



Structure and conformational dynamics of formamide molecule in the ground and lowest excited electronic states

Nickita V. Tukachev^{*1}, Vadim A. Bataev, Alexander V. Abramenkov, Igor A. Godunov

Lomonosov Moscow State University, Chemistry Department, 119991 Moscow, Leninskie gori, 1, Russian Federation



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ABSTRACT

Electronic state calculations, such as equilibrium geometry parameters, harmonic vibrational frequencies and potential barriers to conformational transitions (as well as conformer energy differences in excited states), using *ab initio* methods, such as MP2, CCSD(T), CASSCF, CASPT2 and MRCI, were carried out on the formamide molecule in the ground (S_0) and the lowest excited singlet (S_1) and triplet (T_1) states. One-, two- and three-dimensional PES sections corresponding to different large amplitude motions (LAMs) were calculated using the MP2/aug-cc-pVTZ (S_0) and CASPT2/cc-pVTZ (S_1 , T_1) methods. In each excited electronic state, six minima with comparatively small potential barriers to internal rotation (less than 15 kJ/mol) between them were discovered. Using PES sections, the anharmonic vibrational problem was solved, and the frequencies of the LAMs were determined.

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1. Introduction

Formamide (HCONH_2) is the simplest molecule containing a peptide bond, so its structure and spectral characteristics in the ground electronic state (S_0) have been a target of numerous theoretical and experimental investigations (see [1–5] and references therein).

In ref. [6], microwave spectra of 14 formamide isotope substituents were investigated in detail, and as a result, the r_s -structure of formamide was established. The formamide molecule was shown to be planar; however, the potential energy surface (PES) section corresponding to the out-of-plane NH_2 vibrational coordinate had a very wide and shallow minimum. This conformation was confirmed later by the results of rovibrational spectra analyses [1,7]. It was also noted that the CNH_2 fragment in formamide exhibits a strong coupling of internal rotation and out-of-plane vibration [7].

There are many works devoted to analyzing the vibrational spectra of the formamide molecule in different phases (see [1,2] and references therein). In particular, all assignments for formamide fundamentals in vapor were listed in [1] as one-dimensional (1D) potential function for out-of-plane NH_2 vibration based on experimental energy levels. In addition, in [3], the

frequencies of torsion and out-of-plane NH_2 vibrations were estimated using a two-dimensional (2D) approximation by considering their apparently strong coupling.

The structure of formamide in excited electronic states has been investigated to a lesser extent. Electronic excitation energies of formamide to the lowest triplet and singlet electronic states T_1 ($n\pi^*$), S_1 ($n\pi^*$), T_2 ($\pi\pi^*$) and S_2 ($\pi\pi^*$) were obtained both experimentally ([8,9]) and by use of *ab initio* methods (see [10–13] and references therein). However, no experimental data describe the geometry parameters or vibrational frequencies of formamide in excited electronic states [14].

Earlier calculations ([12,15,16]) predicted that the formamide transition from the ground (S_0) to the lowest excited singlet (S_1) and triplet (T_1) electronic states causes geometrical relaxation resulting in the pyramidalization of both the HCON and CNH_2 fragments. Harmonic vibrational frequencies of the formamide molecule in some excited electronic states were calculated in [16]; however, the method used (namely, MNDOC-CI) is now considered valid only for qualitative results. In addition, there are no data in the literature dealing with possible anharmonic effects for LAMs in formamide in excited electronic states.

For peptides and simple amides (such as *N*-methylacetamide), photoisomerization in aqueous solution to the less stable *cis* conformer as observed experimentally (see Refs. [1] and [2] in [17]). Computational investigation of this isomerization's possible mechanism was carried out in [17] by calculating the minimal energy configurations of formamide and *N*-methylacetamide in the T_1 ($n\pi^*$), S_1 ($n\pi^*$) and S_2 ($\pi\pi^*$) electronic states. Geometry parameters

* Corresponding author. Fax: +7 (095) 939 3689.

E-mail addresses: tukachev.nikita@mail.ru (N.V. Tukachev), v.a.bataev@gmail.com (V.A. Bataev), a.v.abramenkov@gmail.com (A.V. Abramenkov), godunov@phys.chem.msu.ru (I.A. Godunov).

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were optimized with the Unrestricted Hartree-Fock (UHF) method for the T_1 state and the Configuration Interaction Singlets (CIS) method for the S_1 and S_2 states. The basis set used for all of these calculations was 6-31G*.

It was found that the $S_0 \rightarrow T_1$ and $S_0 \rightarrow S_1$ electronic transitions caused pyramidalization of HCON and CNH₂ fragments as well as their rotation around the CN bond. As a result, in the T_1 , S_1 , and S_2 excited electronic states, there were a few different conformers with potential barriers to internal rotation around the CN bond approximately equal to 5 kcal/mol (21 kJ/mol) in the S_1 state and 3 kcal/mol (13 kJ/mol) in the T_1 state [17]. Space models of the lowest energy conformers were also shown in [17], but there was no detailed information about the quantity and geometry parameters for any of the conformers in the T_1 , S_1 , and S_2 excited electronic states.

Large amplitude motions (LAMs) such as internal rotations, inversions and some other out-of-plane vibrations play a very important role in conformational analysis. Conformational transitions usually occur due to these intramolecular motions. That is, one of the main focuses of present paper is to investigate these motions in formamide.

In the present work, a detailed investigation of the structure of the formamide molecule in the ground (S_0) and lowest excited singlet (S_1) and triplet (T_1) electronic states was carried out. In particular, 1D, 2D and 3D PES sections corresponding to different large amplitude motion (LAM) coordinates in excited states of formamide were calculated. Then, the corresponding vibrational problems were solved, and the vibrational levels' energies were determined.

2. Computational details

Calculations on formamide in the S_0 state were performed by *ab initio* methods such as MP2, QCISD(T) and CCSD(T) as well as CASPT2 to compare geometry parameters and vibrational frequencies in the S_0 , S_1 and T_1 states and to estimate electronic transition energies. As the main method used for excited states calculations, we chose CASPT2/cc-pVTZ (Data obtained by the CASSCF and MRCI methods are also presented in this paper for comparison.).

Sections of the PES of formamide in the S_0 state were calculated using the MP2/aug-cc-pVTZ method. This method was shown to reproduce experimental geometry parameters quite well while also requiring less time than QCISD(T) and CCSD(T) to optimize the structure. These last two methods were applied for point calculations to verify the MP2 results.

The active space (6-5) for the CASSCF, CASPT2 and MRCI methods consisted of 5 molecular orbitals occupied by 6 electrons. These molecular orbitals are generally located around carbonyl group nuclei and thus can be classified as σ_{CO} , π_{CO} , n_O , π_{CO}^* , σ_{CO}^* . To verify these results, test calculations in a wider (10-8) active space were also performed. This active space was produced by expanding the 6-5 active space with orbitals located on the nitrogen nucleus (σ_{CO} , σ_{CN} , π_{CO} , n_O , n_N , π_{CO}^* , σ_{CN}^* , σ_{CO}^*). All CASSCF and CASPT2 calculations were state specific. In the CASSCF calculations, the problem of variational collapse was avoided by thoroughly controlling the initial and obtained molecular orbitals. We used an internally contracted MRCI in which only the double excitations were contracted, while the reference functions and the single excitations were left uncontracted.

The geometry parameters and energy differences of the conformers calculated in these active spaces were found to be close. However, smaller complete active space (6-5) is characterized by better convergence of iteration procedures and higher stability towards essential changes to internuclear angles.

All *ab initio* computations were performed using the Molpro.2010 software program package [18]. All cut-offs used in our

calculations were defaults except for the energy (10^{-8} Hartree) and its gradient (10^{-5}) in the iterative optimization procedure.

Frequencies of all 12 formamide fundamentals were obtained by use of harmonic approximation. Among formamide fundamentals in the excited S_1 and T_1 electronic states, there are three LAMs: internal rotation around the CN bond and inversions of both pyramidal HCON and CNH₂ fragments. To describe these LAMs more correctly, we solved different anharmonic vibrational problems. The model under consideration is based on separating intramolecular LAMs from both small vibrations and the rotation of the whole molecular framework (e.g., [19–21]).

The formamide molecule is very flexible, and therefore the choice of essential coordinates for the vibrational problem is not trivial. Some examples of the coordinate choices are presented in [7,22]. We described the geometry parameters of the molecule using the imaginary atom A (see Fig. 1) to account for the symmetry of the molecule. The location of atom A was defined as follows: the segment AN lied in plane with the NH₂ bond, and it was perpendicular to the NC bond. As a result, the coordinate of the out-of-plane NH₂ vibration was defined as the angle of NH₂ rotation around the AN axis in relation to the NC bond, and the angle between the NC bond and the NH₂ plane was denoted as $\angle NC$. Internal rotation around the CN bond was described as the change of the dihedral angle $\angle OCNA$, and the inversion of the HCON fragment in the excited electronic states was defined as the change of the angle between the CH bond and the OCN plane (thereafter denoted as $\angle CH$). The planar configuration of the molecule corresponded to a configuration where all of the coordinates under consideration were equal to zero.

The model Hamiltonian can be written as

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

where $n = 1, 2, 3$ is the dimension of problem considered (which is denoted later as 1D, 2D, and 3D, respectively), i.e., the number of coordinates φ_i , B_{ij} in the kinematic parameters ($B_{ij} = B_{ji}$), and V is the potential function.

Both B_{ij} and V calculated for different geometrical configurations of the molecule were approximated by periodic functions of three angular variables φ_i constructed with the regard to symmetry considerations. One can suppose following symmetry restrictions for the potential function $V = V(\varphi_1, \varphi_2, \varphi_3)$, where φ_1 is the angle of internal rotation around the CN bond, φ_2 is the coordinate of the HCON inversion, and φ_3 is the coordinate of the CNH₂ inversion:

$$V(\varphi_1, \varphi_2, \varphi_3) = V(\varphi_1 + \pi, \varphi_2, -\varphi_3), \quad (2)$$

$$V(\varphi_1, \varphi_2, \varphi_3) = V(-\varphi_1 - \varphi_2, -\varphi_3) \equiv V(2\pi - \varphi_1, -\varphi_2, -\varphi_3) \quad (3)$$

Eq. (2) shows that the 180° rotation of the amino group around the CN bond that resulted in the CNH₂ inversion produced an identical molecule configuration. Based on these two general equations, more specific equations were found dealing with 2D PES sections by internal rotation and inversion coordinates. (More detailed information is given in [Supplementary Materials 1](#).)

The kinematic parameters $B_{ij}(\varphi_1, \varphi_2, \varphi_3)$ and the potential function $V(\varphi_1, \varphi_2, \varphi_3)$ were calculated in the ranges $0 \leq \varphi_1 \leq 360^\circ$, $-60^\circ \leq \varphi_2 \leq 60^\circ$, and $-70^\circ \leq \varphi_3 \leq 70^\circ$ with a 10° step size for the inversion and out-of-plane vibrations and 15° for the torsion coordinates. The coefficients in the corresponding approximations are presented in [Supplementary Materials 2](#).

The energy levels and their corresponding wave functions for the 1D, 2D and 3D model Hamiltonians such as Eq. (1) were computed variationally by means of Vib3D program written by

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