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Acetamide as the model of the peptide bond: Nonadiabatic photodynamical simulations in the gas phase and in the argon matrix

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ABSTRACT

The short-time photodynamics of acetamide in the gas phase and in the Ar-matrix starting from the first excited singlet S_1 ($n-\pi^*$) and S_2 ($\pi-\pi^*$) states was explored by the direct trajectory surface hopping method based on multiconfigurational ab initio calculations. For the $n-\pi^*$ state effect of embedding into Ar matrix employing hybrid QM/MM approach on the lifetime and dissociation paths was also discussed. The calculations show that nonadiabatic deactivation from the S_1 to the ground state occurs within 785 fs via the crossing seam related to the C–N bond stretching MXS. The major products in the gas phase are $\text{NH}_2 + \text{CH}_3\text{CO}$ radicals which partially undergo further dissociation of the CH_3CO or recombination to the parent molecule. The embedding of the molecule in the Ar matrix considerably suppresses the C–N dissociation and prevents dissociation of the CH_3CO radical.

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1. Introduction

Interaction of small amides with ultraviolet light is continuing to attract substantial interest both experimentally [1–7] and computationally [8–16] mostly because the low molecular weight products of their photodegradation have been recognized as the active precursors in prebiotic synthesis of proteins [17]. Formamide and acetamide are particularly challenging in this regard since they are the only naturally occurring molecules containing a peptide bond which provides linkage to polymerization of aminoacids into proteins that have been detected in the interstellar medium. It is interesting to mention in this context that acetamide is the largest amide found in the interstellar medium so far [18]. Consequently, understanding of their behavior toward UV irradiation is crucial for enlightening the role of small amides in the prebiotic formation of aminoacids [19] and to learn about their survival conditions under light irradiation in an astrophysical content. In addition, the study of the mechanism of their dissociative photoionization has significant implications in many other fields, to mention only use of mass spectrometry in peptide sequencing [20–22], laser surgery [23] or photodegradation of biopolymeric materials [24].

As a part of our interest in this topic we have previously reported on dynamics simulation of formamide (here denoted as FOM) photodissociation in the gas phase [11], in solution [25]

and in Ar-matrix [15], as well as on the effect of protonation [13] and replacing the amino hydrogen atoms in formamide with the methyl groups leading to *N,N*-dimethylaminoformamide (DMF) [14]. Most important results of this work were summarized in two recent reviews [26,27]. Recently, effect of a methyl substitution, using *cis*- and *trans*-*N*-methylformamide (*cis/trans* MF) in the gas phase and in Ar matrix was reported by Sander and Barbatti [28]. The latter studies showed that substitution by the methyl group at the NH_2 site has profound effect on lifetime and efficacy of dissociation. In the present paper dynamics simulation of photodissociation of acetamide (denoted hereafter as AC) is carried out with the focus on the effect of methylation of the carbonyl group on the mechanism of photodissociation of the C–N bond from the S_1 state in the gas phase and in the argon matrix. This is of some interest since the attachment of the methyl group at the carbon atom and the NH_2 site in formamide is expected to have opposite effect on the strength of the central C–N bond. In AC the C–N bond will elongate to some extent in comparison to the C–N bond in the parent formamide due to the weakening of the $p-\pi$ interaction in the $-\text{N}-\text{C}=\text{O}$ moiety. On the other hand presence of the methyl group(s) at the amino nitrogen atom in MF and DMF causes strengthening of the $p-\pi$ interaction resulting in the slight shortening and thus strengthening of the C–N bond. Our second aim in carrying this work was to provide an insight into effect of methyl group attached to the C-termini of the peptide bond on efficacy of photodissociation in the Ar matrix. These calculations will be limited to dissociation from the S_1 state. Finally, for the sake of comparison with the results obtained for formamide the effect of the

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methyl group attachment on photodissociation from the S_2 state will be also considered. In this way the present work complements previous computational studies on photodissociation of the peptide model compounds in the $n-\pi^*$ and $\pi-\pi^*$ singlet excited states, by providing qualitative insight into effect of blocking the N- or the C- termini of the peptide bond with the methyl groups, which to some extent mimic the effect of incorporating peptide bond into protein chain, in different environment.

Photolysis of acetamide has been subject of several studies in the gas phase and in solution. In both media the C–C and the C–N bond fissions were proposed as the primary photodissociation channels. Thus, gas phase photolysis has been shown to produce CH_3 , CO and NH_2 radicals, and in addition direct molecular formation of CH_3CN and H_2O was observed [29]. In aqueous solution the photolysis was claimed to lead to formation of NH_2 and CH_3CO radicals, followed by subsequent decomposition of the latter [5]. On the other hand in dioxane and hexane, the primary decomposition path has been reported to be non-free radical, but occurring via direct formation of CO and CH_3NH_2 [30]. More recently Duverny et al. reported on photochemical dehydration of acetamide upon irradiation in an argon matrix at 110 K [31]. They identified several primary photoproducts, including $\text{HNCO}:\text{CH}_4$ and $\text{CO}:\text{CH}_3\text{NH}_2$ molecular complexes and acetimidic acid. They also demonstrated that acetimidic acid is an intermediate in the dehydration process leading to $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ molecular complex. Formation of acetimidic acid in the course of dehydration was also proposed by Chen and coworkers in their theoretical study [9]. Thus, Chen and coworkers reported a comprehensive computational study of acetamide photodissociation at DFT (for the ground and triplet states) level and using the CASSCF/cc-pVDZ method followed by CASSCF/MR-CISD single point calculations (for the singlet excited states). On the basis of calculated energetic properties of the transition structures and the minima on the crossing seams the authors concluded that the C–C and C–N bond cleavage, as well as dehydration takes place in the T_1 state, whereas from the S_1 state molecules can relax via three nonradiative channels, besides radiation decay. They were identified as internal conversion to the ground state, internal system crossing to the T_1 state and direct dissociation in the S_1 state. They also proposed that the C–C bond dissociation in the S_1 state does not compete with the C–N dissociation due to much larger barrier. However, as their work was limited to static calculations they were not able to clarify the role of various available reaction pathways.

2. Computational details

Calculations were carried out following procedures described in our previous papers [11–15]. For the sake of brevity, only a short summary will be presented here and the more extensive description is given in [Suppl. Data](#). Briefly, the energies of the stationary points in the ground state and the lowest singlet excited states potential energy surfaces of acetamide were computed with the state-averaged complete active space self-consistent field (SA-CASSCF) method. The active space consisted of ten electrons in eight orbitals, comprising two σ/σ^* -pairs, two nonbonding lone pairs and one π/π^* pair of orbitals (see [Fig. S1 in Suppl. Data](#)). This active space was found to be a good compromise between accuracy and computational efficiency for adequate characterization of the low-lying valence states and photodissociation processes in our previous studies on formamide and its derivatives. State averaging was performed over the three lowest singlet states corresponding to the π^2 closed shell ground state (S_0), $n-\pi^*$ (S_1) and $\pi-\pi^*$ (S_2) excited states with equal weights. Intermediate Rydberg states were not taken into account. The critical points were reoptimized with multireference configuration interaction method with singles and

doubles (MR-CISD) and their energies were scaled by Davidson correction (MR-CISD + Q) [32,33] in order to validate CASSCF results. In these calculations the total configuration state function (CSF) space was constructed by applying single and double excitations from all internal (active and double occupied) orbitals into all virtual orbitals for all reference CSFs. The reference space comprised CAS(8,6) CSFs, while four 1s orbitals were kept in the frozen core. The stationary points and the minima on the crossing seam (MXS) were calculated using analytic gradients and nonadiabatic coupling vectors computed by the procedures described previously [34–36]. The nature of minima and saddle points was proved by vibrational analysis at the CASSCF level. The same method was used to calculate ZPVE values. Cartesian coordinates for the minima, transition structures and conical intersections are gathered in [Table S3 in Supplementary Data](#).

Nonadiabatic dynamics simulations were performed using the direct trajectory surface hopping approach based on ab initio calculations of the electronic energies and CASSCF wavefunctions. The ground state equilibrium geometry and vibrational modes used in the initial condition generation in dynamics simulations were calculated by the density functional theory DFT(B3LYP)/SV(P) [37,38] method using the TURBOMOLE [39] program since this approach gives more reliable vibrational frequencies. The 6-31G(d) basis set [40,41] was employed in all calculations. The dynamics simulations were performed using the NEWTON-X program package [42,43] interfaced with the COLUMBUS [44] suite of programs.

For the simulations in argon matrix the QM/MM approach as implemented in the NEWTON-X program was employed [45–47]. The acetamide was treated fully quantum mechanically, while the argon matrix and the acetamide–argon interaction were treated by means of Lennard–Jones potential using energies and gradients from TINKER [48] applying OPLSAA force field [49]. The acetamide was placed in the argon matrix using the VEGA ZZ [50] program. Initial conditions for a dynamics starting in the S_1 state were generated with the mixed scheme described in Ref. [15]. In this scheme a Wigner distribution is employed for the QM region and thermalized structures and velocities to the MM region. The number of calculated trajectories in this set of calculations was 70 and the maximum simulation time was restricted to 3 ps. All simulations in argon were performed at temperature of 18 K.

3. Results and discussion

3.1. Characterization of the potential energy surface

As mentioned earlier PES for dissociation of the C–N and the C–C bonds in AC in the T_1 and S_1 states was previously calculated at the CASSCF(8,7)/cc-pVDZ level of theory [9]. As we are primarily interested in comparison of photodissociation mechanism of AC with that of the parent formamide, we reoptimized the critical points for possible dissociation paths at the S_1 and S_2 PES using the same approach as in Refs. [11,14] i.e. by employing CASSCF(10,8)/6-31G(d) and MR-CISD methods. To calculate vertical excitation energies and relative energies (E_{rel}/eV) of the stationary points in the S_1 and the S_2 electronic state of acetamide the geometry of acetamide in the ground state was also calculated at the same levels of theory. These methods, as anticipated, predict ground state structure for acetamide to be non-planar (Table S1) what is in contrast to the planar structure observed experimentally [51–55]. However, this is not expected to influence the energies of the stationary points in the excited states to great extent since e.g. at the CASSCF level the energy of the planar form was found to be only slightly higher (by 0.03 eV) than the fully optimized non-planar structure. Starting with the CASSCF results vertical excitation

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