

Invited feature article

Photochemical deactivation pathways of microsolvated hydroxylamine



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ABSTRACT

Hydroxylamine is a prototypical molecule displaying OH and NH bond interactions. Despite the early interest in the photolysis of NH_2OH the primary mechanism of photodissociation remained unclear. Here we perform nonadiabatic trajectory-surface-hopping dynamics simulations based on the algebraic diagrammatic construction method to the second order (ADC(2)) together with reaction path calculations based on the multi-state complete active space second-order perturbation theory (CASPT2) method to identify the dominant deactivation channel of NH_2OH . By considering the photoinduced dynamics of hydroxylamine hydrates, ranging from monohydrates to tetrahydrates we show how this channel is modified by site-specific addition of water.

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1. Introduction

In the last two decades much effort has been devoted to the characterization of decay mechanisms of molecules which are constitutive subunits of important biomolecular chromophores [1–4]. Prominent examples include chromophores such as pyrrole, imidazole or phenol, whose non-reactive decay is mediated by low-lying dissociative $\pi\sigma^*$ states [5–10]. Interestingly, much less is known about the excited state dynamics of simpler chromophores such as hydroxylamine, NH_2OH whose photochemistry is dominated by Rydberg states.

Apart from being of considerable technological interest [11–13], hydroxylamine is a prototypical example of a system displaying NH and OH bond interactions. In the context of fundamental molecular interactions between functional groups, the system has been intensively investigated in the ground electronic state [14–18]. Specifically, details of the intramolecular dynamics including: timescales of vibrational redistribution in high-frequency

stretching and bending motion, energy flow between the NH_2 and OH moieties, and the mechanism of the torsion-inversion dynamics have been revealed by rovibrational spectroscopy [17,18].

The dynamics of hydroxylamine in the excited electronic states has received less attention. The vacuum ultraviolet (VUV) absorption spectrum of hydroxylamine vapor in the range between 160 and 250 nm has been first reported by Betts and Back [19]. The same authors have investigated the photolysis of NH_2OH showing that $\text{NH}_2 + \text{OH}$ and $\text{NH}_2\text{O} + \text{H}$ are the primary processes of direct photolysis (Zn spectral lamp at 213 nm) with yields of 40% and 60%, respectively. On the other hand, mercury-sensitized decomposition of hydroxylamine yielded NH_3 as a major product suggesting a primary decomposition into $\text{NH}_2 + \text{OH}$. More recently, Gericke et al. [20] confirmed that the H atom channel dominates the photo fragmentation of hydroxylamine at 193 nm. The quantum efficiency of the $\text{NH}_2 + \text{OH}$ channel was found to be less than 0.10. The importance of H-atom formation at 193 nm was also confirmed by Crim and coworkers [21]. At 240 nm, however, NO bond dissociation became the main channel of hydroxylamine photodissociation. From the theoretical side, the authors have shown that the two lowest excited electronic states cross along the NO stretching coordinate implying nonadiabatic deactivation [21]. In aqueous solution, the stoichiometry of NH_2OH photolysis $3\text{NH}_2\text{OH} \rightarrow \text{NH}_3 + 3\text{H}_2\text{O} + \text{N}_2$ and the detection of NHOH suggests that NO bond fission is again the primary

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photodissociation process [22]. However, considering the complexity of the mechanisms leading to the final stoichiometry alternative primary processes can be envisaged. Here these processes will be investigated.

This work presents results of a computational study directed toward understanding the mechanisms of excited state deactivation of hydroxylamine and of small hydroxylamine–water clusters, $\text{NH}_2\text{OH}(\text{H}_2\text{O})_n$ with $n = 1\text{--}4$. Understanding the role of water location and cluster size in the photofragmentation dynamics of hydroxylamine is an important issue for acid–base chemistry as hydrogen bond formation may modify the ordering and character of the excited electronic states as well as the accessibility of the conical intersections (CI). In addition, by increasing the size of the system interesting aspects of the competition between intrinsic relaxation of the chromophore, excited state proton transfer and redistribution of excess vibrational energy to the solvent can be studied in details.

2. Computational methods

The initial ground state geometries of several of $\text{NH}_2\text{OH}(\text{H}_2\text{O})_n$ clusters have been generated using the test particle model (T-model) [23–25]. Briefly, the energy of the interacting system ($\text{NH}_2\text{OH} \cdot \text{H}_2\text{O}$) is given as

$$\Delta E^{\text{T-model}} = \Delta E_{\text{SCF}}^1 + \Delta E^{\text{r}} \quad (1)$$

where E_{SCF}^1 is the first order interaction energy accounting for the electron exchange and electrostatic energies. Parameters entering the analytic expression for E_{SCF}^1 are obtained probing molecules of interest with suitable test particles. The second term, E^{r} , accounts for dispersion and polarization parts. Subsequently the RI-MP2/aug-cc-pVDZ method has been used to optimize the ground state structures of these initial clusters and compute the Hessians which are needed for the generation of initial conditions in the dynamics simulations. Excited state computations were performed using the algebraic diagrammatic construction method to the second order, ADC(2) [26,27], with the resolution of identity approximation (RI) and the aug-cc-pVDZ basis set [28–30]. The method was also used for nonadiabatic (NA) dynamics simulations. Further, the potential energy surface of NH_2OH was explored along OH and NO stretching coordinates using the multi-state complete active space second-order perturbation theory method (CASPT2) as implemented in the Molcas 8.0 package [31]. An active space of 10 electrons in 11 orbitals has been used. The lowest five states were calculated with equal weights in the multi-state calculation. A level shift of $0.3 E_h$ was used in the calculations. All calculations have been performed with the aug-cc-pVTZ basis set.

NA dynamics trajectory simulations have been performed using an in-house software [32–35] based on Tully's fewest switching surface hopping algorithm [36,37] with a decoherence correction of $\alpha = 0.1 E_h$ [38]. The program is interfaced to Turbomole 7.0 [39]. Newton's equations were integrated in time steps of $\tau_1 = 0.5$ fs using the velocity-Verlet algorithm, whereas the time-dependent Schrödinger equation was integrated in steps of $\tau_2 = 5 \times 10^{-5}$ fs [40]. The initial conditions were selected from the ground state (S_0) through Wigner distribution [41] as explained in a recent work [42]. In order to simulate the photolysis of isolated hydroxylamine at 240 nm and 193 nm, NA trajectories have been started from the S_1 , and $S_1\text{--}S_3$ states, respectively, and propagated in the manifold of the ground and four excited electronic states. All simulations of $\text{NH}_2\text{OH}(\text{H}_2\text{O})_n$ clusters were initiated in the S_1 state.

3. Results and discussion

3.1. Electronic structure calculations

In the ground electronic state the minimum energy geometry of NH_2OH is *trans* with C_s symmetry. Fig. 1 displays the minimum energy structure of four hydroxylamine hydrates as optimized at the MP2/aug-cc-pVDZ level of theory. The structures are denoted as HWN-X with $n = 1\text{--}4$ and the index X ranging from 1 to k orders structures with respect to energy. The minimum energy structure is indicated by $\text{HWN-}[1]$. The relevant geometry parameters are collected in Table 1. The relative energies of several local minima and the corresponding structural parameters are given in Table S1. These are found significantly higher in energy and will not be considered further. For example, the structure $\text{HW1-}[2]$ (see Fig. S1) in which the water molecule is H-bonded only to the hydroxyl group is found $2.06 \text{ kcal mol}^{-1}$ higher in energy. In going from $\text{HW1-}[1]$ to $\text{HW4-}[1]$ one notices the prolongation of the OH bond from 0.97 to 0.99 Å whereas the NO bonds remained virtually unaffected. Strengthening of the hydrogen bond with the closest water molecule can be followed also by monitoring the $\text{O} \cdots \text{O}$ distance which decreases from 2.85 Å in $\text{HW1-}[1]$ to 2.73 Å in $\text{HW4-}[1]$.

Basic excited state information is collected in Table 2. The vertical excitation energy of NH_2OH to the S_1 state of 6.25 eV (198 nm) finds good agreement with the experimental absorption maximum of hydroxylamine vapor at around 188 nm [19,21]. The S_1 state is of $n\text{Ryd}$ character and corresponds to excitation from the lone pair orbitals on the O and N atoms to dominantly a 3s-like Rydberg orbital. In the hydrates vertical excitations are in the range between 6.27 eV in $\text{HW3-}[1]$ and 6.69 eV in $\text{HW4-}[1]$. The lowest $n\text{Ryd}$ state is predominantly a HOMO \rightarrow LUMO transition with the HOMO localized on NH_2OH . The frontier orbitals are shown in Fig. 2 whereas the molecular orbitals involved in the four lowest singlet transitions are shown in Figs. S2–S6. In going from $\text{HW1-}[1]$ to $\text{HW4-}[1]$ the transitions originating from excitation from the lone pair orbitals of the O atoms on the water molecules to delocalized Rydberg orbitals get stabilized. Specifically, the S_2 state of $\text{HW4-}[1]$ corresponds to such a state and found only 0.38 eV above S_1 has direct implications for the dynamics.

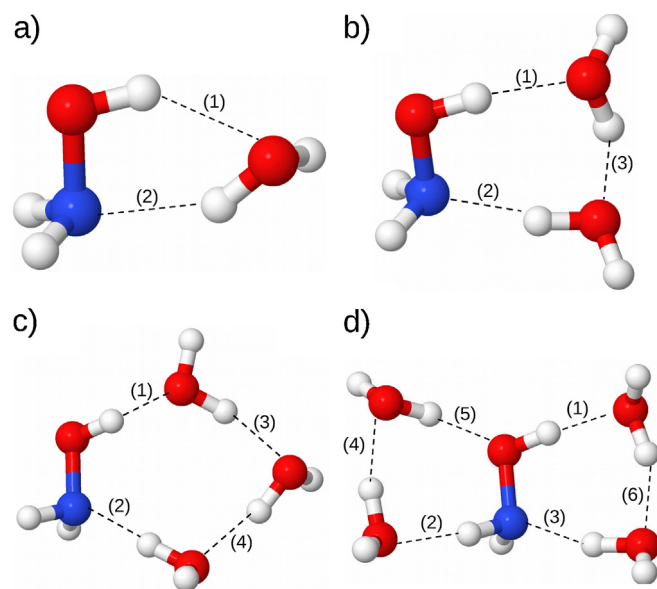


Fig. 1. Minimum energy structures of $\text{NH}_2\text{OH}(\text{H}_2\text{O})_n$ with $n = 1\text{--}4$ as optimized using the RI-MP2(aug-cc-pVDZ) method. Top (a) $\text{HW1-}[1]$, (b) $\text{HW2-}[1]$, bottom (c) $\text{HW3-}[1]$ and (d) $\text{HW4-}[1]$. The numeration of hydrogen bonds (1)–(6) is given to facilitate the comparison of the structural parameters given in Table 1.

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