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# On large amplitude motions of simplest amides in the ground and excited electronic states

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**Abstract.** For the formamide, acetamide, N-methylformamide and N-methylacetamide molecules in the ground ($S_0$) and lowest excited singlet ($S_1$) and triplet ($T_1$) electronic states equilibrium geometry parameters, harmonic vibrational frequencies, barriers to conformational transitions and conformer energy differences were estimated by means of MP2, CCSD(T), CASSCF, CASPT2 and MRCI ab initio methods. One-, two- and three-dimensional potential energy surface (PES) sections corresponding to different large amplitude motions (LAM) were calculated by means of MP2/aug-cc-pVTZ ($S_0$) and CASPT2/cc-pVTZ ($S_1$,$T_1$). For these molecules, in each excited electronic state six minima were found on 2D PES sections. Using PES sections, different anharmonic vibrational problems were solved and the frequencies of large amplitude vibrations were determined.

The simplest amides (RCONHR') in the ground electronic state prove to be suitable in modelling the structure and properties of peptides, which are abundant in nature and play crucial role in many biochemical processes. The investigation of the amides in the lowest excited electronic states is important considering different photophysical and photochemical processes in which amides take part. For instance, peptides and monosubstituted amides photoisomerize in aqueous solution to the less stable *cis* isomers during 220 nm ultraviolet resonance Raman experiments ([1]). Thus, the describing of the structure and conformational dynamics of the amide molecules in different electronic states is an important and actual problem.

The results presented in this paper are devoted to formamide ($HCONH_2$), acetamide ($CH_3CONH_2$), *N*-methylformamide ($HCONHCH_3$) and *N*-methylacetamide ($CH_3CONHCH_3$) in the ground ($S_0$) and lowest excited singlet ($S_1$) and triplet ($T_1$) electronic states.

In $S_0$ electronic state the heavy atoms' frame of these molecules is planar though the potential functions of out-of-plane CNHR' vibration have a very shallow minima. Electronic excitation to $S_1$ and $T_1$ states was previously shown to cause strong pyramide-like deformation of both CNHR' and OCNR fragments and their rotation one around another in formamide and *N*-methylacetamide [2].

Among all amide vibrations, there are so-called large amplitude motions (LAM). These motions are known to play important role in describing the dynamics of conformationally non-rigid molecules. A few LAM could be considered in these molecules, namely: asymmetric (around "central" CN bond) and symmetric (the methyl top) internal rotations

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for all aforementioned electronic states, out-of-plane vibrations of CNHR' fragment in $S_0$ electronic state and the inversions of both CNHR' and OCNR fragments in excited electronic states.

In order to describe these LAM correctly, 1D, 2D and 3D vibrational problems were solved using following model Hamiltonian:

$$\hat{H}(\varphi_1,\ldots,\varphi_n) = -\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\partial}{\partial\varphi_i}B_{ij}(\varphi_1,\ldots,\varphi_n)\frac{\partial}{\partial\varphi_j} + V(\varphi_1,\ldots,\varphi_n)$$

where $n$ is the dimension of the problem (i.e. the number of vibrational degrees of freedom considered), $\varphi_i$ — natural coordinates used in describing LAM, $B_{ij}$ — kinematic parameters, and $V$ — potential function (i.e. PES section).

*Ab initio* quantum chemistry methods used in this work for calculating various 1D, 2D and 3D PES sections along the LAM coordinates were MP2 ($S_0$) and CASPT2 ($S_1$, $T_1$) with basis sets aug-cc-pVTZ and cc-pVTZ, respectively. The active space (6-5) for the CASSCF and CASPT2 methods consisted of 5 molecular orbitals occupied by 6 electrons. These molecular orbitals are located on the carbonyl group and can be classified as $\sigma_{CO}$, $\pi_{CO}$, $n_O$, $\pi^*_{CO}$, $\sigma^*_{CO}$. All CASSCF and CASPT2 calculations were conducted as state specific.

Solving different vibrational problems with previously calculated PES sections as the potentials yields the vibrational levels' energies and vibrational wave functions. For $S_0$ electronic states anharmonic vibrational frequencies of formamide and acetamide are in good agreement with available experimental data [3,4]. For *N*-methylformamide, 2D (with internal rotation around the "central "CN bond and the NH out-of-plane vibration) and 3D vibrational frequencies of these two motions are in satisfactory agreement with each other and with harmonic approximation. However, the discrepancy revealed in the comparison of calculations and experiment [5] is significant enough to understand the importance of conducting more complicated and modern experiments [6]. For all considered molecules in $S_0$ electronic state there is a sufficient correlation between the internal rotation of "central" CN bond and out-of-plane CNHR' vibration.

On 2D PES sections of investigated amides in $^{1,3}(n,\pi^*)$ electronic states *ab initio* calculations predict six minima to exist (corresponding to 3 pairs of mirror symmetry conformers in the case of formamide and acetamide and to 6 entirely different conformers for *N*-methylformamide and *N*-methylacetamide). When compared to $S_0$ electronic state, in $S_1$ and $T_1$ electronic states the rotation around CN bond does not lead to essential changes in geometry structure of CNHR' fragment. In general, it could be said that the amide molecules in the lowest excited electronic states are less flexible than in ground electronic state. In excited electronic states of amide molecules increasing the dimension of vibrational problem solved (at least, from 1D up to 3D) does not lead to considerable changes of the lowest torsion levels energies. Vibrational wave functions in excited electronic states are more sophisticated than those in the ground electronic state: they are delocalized. This is the case due to close locations of PES minima and relatively low barriers to conformational transitions (compared to the ground electronic state).

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