibrations in DMFA on the DMFA concentration in various solutions: for the isotropic component in  $\text{CCl}_4$  (1) and DMSO (4) solvents, and for the anisotropic one in DMSO (2) and  $\text{CCl}_4$  (3) solvents

of the other imposed band. The frequency difference between the maxima of the observed resulting bands  $I_{\parallel}(\nu)$  and  $I_{\perp}(\nu)$  should vary in this case.

A noticeable modification of the width of the resulting C=O bond vibration band with the variation of the DMFA content in the mixture is connected to the change of the relation between the numbers of monomer and aggregated formations and, therefore, to the variation of the intensity relation between the bands corresponding to those formations. At the dilution of DMFA within the investigated range of concentrations, the decrease or increase of the band width or its passage through a maximum can be observed depending on the direction of a variation of the relative content of monomers and aggregates in the liquid and the ratio between the intensities of the corresponding bands  $I_{\parallel}(\nu)$  and  $I_{\perp}(\nu)$  (see Fig. 4).

The behavior of the C=O band in the DMFA–DMSO solution, as distinct from that in the DMFA– $\text{CCl}_4$  one [1], is connected to an opportunity for the formation of a dimer from diverse molecules. According to the calculations discussed above, such molecules are responsible for the lower-frequency band, in comparison with the monomer-induced one, with a smaller value of the depolarization factor. When DMFA is more diluted in DMSO, the relative content of monomers decreases.

Both the dimer and monomer bands are shifted towards higher frequencies, but, due to the reduction of the monomer content and the reduction of their contribution into the intensity of the resulting band, there is an impression that the maximum of  $I_{\parallel}(\nu)$  is displaced towards higher frequencies, and the maximum of  $I_{\perp}(\nu)$  moves insignificantly towards lower ones.

Thus, we see that the calculations are in rather a good agreement with experimental data. Not depreciating the role of the resonant interaction of molecules with the transfer of the vibrational energy, we come to a conclusion that the aggregation of molecules and molecular modifications caused by this aggregation are not less important when considering the effect of the frequency discrepancy between the  $I_{\parallel}(\nu)$  and  $I_{\perp}(\nu)$  maxima.

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АГРЕГАЦІЯ МОЛЕКУЛ У РІДКОМУ  
ДИМЕТИЛФОРМАМІДІ ТА ЙОГО  
РОЗЧИНАХ: НЕЕМПІРИЧНІ РОЗРАХУНКИ  
І СПЕКТРИ КОМБІНАЦІЙНОГО РОЗСІЯННЯ

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Резюме

На основі *ab initio* розрахунків, проведених за програмою Gaussian 98W у наближенні самоузгодженого поля Хартри — Фока з використанням базису гауссівських функцій 6-31G (d), встановлено можливість формування ізольованих димерних утворень з молекул диметилформаміду (ДМФА) та молекули ДМФА і молекули диметилсульфоксиду (ДМСО). Міжмолекулярний комплекс ДМФА являє собою замкнутий димер, утворення якого зобов'язане наявністю двох слабких міжмолекулярних водородних зв'язків і взаємодії зарядів молекул. Енергія димеризації дорівнює 8 ккал/моль, дипольний момент агрегату нульовий. Внаслідок утворення міжмолекулярного комплексу змінюються довжини зв'язків у молекулах і перерозподіляються заряди між атомами. Наближене врахування взаємодії з найближчим оточенням для мономерів і димерів ДМФА проведено за моделлю Онзагера. У спектрах комбінаційного розсіяння світла для С=О-коливань димерів у рідкому стані виявлено зміщення смуги у бік менших частот і зміну, у порівнянні з мономерними молекулами, коефіцієнта деполаризації смуги. Наявність у рідині і мономерних, і димерних молекул, які перебувають у певній рівновазі, повинно привести до прояву у спектрах і смуги мономерів, і смуги агрегатів. У разі невеликої різниці частот С=О-коливань цих утворень накладання смуг, різниця їхніх коефіцієнтів деполаризації та різний склад паралельної і перпендикулярної складових розсіяного світла повинні привести до незбігу частот максимумів результатуючих смуг у цих двох поляризаціях, що і спостерігається в експерименті.