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Conformational analysis of acetamide in the ground and lowest excited electronic states



N.V. Tukachev*, V.A. Bataev, I.A. Godunov

Lomonosov Moscow State University, Chemistry Department, Leninskie gori, 1, 119991 Moscow, Russia

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ABSTRACT

For acetamide molecule (CH_3CONH_2) in the ground (S_0) and lowest excited singlet (S_1) and triplet (T_1) electronic states calculations of equilibrium geometry parameters, harmonic vibrational frequencies and barriers to conformational transitions (also conformer energy differences in excited states) using following *ab initio* methods: MP2, CCSD(T), CASSCF, CASPT2 and MRCI were performed. One-, two- and three-dimensional potential energy surface (PES) sections by different large amplitude motions (LAM) coordinates were calculated by means of MP2/aug-cc-pVTZ (S_0) and CASPT2/cc-pVTZ (S_1 , T_1). As a result of electronic excitation, both CON and CNH_2 fragments become pyramidal. On 2D PES sections by torsion (CN) and inversion coordinates there are six minima forming three pairs of enantiomers. Using PES sections different anharmonic vibrational problems were solved and the frequencies of large amplitude vibrations were estimated.

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1. Introduction

Acetamide (CH_3CONH_2) is one of the simplest amide molecules and it was studied both by experimental and theoretical methods due to its importance as a model for the peptide bond in biological molecules.

Microwave spectra of acetamide were thoroughly investigated in literature [1–3, review 4]. However, there are still not enough information to obtain full r_s structure of acetamide and the only available experimental geometry parameters were obtained by gas electron diffraction in 1973 [5]. It was assumed [5] (from the analysis of related molecules) that this molecule belongs to the C_s point group of symmetry with all nuclei excluded two hydrogens of methyl group located on the plane of symmetry. Later, the absence of *c*-type transitions and non-planar component of dipole moment confirmed mentioned supposition. It should be noted also that the barrier to internal rotation of methyl top in acetamide was found to be very low: 24 cm^{-1} [1].

Geometry parameters of acetamide calculated by different *ab initio* methods are generally in satisfactory agreement with each other. Comprehensive review of different quantum chemistry computations is presented in work [6]. It was shown [6] that MP2 calculations yield for orientation of methyl top *syn*-conformation in relatively small basis sets and *anti*- in larger ones, while CCSD calculations tend to give *perpendicular* conformation (see Fig. 1).

Taking into account the very low barrier to internal rotation around CC bond in acetamide one should understand that *ab initio* methods are unable to definitely predict the orientation of methyl group. Detailed investigation of rotational structure of first three vibrational A-levels of methyl top was conducted in work [7]. Potential function of internal rotation around CC bond was calculated as a result of inverse vibrational problem and found to have very shallow form around minima.

According to some *ab initio* calculations, CNH_2 fragment is planar; other methods predict it to be pyramidal (with very low barrier $< 3\text{ cm}^{-1}$ to corresponding conformational transition) [8].

IR spectra of acetamide in vapour was investigated in works [9–11]. It is reported [10] that IR spectra of acetamide (with resolution equal to 2 cm^{-1}) qualitatively correspond to IR spectra of formamide (HCONH_2) with the exception of the lowest energy transition' line splitting. With higher resolution, one can observe small splittings for the lines in a range $200\text{--}300\text{ cm}^{-1}$; peak corresponding to frequency 259 cm^{-1} seemingly consists of a few overlapping lines. Authors [10] explain these splittings as the consequence of interaction of out-of-plane vibrations of amino group with methyl top rotation (which as pointed above has a very low barrier). This interaction could provide difficulties for correct interpretation of both microwave and IR spectra. In work [12] IR spectra of acetamide and its deuterated substituents were observed in argon matrix. Vibrational frequencies were found to be close to those obtained in vapour phase. Using the force constant of torsion CN vibration the barrier to internal rotation around CN bond was estimated to be 6771 cm^{-1} . Frequency of the methyl top rotation was not observed in IR spectra but was estimated to be

* Corresponding author.

E-mail address: tukachev.nikita@mail.ru (N.V. Tukachev).

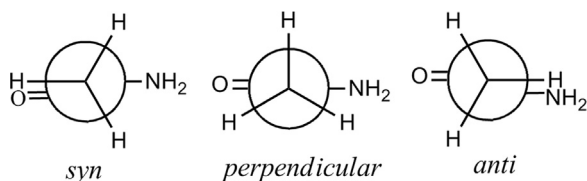


Fig. 1. Possible stable orientations of methyl top in acetamide in S_0 electronic state.

less than 100 cm^{-1} due to the absence of corresponding line in technically available frequency range.

Theoretical attempts to model vibrational spectrum of acetamide did not go beyond harmonic approximation. In work [6] harmonic vibrational frequencies were calculated by means of HF/6-31+G**, HF/6-311++G**, MP2/6-311++G**, MP2/cc-pVTZ, DFT/6-311++G** *ab initio* methods. It is worth mentioning that frequencies of torsion (CC) and out-of-plane NH_2 vibrations calculated by different methods could differ up to three times.

Excited electronic states of acetamide are less investigated both experimentally and theoretically. Electronic spectrum of acetamide in gas phase reported in [13] shows an intense and broad band peaking at 7.4 eV that was assigned to the ($\pi \rightarrow \pi^*$) transition. A weak transition in the red edge of the spectrum was observed at 5.44 eV in dioxane and characterized as ($n \rightarrow \pi^*$) [14]. Vertical absorption spectra were computed by CASSCF and CASPT2 methods [15]; results obtained were found to be in good agreement with available experimental data. Earlier, MNDOC-CI calculations [16] predicted that electronic transition from the ground (S_0) to the lowest excited singlet (S_1) and triplet (T_1) electronic states causes (after relaxation of geometry parameters) pyramidalization of both the CCON and CNH_2 fragments. Due to the possibility of inversion of these two pyramidal fragments the existence of two conformers – cisoid and transoid – was proposed and then found for acetamide in S_1 and T_2 states. Harmonic vibrational frequencies of the acetamide molecule in S_1 , T_1 and T_2 electronic states were also estimated in [16].

Internal rotations in CONH fragments in peptides are reported to induce electronic relaxation through excitation transfer from other chromophore groups (e.g. like in phenylalanine [17] it was resulted in non-radiative transition from excited aromatic residue to excited –CONHR part). Due to this peculiar feature, the investigation of large amplitude motions (LAMs) in excited electronic states of amides could be important in describing possible fluorescence quenching mechanisms of related molecules. However, there are no data in literature dealing with possible anharmonic effects for LAMs in acetamide in excited electronic states.

The aim of present work is detailed conformational analysis of the lowest excited S_1 and T_1 electronic states and re-investigation of the ground electronic state S_0 of acetamide. In our work we study not only the inversion like in [16] but also the internal rotation around CN bond as the internal motion accounting for the conformer' formation. As a result we find out that there are three pairs of different conformers in acetamide in S_1 and T_1 electronic states. In order to investigate the shape of potential energy surfaces in aforementioned electronic states, 1D, 2D and 3D PES sections corresponding to different LAM coordinates are calculated. To account for possible anharmonicity of LAM the corresponding vibrational problems are solved producing the vibrational levels' energies and wave functions.

2. Computational details

Calculations on acetamide in the S_0 state were performed by *ab*

initio methods such as MP2 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. A few stationary points on PES were also computed by MRCI-SD method in cc-pVTZ basis set for comparison. PES sections of acetamide in the S_0 state were calculated using the MP2/aug-cc-pVTZ method. This method was shown to reproduce experimental geometry parameters of related molecules quite well while also requiring less time than CCSD(T) to optimize the structure [18].

The active space (6-5) for the CASSCF, CASPT2 and MRCI methods consisted of 5 molecular orbitals occupied by 6 electrons (for the latter two, reference wave function used was from CASSCF). These molecular orbitals are generally located on the carbonyl group and can be classified as σ_{CO} , π_{CO} , n_{O} , π^*_{CO} , σ^*_{CO} . All CASSCF, CASPT2 and MRCI calculations were conducted as state specific. In the CASSCF calculations, the problem of variational collapse was avoided by thoroughly controlling the initial and obtained molecular orbitals.

All *ab initio* computations were performed using the Molpro.2010 software program package [19]. 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 21 acetamide fundamentals were calculated in harmonic approximation. There are a few LAMs: internal rotations around the CN and CC bonds, out-of-plane CNH_2 vibration in the ground state and inversions of both pyramidal CCON and CNH_2 fragments in excited states. To properly describe these LAMs we solved different anharmonic vibrational problems. The model under consideration is based on separating intramolecular LAMs from both small-amplitude vibrations and the rotation of the molecule as a whole (e.g., [20,21]).

To account for the permutation symmetry of two amino group' hydrogens we describe molecular geometry parameters using the imaginary atom A (see Fig. 2). The location of atom A is defined as follows: the segment AN lied in plane with the NH_2 bond, and it is perpendicular to the NC bond. Internal rotation around the CN bond is described as the change of the dihedral angle $\angle \text{ANCC}$ (φ_1), and the inversion of the CCON fragment in the excited electronic states was defined as the change of the angle between the CO bond and the NCC plane (φ_2). The coordinate of the out-of-plane NH_2 vibration (and inversion of CNH_2 fragment in excited electronic states) is defined as the angle of NH_2 rotation around the AN axis in relation to the NC bond, and the angle between the NC bond and the NH_2 plane is denoted as φ_3 . The internal rotation around CC bond is presented as a change of $\angle \text{H}_2\text{CCN}$ dihedral angle (φ_4). C_3 dynamic symmetry of the methyl top is effectively considered in potential and kinematics approximations by using functions $\cos(3k\varphi_4)$ or $\sin(3k\varphi_4)$. Two possible C_s configurations of the molecule correspond to a configurations where φ_1 is equal

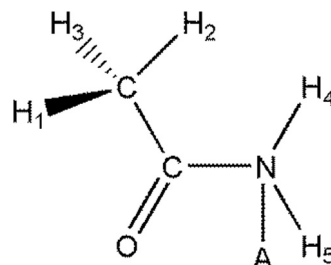


Fig. 2. Structure of acetamide. A is the imaginary atom.

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