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Water Complex of Imidogen

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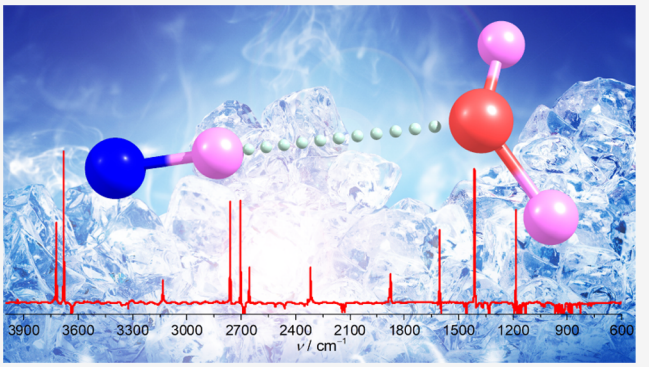
ABSTRACT: Imidogen (NH) is the simplest nitrogen hydride that plays an important role in combustion and interstellar chemistry, and its combination with H_2O is the prototypical amidation reaction of O−H bonds involving a nitrene intermediate. Herein, we report the observation of the elusive water complex of NH, a prereaction complex associated with the amidation reaction in a solid N_2 matrix at 10 K. The hydrogen-bonded structure of NH···OH_2 (versus HN···HOH) is confirmed via IR spectroscopy with comprehensive isotope labeling (D, ^{18}O, and ^{15}N) and quantum chemical calculations at the UCCSD(T)/aug-cc-pVQZ level of theory. In line with the observed absorption at 350 nm, irradiation of the complex at 365 nm leads to O−H bond insertion, yielding hydroxylamine NH_2OH.



1. INTRODUCTION

Imidogen (NH) is the simplest nitrogen hydride that serves as a transient intermediate in the combustion of nitrogen-bearing compounds[1] and in the decomposition of ammonia.[2] This diatomic species is also a key building block in the formation of prebiotic molecules such as isocyanic acid (HNCO) and hydrogen isocyanide (HNC) in the interstellar medium (ISM), and NH has been found in the atmospheres of the Earth,[3] the Sun,[4] and a variety of other astronomical objects such as comets,[5] cold molecular clouds (MCs),[6] and massive star-forming regions.[7] As the parent molecule of synthetically useful nitrenes,[8] NH adopts a triplet ground state in which the two unpaired electrons on the monovalent nitrogen atom have parallel spins, singly occupying pure p_x and p_z orbitals, while the singlet state with antiparallel spins is higher in energy, with a singlet-triplet gap (ΔE_{ST}) of 36 kcal mol^{-1}.[9] This gap is significantly larger than that of the isoelectronic carbene CH_2 (ΔE_{ST} = 9 kcal mol^{-1}),[10] in which the two nonbonding electrons occupy an sp^2 orbital as well as an orbital with largely p character. Due to the triplet spin multiplicity, NH is magnetically trappable and is considered as a prototypical molecule for the study of ultracold chemical reactions at millikelvin temperatures.[11]

Chemically, NH is very reactive, and its reactions with small molecules have been extensively explored. For instance, the oxidation of NH by O_2 in solid Xe occurs spontaneously at 50 K by overcoming a barrier of approximately 1 kcal mol^{-1}, yielding the peroxide HNOO.[12] Similar oxidation reactions have also been observed for other nitrenes, such as phenylnitrene[13] and borylnitrene,[14] as well as the carbene analogue CH_2.[15] In contrast, the spin-forbidden reactions of NH with closed-shell molecules such as N_2 and CO can only occur upon irradiation.[16] As a model for the synthesis of hydroxyl amines through the amidation of O−H bonds by nitrenes,[17] the mechanism for the spin-allowed reaction between singlet NH and H_2O to form hydroxylamine (NH_2OH) through O−H bond insertion has been extensively explored by quantum chemical calculations.[18] It was suggested that the insertion occurs by the initial formation of a high-energy intermediate H_2O−NH via a donor−acceptor interaction between the water oxygen lone pair and the electron-deficient nitrene center, followed by highly exothermic isomerization to NH_2OH via an intramolecular 1,2-H shift, with a calculated barrier of 5 kcal mol^{-1}. This elusive ylide-like intermediate has also been proposed as a key intermediate in the decomposition of NH_2OH,[19] which is an important nitrogen-containing species involved in the atmospheric nitrogen cycle.[20] A similar ylide-like intermediate (H_2C−OH_2) has also been proposed in the reaction between CH_2 and H_2O.[21]

Interestingly, very recent theoretical studies on the mechanism of the photodecomposition of NH_2OH using the complete active space second-order perturbation theory (CASPT2) reveal the additional involvement of several other intermediates, including hydrogen-bonded complexes consist-

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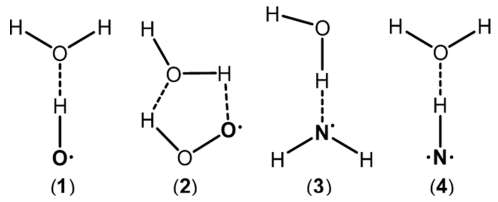
ing of the fragments NH, H_2O, NH_2, and OH, all of which are lower in energy than the ylide-like isomer H_2O−NH.[19e] Among these complexes, the water−imidogen complex NH···OH_2 (Scheme 1) is of particular interest since it is a rare water

Scheme 1. Examples of Water Complexes of OH (1),[22g−i] OOH (2),[22c] NH_2 (3),[22j] and NH (4)



complex of a triplet nitrene (NH), which can also be viewed as a model for the microsolvation of nitrenes. Due to the ubiquity of water molecules in the universe, hydrogen-bonded water complexes have attracted enormous interest.[22] In particular, a number of water complexes with atmospherically relevant radicals, such as OH (**1**),[22g−i] OOH (**2**),[22c] and NH_2 (**3**),[22j] have been spectroscopically identified, in which the water molecule may act as a hydrogen bond donor and/or acceptor. Herein, we report the generation and spectroscopic characterization of NH···OH_2 ($^3A_2$) in a solid N_2-matrix at 10 K, and its photoinduced interconversion with NH_2OH is also observed.

2. RESULTS AND DISCUSSION

To estimate the relative stability of the intermediates on the potential energy surface (PES) of NH_2OH, their structures and energies (Figure 1) were calculated at the (U)CCSD(T)/aug-cc-pVQZ level of theory. The ylide-like isomer H_2ONH containing a long O−N bond (1.662 Å) is significantly higher in energy than the global minimum (NH_2OH) by 60.4 kcal mol^{-1}, and it is highly unstable due to its exothermic dissociation to NH and H_2O by releasing 25.6 kcal mol^{-1}. In contrast, the two water−radical complexes NH···OH_2 (C_{2v}, $^3A_2$) and HN···HOH (C_s, $^3A''$) in the triplet ground state bearing short intermolecular hydrogen bonds with lengths of 2.193 and 2.160 Å are significantly lower in energy, with binding energies of approximately 2 kcal mol^{-1}, and the former is relatively more stable by 0.5 kcal mol^{-1}. The hydrogen-bonded radical pair (H_2N···HO, $^3A_2$) of NH_2 and OH has a binding energy of 3.9 kcal mol^{-1}, and it is higher in energy than the two water−radical complexes by more than 20 kcal mol^{-1}. Notably, the putative *N*-oxide H_3NO[23] is the second most stable isomer.

Considering the major UV absorption of NH_2OH at approximately 180 nm, photolysis of this compound in a solid N_2-matrix at 10 K was performed with an ArF excimer laser (193 nm). The corresponding IR spectra (Figure 2A) reflect the fast depletion of NH_2OH (**a**) to mainly yield a new species (**b**) with two intense IR bands at 3722.3 and 1605.9 cm^{-1}, which are very close to those of unperturbed H_2O (as an impurity in the matrix) at 3727.3 and 1597.2 cm^{-1}, corresponding to the antisymmetric stretching (ν_{asym}(HOH)) and bending (δ(HOH)) modes, respectively. After 50 min of irradiation, another weak IR band of **b** at 3134.6 cm^{-1} was observed in the difference spectrum (Figure 2B). It was blue-shifted ($\Delta\nu$) by +12.4 cm^{-1} in comparison to the stretching frequency of N_2-matrix isolated NH (3122.2 cm^{-1}),[12a] implying the formation of improper hydrogen bond[24] of the highly electron-deficient imidogen bond upon lone-pair electron sharing by water. The observed shift (+12.4 cm^{-1}) is in good agreement with the UCCSD(T)/aug-cc-pVQZ-calculated value (+15.9 cm^{-1}, Table S1) for NH···OH_2, whereas the calculated shift for the NH stretching mode in the less stable HN···HOH (+34.6 cm^{-1}) is significantly larger. Concomitantly, NO (1875.0 cm^{-1}) was formed via the photolytic dehydrogenation of NH_2OH.

In sharp contrast to the photochemistry of NH_2OH in the N_2-matrix, its photolysis at 193 nm in an Ar matrix mainly yields the dehydrogenated fragments NO and HNO. Additionally, weak IR bands for the OH_2···NH_2 (**c**) complex at 3532.3 and 1498.6 cm^{-1} were observed (Figure S1).[22j] The presence of triplet NH among the photolysis products in the Ar matrix can only be evidenced by its absorption at approximately 345 nm (λ_{max}) in matrix-isolation UV−vis spectra (Figure 2C). Similar absorption has been observed for

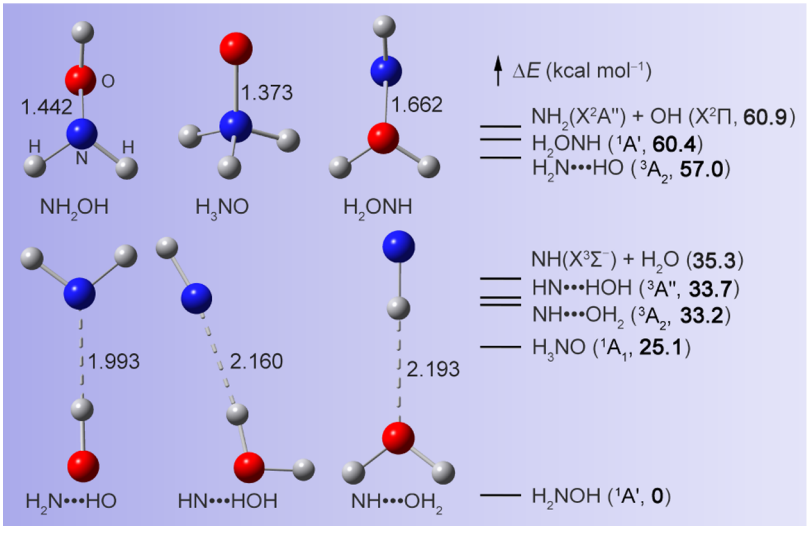


Figure 1. Molecular structures of NH_2OH, H_3NO, H_2ONH, and three radical complexes at the (U)CCSD(T)/aug-cc-pVQZ level of theory. The intermolecular hydrogen bonds in the complexes are shown in Å, and the calculated relative energies (kcal mol^{-1}) with zero-point vibration energy (ZPVE) corrections are given in parentheses.

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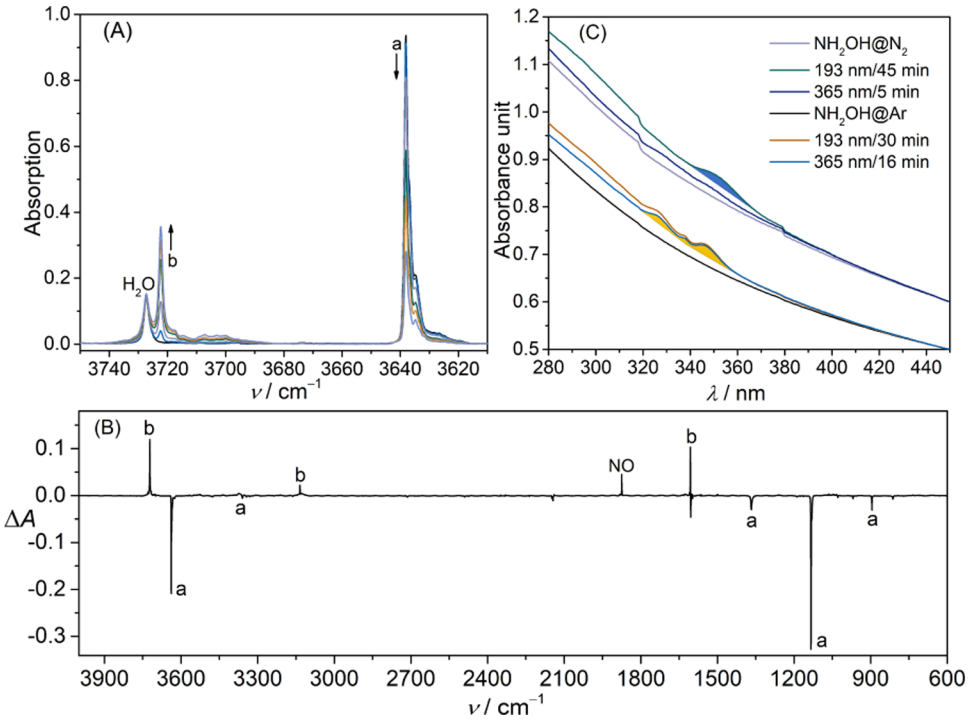

Figure 2. Panel A: Region of the IR spectra (3743−3617 cm^{-1}) showing the photodecomposition of NH_2OH (**a**) to $NH\cdots OH_2$ (**b**) in a solid N_2-matrix at 10 K over a time period of 50 min. The IR band at 3727.3 cm^{-1} attributed to the impurity H_2O in the matrix is marked. Panel B: IR difference spectrum (4000−600 cm^{-1}) showing the decomposition of NH_2OH (**a**) in a solid N_2-matrix (10 K) upon irradiation at 193 nm (15 min). Panel C: Region of the UV−vis spectra (280−450 nm) showing the photodecomposition of NH_2OH (**a**) in Ar- and N_2-matrices (10 K). For clarity, the spectra are arbitrarily shifted along the vertical axis.

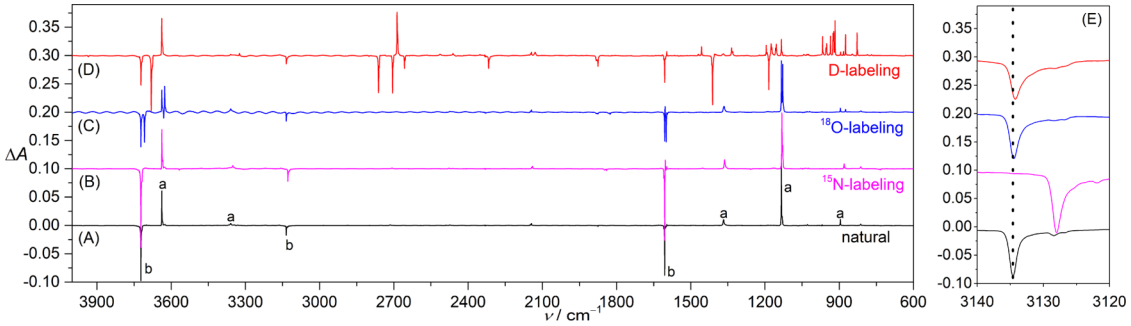

Figure 3. IR difference spectra (4000−600 cm^{-1}) showing the photoinduced (365 nm, 5 min) conversion from $NH\cdots OH_2$ (**b**) to NH_2OH (**a**) in solid N_2-matrices (10 K) for the natural (panel A), ^{15}N-labeled (panel B), ^{18}O-labeled (panel C), and D-labeled (panel D) species. For clarity, the expanded spectra in the range of 3140−3120 cm^{-1} are depicted in panel E.

NH during the photolysis of HN_3 in the Ar matrix.[8a] The absence of absorption for NH_2 in the range of 500−700 nm[25] implies a minor contribution to the decomposition, although dissociation to NH_2 and OH is the lowest-energy pathway for the photolysis of NH_2OH in the gas phase.[19f] Consistent with the IR spectroscopic observation in the N_2-matrix, a weak absorption peak at 350 nm for **b** appeared in the UV−vis spectrum after laser photolysis of the N_2-matrix isolated NH_2OH (Figure 2C). This band vanished upon subsequent irradiation at 365 nm, whereas the band for NH at 345 nm in the Ar matrix remained unchanged under the same irradiation conditions. The corresponding IR difference spectrum (Figure 3A) reflecting the changes in the photolysis products of N_2-matrix isolated NH_2OH upon further UV-light irradiation at 365 nm showed selective depletion of **b** by the reformation of **a**. Similar photoinduced reversible interconversion between **a** and **b** was fully reproducible for the ^{15}N-, ^{18}O-, and D-labeled isotopologues (Figure 3B−D), thus allowing unambiguous identification and assignment of the IR bands to the $NH\cdots OH_2$ complex.

According to the isotope labeling experiments, the two prominent bands at 3722.3 and 1605.9 cm^{-1} were assigned to the ν_{asym}(HOH) and δ(HOH) modes of the H_2O moiety in the complex. The former underwent a negligible ^{15}N isotopic shift (Figure 3B) but a clear ^{18}O isotopic shift of 14.0 cm^{-1} (Figure 3C), comparable to the shift of 14.3 cm^{-1} for the same mode in free H_2O. Importantly, the observed splitting pattern for this band when using an isotopically scrambled mixture of NH_2OH/NNDOH/NH_2OD/NHDOD/ ND_2OD (approximately 1:1:1:1:1 ratio) as the precursor in photochemistry provides useful information for discrimination of the two isomeric structures $NH\cdots OH_2$ (C_{2v}) and $HN\cdots HOH$ (C_s, Figure 1). As seen in Figure 3D, these vibrational modes appeared as three components at 3722.0, 3680.6, and 2761.9

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cm^{-1} with a ratio of approximately 1:2:1 based on the band intensities, strongly supporting the assignment to the C_{2v}-symmetric NH···OH_2 structure (Figure 1) in which the two hydrogen atoms in the complexed water molecule are structurally equivalent with respect to the vertical molecular symmetry plane. The experimental D-isotopic shifts of 0.3, 41.7, and 961.4 cm^{-1} (Table S2) are in good agreement with the UCCSD(T)/aug-cc-pVQZ-calculated values (0, 51.9, and 1051.7 cm^{-1}) for the ν_{asym}(HOH), ν_{asym}(DOH), and ν_{asym}(DOD) modes in the isotopologues NH···OH_2/ND···OH_2, NH···OHD/NH···ODH/ND···OHD/NH···ODH and NH···OD_2/ ND···OD_2, respectively. In contrast, all of the hydrogen atoms in the HN···HOH structure are nonequivalent, leading to a mixture of 10 isotopologues with distinct D-isotopic shifts (Table S3). A similar 1:2:1 isotopic pattern was also observed for the δ(HOH) mode at 1605.9 cm^{-1} in NH···OH_2, with the observed shifts (0, 193.9, and 421.7 cm^{-1}) nicely agreeing with the calculated results (0, 198.6, and 433.0 cm^{-1}, Table S2), further supporting the C_{2v} symmetry of the complex. D-isotope labeling in NH···OH_2 also allowed clear identification of the ν_{sym}(HOD) and ν_{sym}(DOD) modes at 2705.2 and 2657.2 cm^{-1} in NH···OHD/NH···ODH/ND···OHD/ NH···ODH and NH···OD_2/ND···OD_2, respectively. However, the bands for the ν_{sym}(HOH) mode in NH···OH_2/ND···OH_2 overlapped with the broad IR band at 3638.2 cm^{-1} attributed to the OH stretching mode of NH_2OH.

The N−H stretching mode (ν(NH)) of NH···OH_2 at 3134.6 cm^{-1} shifted to 3128.0 cm^{-1} upon ^{15}N labeling, and the corresponding shift (6.6 cm^{-1}) agreed with the calculated value of 5.5 cm^{-1}. Interestingly, very small but distinguishable shifts of 0.1 and 0.4 cm^{-1} were observed (Figure 3E) for this vibrational mode upon ^{18}O- and D-labeling, respectively, implying noticeable intermolecular NH···O hydrogen-bonding interactions between NH and H_2O. In contrast, the ν(NH) mode in the less stable HN···HOH complex was expected to be less perturbed by ^{18}O and D enrichment of the water molecule (Tables S3 and S4). The reversible photoisomerization between NH···OH_2 and NH_2OH also permitted clear identification of two weak IR bands at 7444.6 and 5326.2 cm^{-1} for the complex (Figure S2). The former was attributed to the overtone of the ν_{asym} (HOH), and the latter corresponds to the combination of the ν_{asym} (HOH) and δ(HOH).

The UV light (365 nm)-induced conversion of NH···OH_2 to NH_2OH was consistent with the observed absorption at 350 nm (Figure 2C) and the calculated vertical transition at 350 nm (Table S5) for the complex. Attempts were made to stimulate the transformation of the hydrogen-bonded complex through vibrational excitation of the fundamental and overtone bands of the OH and NH stretching modes using an optical parametric oscillator (OPO). However, neither O−H bond insertion (NH···OH_2 → NH_2OH) nor O−N bond formation (NH···OH_2 → H_2O−NH) was observed, indicating that the observed spin-forbidden conversion upon irradiation at 365 nm likely proceeded through initial photoexcitation of triplet NH ($^3X\sum$) in the prereaction complex NH···OH_2 to the higher-energy triplet excited state (ΔE_{ST} = 36 kcal mol^{-1}), followed by relaxation to the reactive singlet state via intersystem crossing (ISC) in the cryogenic solid N_2-matrix. According to the calculation at the (U)CCSD(T)/aug-cc-pVQZ level of theory (Figure S3), the subsequent reaction of singlet NH with H_2O (X^1A_1) is highly exothermic (49.2 kcal mol^{-1}), with a low barrier of 4.3 kcal mol^{-1} and a donor−acceptor intermediate complex H_2O−NH. Note that the prereaction complex NH···OH_2 in the closed-shell singlet state was not observed as a minimum on the singlet PES, and its structural optimization in the singlet state led to spontaneous O−N bond formation. Further theoretical study is desirable to fully understand the mechanism for the spin-forbidden reaction between triplet NH and H_2O via the intermediacy of the hydrogen-bonded complex NH···OH_2. The absence of H_2O−NH in the photoreaction of NH with H_2O was probably due to fast isomerization under irradiation conditions (365 nm).

3. CONCLUSIONS

In summary, the hydrogen-bonded NH···OH_2 complex in the triplet ground state, a common intermediate in the hydration/microsolvation of the imidogen radical (NH) and in the O−H bond insertion by a triplet nitrene intermediate, has been generated and characterized in a solid N_2-matrix at 10 K. The IR spectra of NH···OH_2 and its isotopologues confirmed the C_{2v} molecular symmetry of the complex in which the imidogen acts as a proton donor, whereas the isomeric triplet HN···HOH complex in which the radical acts as a proton acceptor is less stable by 0.5 kcal mol. The formation of a molecular complex between NH and H_2O in solid N_2 ice at 10 K and its subsequent photoisomerization to NH_2OH might be of interest for understanding the chemical evolution of nitrogen-containing molecules (NH and NH_2OH) in cold molecular clouds (10−30 K) in the interstellar medium,[26] where water molecules are abundant and low-barrier reactions involving OH, HCO, HOCO, NH, and NH_2 radicals for the formation of prebiotic complex organic molecules (COMs) have been proposed in laboratory studies.[27] In particular, the reaction of the interstellar species NH and H_2O via the NH···OH_2 complex in astronomical ice may provide an alternative pathway for the formation of the important peptide precursor NH_2OH, for which the underlying mechanism remains unclear, although several pathways, including the reactions of NH_3 + O_2, NO + H_2, and NH_2 + OH, have been suggested.[28]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c12808.

Experimental and computational details, matrix-isolation spectra, calculated vertical transitions, and atomic Cartesian coordinates for the calculated structures (PDF)

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Notes

The authors declare no competing financial interest.

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