Communication: Gas Phase Vibrational Spectroscopy of the Azide-Water Complex

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ABSTRACT: The vibrational spectra of the azide-water complex, $N_3^-(H_2O)$, and its fully deuterated isotopologue are studied using infrared photodissociation (IRPD) spectroscopy (800-3800 cm^{-1}) and high-level *ab initio* computations. The IRPD spectrum of the H_2-tagged complex exhibits four fundamental transitions at 3705, 3084, 2003 and 1660 cm^{-1}, which are assigned to the free OH stretching, the hydrogen-bonded O-H stretching, the antisymmetric N_3 stretching and the water bending mode, respectively. The IRPD spectrum is consistent with a planar, singly hydrogen-bonded structure according to an MP2 and CCSD(T) anharmonic analysis via generalized second-order vibrational perturbation theory. The red-shift of the hydrogen-bonded OH stretching fundamental of 623 cm^{-1} associated with this structure is computed within 6 cm^{-1} (or 1%) and is used to estimate the proton affinity of azide (1410 kJ mol^{-1}). Born-Oppenheimer molecular dynamics simulations show that large amplitude motions are responsible for the observed band broadening at cryogenic temperature. Temperature-dependent (6 – 300 K) IR multiphoton dissociation spectra of the untagged complex are also presented and discussed in the context of spectral diffusion observed in the condensed phase.

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The azide anion, N_3^-, is a triatomic, monovalent, closed-shell anion with $D_{\infty h}$ symmetry. This pseudohalide is important in organic and inorganic synthesis[1] (see the early works of Paitai and later by Fehlhammer and Beck for other applications).[2-4] It was initially characterized in the condensed phase by infrared (IR)[5, 6] and Raman[7] spectroscopy. The gas phase formation of the azide anion and its electron affinity (2.69 eV) was first reported in the photodetachment studies of Brauman and coworkers,[8] which was later reproduced by density functional theory (DFT) computations.[9] Subsequently, the vibrational frequency of the antisymmetric N_3 stretching fundamental was determined in the gas phase (1986.5 cm^{-1}), using velocity modulation laser spectroscopy,[10] and later in an N_2-matrix (2003.5 cm^{-1}).[11] Recent spectroscopic investigations by Yang *et al.* have reported gas phase photoelectron spectra (PES) of $N_3^-(H_2O)_n$, where $n = 0 - 16$, and assigned structural motifs to experimental data based on vertical detachment energies (VDEs) from DFT computations.[12] For $n = 1$, they found evidence for a singly hydrogen-bonded structure with a nearly linear N···HO hydrogen bond (~169°), which is similar to that of the nitrogen-water dimer (~170°),[13] rather than the covalent N-N-H angle in neutral hydrazoic acid of 109°.[14]

The present work explores the structure of azide-water complexes from cryogenic temperatures up to room temperature using gas phase vibrational action spectroscopy combined with high-level electronic structure calculations (see the Supplementary Material for experimental and computational details). Two energetically competitive C_s structures of the H_2-tagged $N_3^-(H_2O)$ complex have been identified on the MP2/haTZ and CCSD(T)/haTZ potential energy surfaces, where haTZ stands for the heavy-aug-cc-pVTZ basis set. The two isomers differ by their hydrogen bond topology, where the global minimum exhibits a single ionic hydrogen bond (SIHB) and the local minimum a double ionic hydrogen bond (DIHB). The SIHB and DIHB structural isomers are virtually isoenergetic. CCSD(T)/haTZ computations indicate the two isomers lie with 0.20 kJ mol^{-1} of each other when comparing electronic energies (with and without zero-point vibrational energy correction) or 0.50 kJ mol^{-1} when including Gibbs free energy at 298 K. There is insignificant change in the electronic energy difference near the complete basis set limit (CCSD(T)-F12/ha5Z). The following discussion focuses on the characterization of the SIHB global minimum (see Figure 1) because it is consistently lower in energy that the DIHB isomer and because there is no evidence for the population of the DIHB isomer in the experimental spectra presented here. Structural and vibrational data for the DIHB isomer are reported in the Supplementary Material.

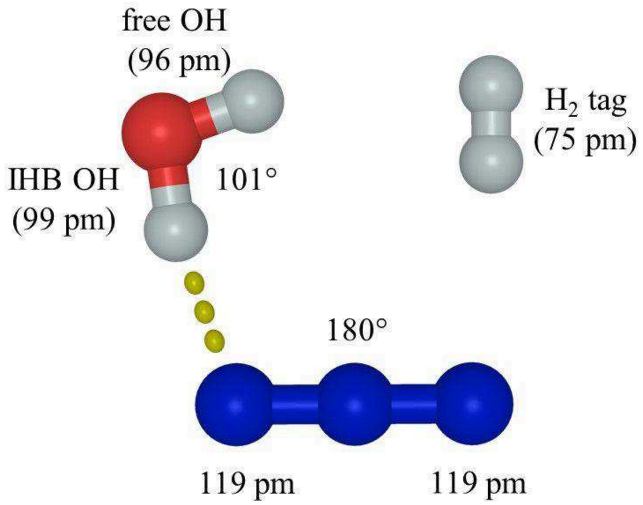

FIG. 1 Global minimum energy structure of the H_2-tagged $N_3^-(H_2O)$ complex (SIHB motif) at the CCSD(T)/haTZ level of theory.

The IRPD spectra of the H_2-tagged $N_3^-(H_2O)$ complex and the corresponding D_2-tagged deuterated isotopologues, $N_3^-(D_2O)$, are shown in Figure 2 and band positions, assignment and H/D frequency ratios are listed in Table 1. For a direct comparison of the bands associated with the vibrational modes involving the H_2O/D_2O moiety, i.e. bands with an H/D frequency ratio close to 1.36, the spectra are plotted against opposing ordinates and the abscissa (for the all-D isotopologue) has been scaled accordingly (by 1.36), which compensates for the difference in reduced mass and brings these bands into (near) alignment.

We observe four fundamental transitions. The antisymmetric N_3 stretch of the azide moiety is found at 2003 cm^{-1} (**a_5**, all-H spectrum) and 2006 cm^{-1} (**b_5**, all-D spectrum) with a characteristic H/D ratio close to unity and slightly blue-shifted from the gas phase value of the bare anion.[10] The three water modes are identified, by their H/D frequency ratios of > 1.3. These are the free OH stretching mode at 3705 cm^{-1} (**a_1**), the intermolecular hydrogen-bonded OH stretching mode at 3084 cm^{-1} (**a_4**), and the water bend at 1660 cm^{-1} (**a_6**), indicating the presence of a SIHB motif, similar to those reported for related halide- and pseudohalide-water complexes.[15-17]

Also shown in Figure 2 are computed anharmonic IR spectra derived from composite CCSD(T)/haTZ anharmonic frequencies and intensities (see Table 1). This comparison supports the above mentioned assignments and allows assignment of the remaining features. It should be noted that the aforementioned descriptions are slightly oversimplified because there is noticeable coupling of the vibrational motions. By combining these computational results with the information from the experimental all-H and all-D IRPD spectra, the remaining less-intense features can be assigned consistently as follows: (**a$_2$**) symmetric and antisymmetric N_3 stretch combination band at 3339 cm^{-1}, (**a$_3$**) IHB OH stretch and intermolecular stretch (IMS) combination band (ν_{OH+IMS}) centered at 3303 cm^{-1}, (**a$_7$**) the out-of-plane (oop) bend overtone ($2\nu_{oop}$) at 1439 cm^{-1},(**b$_3$**) the deuterium-bonded OD stretch and intermolecular stretch (IMS) combination band (ν_{OD+IMS}) centered at 2438 cm^{-1} and (**b$_7$**) the out-of-plane (oop) bend overtone ($2\nu_{oop}$) at 1058 cm^{-1}.

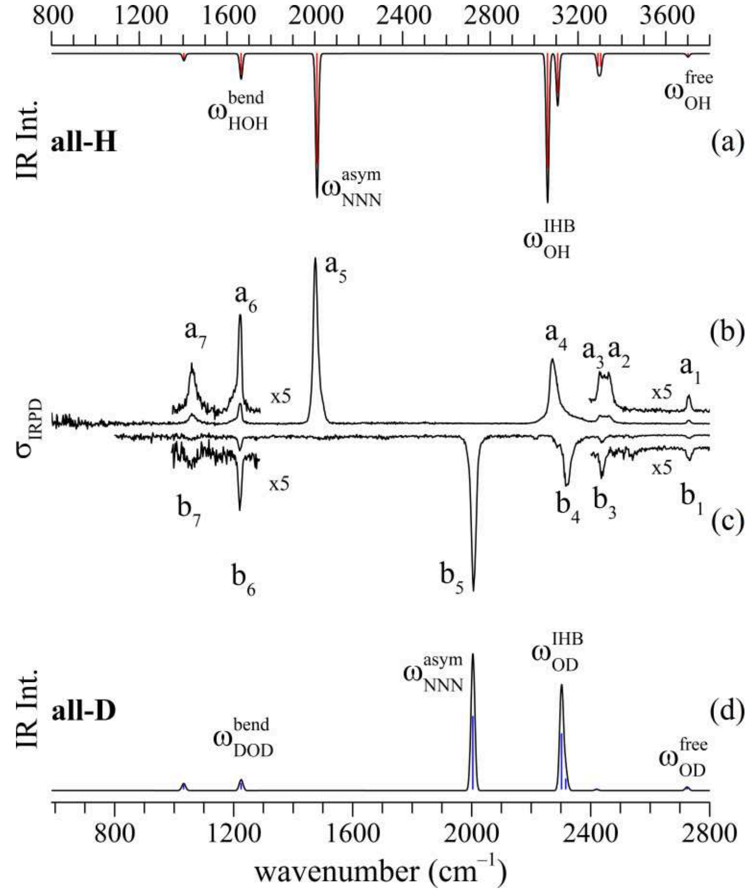

FIG. 2. Comparison of composite CCSD(T) anharmonic frequencies and intensities of the (a) all-H and (d) all-D isotopologues to experimental IRPD spectra of the (b) H_2-tagged $N_3^-(H_2O)$ and (c) D_2-tagged $N_3^-(D_2O)$ complexes. For a direct comparison of the bands assigned to the vibrational modes involving the H_2O/D_2O moiety, the spectra are plotted against opposing ordinates and the abscissa (for the all-D isotopologue) has been scaled by 1.36, which brings the respective bands into near alignment. Note, in this representation bands with similar vibrational energies in the two complexes, like the fundamental of the azide antisymmetric stretching mode (a_5, b_5) near 2000 cm^{-1}, are not aligned. The computed

spectra were convoluted with a Gaussian line function (15 cm^{-1} fwhm) and IR intensities were adapted from composite CCSD(T)/haTZ computations. See Table 1 for band positions and assignments.

TABLE 1. Experimental band positions (in cm^{-1}), H/D wavenumber ratio, and composite CCSD(T)/haTZ anharmonic frequencies (in cm^{-1}). Band assignments of the features observed in the vibrational spectra of the azide-water complexes shown in Figure 2.

All-H		*All-D*		*H / D ratio*		
IRPD	composite CCSD(T)	IRPD	composite CCSD(T)	expt.	theory	Assignment
3705 (**a$_1$**)	3701	2731 (**b$_1$**)	2724	1.36	1.36	free OH/OD stretch
3339 (**a$_2$**)	3291		3233		1.02	sym. N_3 + asym. N_3 stretch
3303 (**a$_3$**)	3303	2438 (**b$_3$**)	2420	1.35	1.36	IHB OH/OD stretch + IMS
	3107		2316		1.34	IHB OH/OD stretch + IMB
3084 (**a$_4$**)	3061	2320 (**b$_4$**)	2302	1.33	1.33	IHB OH/OD stretch
2003 (**a$_5$**)	2010	2006 (**b$_5$**)	2004	1.00	1.00	asym. N_3 stretch
1660 (**a$_6$**)	1664	1221 (**b$_6$**)	1225	1.36	1.36	HOH/DOD bend
1439 (**a$_7$**)	1403	1058 (**b$_7$**)	1032	1.36	1.36	oop bend overtone
	743		539		1.38	oop bend

Hydrogen bond (HB), intermolecular (IM), out-of-plane (oop), symmetric (sym), antisymmetric (asym).

Figure 3 compares the infrared multiphoton dissociation (IRMPD) spectra of the azide-water complex measured at different ion-trap temperatures ranging from 6 K to 300 K to the IRPD spectrum of H_2-tagged $N_3^-(H_2O)$ at 12 K. A minor tag effect is observed. It is most pronounced for bands involving the IHB OH stretching mode (a_3 and a_4), which are shifted to higher energies (10-20 cm^{-1}) upon H_2-tagging of the azide-water complex. T-dependent IRMPD spectra have proven helpful previously to identify the interconversion[18, 19] in-between and to characterize the thermal stability of isomers.[20] In the case of $N_3^-(H_2O)$, we observe a similar spectral evolution with respect to temperature to that of $CN^-(H_2O)$ in which there is no clear evidence for isomerization.[17] Spectra at temperatures exceeding 100 K exhibit typical thermal broadening that can be justified by the population of low-frequency modes and higher rotational levels. The interconversion pathway of the ionic hydrogen bonding between one of the terminal nitrogen atoms of the azide anion to the other has not yet been reported, but our experimental IRMPD spectra at 300 K suggests that the thermal contributions are not sufficient to overcome the isomerization barrier if we consider the characteristic signature of the IHB OH and free OH fundamental stretches.

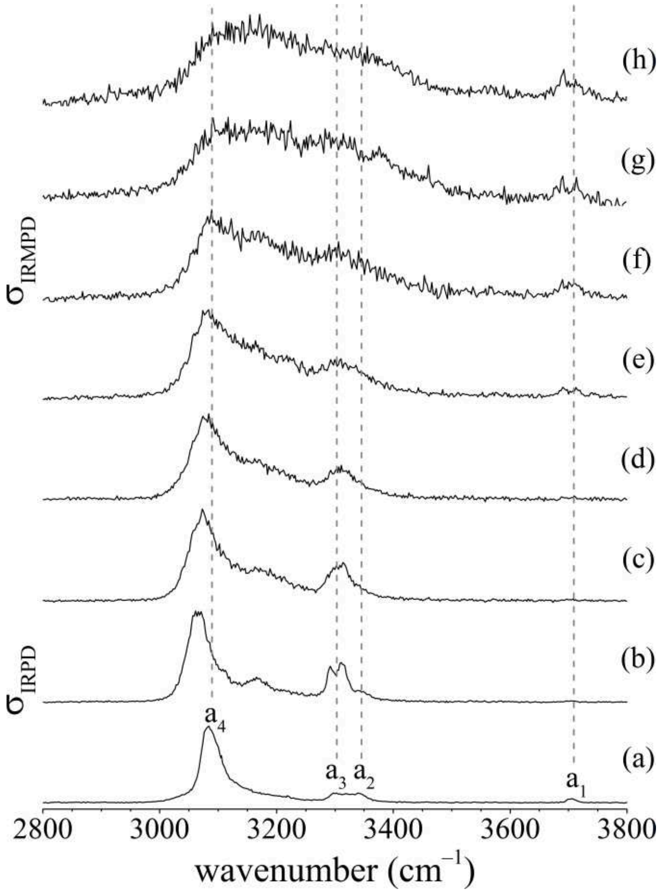

FIG. 3. Comparison of (a) IRPD spectrum of the H_2-tagged $N_3^-(H_2O)$ at 12 K and IRMPD spectra of the $N_3^-(H_2O)$ complex measured at ion-trap temperatures of (b) 6 K, (c) 50 K, (d) 100 K, (e) 150 K, (f) 200 K, (g) 250 K, and (h) 300 K.

In Figure 4 we compare the IRPD spectra of the H_2-tagged $N_3^-(H_2O)$ and D_2-tagged $N_3^-(D_2O)$ to results from Born-Oppenheimer molecular dynamics (BOMD) simulations in the O-H(D) stretching region to characterize the propensity for large amplitude dynamic motions. Rotational band profile simulations (see Figure S2) show that the spectral profile (*e.g.* form and width of bands) observed in the experiment cannot be recovered by assuming a typical rotational temperature of ~50 K. However, the BOMD simulations indicate that the hydrogen-bonded OH(D) bond and the azide anion exhibit correlated behavior over the duration of the simulation and this is the origin of the pronounced broadening of the IHB OH (**a**$_4$) and IDB OD (**b**$_4$) stretching bands.[21, 22] By employing a monomeric component analysis of the computed IR spectra from the BOMD simulations, we can disentangle the contributions of the azide anion (blue traces in Figure 4) in the OH and OD stretching regions (see Figure 4). Azide contributions are predicted to be dominant for band a_2, significant for band a_4 and less significant for band a_1. This also confirms our assignment of band $\mathbf{a_2}$ (denoted by * in Figure 4) as a combination band involving excitation of the N_3 stretching modes (see Table 1). Note, the corresponding band in the all-D spectrum is predicted at 3233 cm^{-1}, *i.e.* outside the spectral range shown in Figure 4.

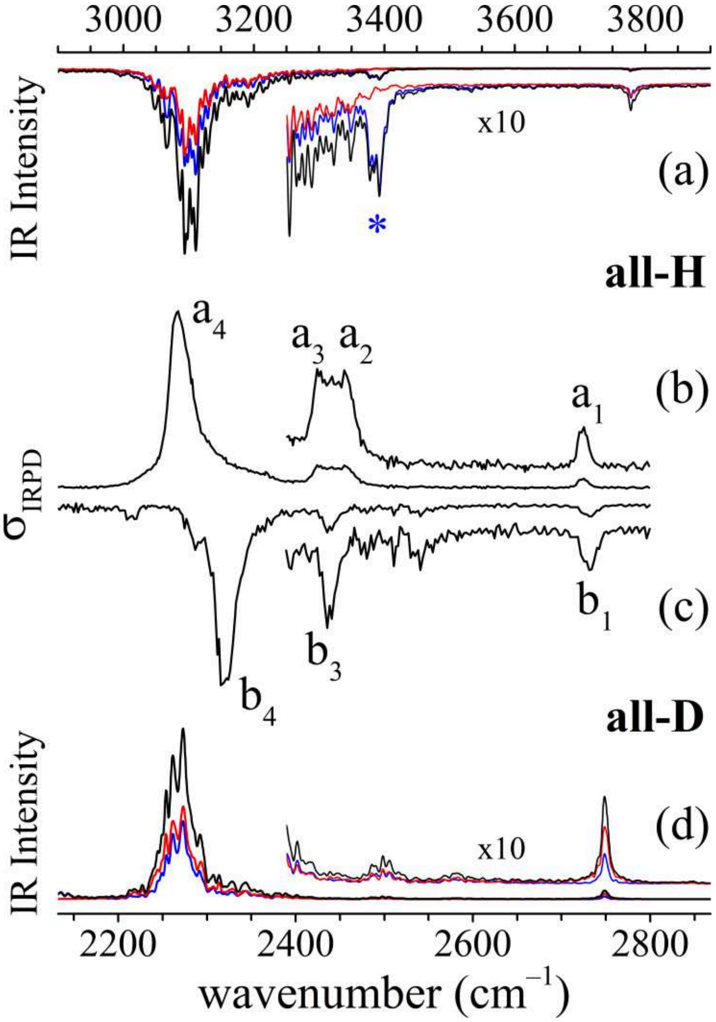

FIG. 4. Comparison of BOMD infrared spectra of the (a) all-hydrogen and (d) all-deuterium azide-water complexes to the IRPD spectrum of the (b) H_2-tagged $N_3^-(H_2O)$ and (c) D_2-tagged $N_3^-(D_2O)$ complex. The BOMD IR spectra were obtained from a time correlation formalism of the fluctuating dipole moment at temperature of 150 K (black traces) with the monomeric component spectra (azide is blue and HOH and DOD are red). For better comparability, the spectra for the all-deuterium isotopologue are plotted against opposing ordinates. Asterisk (*) denotes symmetric and antisymmetric N_3 stretch combination band.

The spectral assignment of the water modes is comparable to those of the monohydrated halide series, $X^-(H_2O)$ where X = Cl, Br, and I, previously reported by Johnson and coworkers.[16] This correlation model correlates the red shift $\Delta\nu_{OH}$ (relative to the centroid of the free H_2O stretching modes: 3707 cm^{-1}) of the IHB OH stretching band to the proton affinity (PA) determined from the thermodynamic cycle: $X^- + HOH \rightarrow XH + OH^-$. Application of this model to the azide-water complex ($\Delta\nu_{OH}$ = 623 cm^{-1}) yields an estimated proton affinity of ~1410 kJ mol^{-1}, similar to that of chloride (PA = 1395 kJ mol^{-1} and $\Delta\nu_{OH}$ = 561 cm^{-1}). The computed red-shift (629 cm^{-1} from the centroid of the water monomer symmetric and antisymmetric stretch) of the hydrogen-bonded OH stretch in the H_2-tagged $N_3^-(H_2O)$ complex is in excellent agreement (within 1%) with the 623 cm^{-1} shift measured experimentally. We can also make a qualitative connection to the results from previous condensed phase vibrational investigations. Two dimensional infrared spectroscopy (2D-IR) studies have shown that there is a large inherent shift in the OH stretching region in aqueous solutions of azide salts.[23, 24] Hochstrasser and coworkers rationalize the fast spectral diffusion of vibrationally excited azide anions in solution to a strong coupling of the antisymmetric N_3^- stretch and the hydrogen-bonded OH mode.[24] Indeed, we interpret large amplitude motions involving the coupled hydrogen-bonded OH stretch and antisymmetric azide stretch oscillators as the onset for spectral diffusion in the binary anion-water complex. Moreover, our temperature dependent spectra quantify the thermal contribution to the spectral diffusion.[17]

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SUPPLEMENTAL MATERIAL

See supplemental material for experimental and computational details and include the Cartesian coordinates of the SIHB and DIHB structures, the harmonic frequencies and the anharmonic frequencies. Anharmonic frequencies embedded with rotational structure for the all-H SIHB and all-D SIDB complexes are compared to IRPD spectra with the computed spectra convoluted with a Gaussian line function (3 cm^{-1} fwhm) and a simulated temperature of 150 Kelvin in the PGOPHER program. The full decomposition of the infrared spectra obtained from BOMD simulations are included.

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