

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

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S u m m a r y

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.