Supplementary Information for:

Isomer-specific cryogenic ion vibrational spectroscopy of the D₂ tagged Cs⁺(HNO₃)(H₂O)_{n=0-2} complexes: Ion-driven enhancement of the acidic H-bond to water

Sayoni Mitra ^a, Chinh H. Duong ^a, Laura M. McCaslin ^b, R. Benny Gerber ^c, and Mark A. Johnson ^a

^a Sterling Chemistry Laboratory, Yale University, New Haven, CT, USA

^b Department of Chemistry, University of California Irvine, Irvine, CA, USA

^c Institute of Chemistry and the Fritz-Haber Center for Molecular Dynamics, The Hebrew University, Jerusalem, Israel

This file includes: Experimental Methods Figs. S1 to S11 Tables S1 to S9 References

Section S1: Experimental Methods

10 mM samples of Cs⁺NO₃⁻ in H₂O(*l*) were pumped through a 50 μ m tapered metal needle held between 2700 and 4000 V into a purge capsule containing $H_2O(I)$ and purged with dry $(H_2O \text{ and } CO_2 \text{ free})$ air. The steep voltage gradient between the needle and a capillary held at an attractive voltage (300 V) accelerates the cations (Cs⁺) in the solution towards the vacuum chamber. During this process, the $H_2O(I)$ evaporates in the capsule and interacts with the charged droplets to form $Cs^+(H_2O)_n$ clusters. Various differential pumping stages remove air and solvent molecules from the initial beam, which is guided by radio frequency (RF) quadrupole and octopole ion guides, and reduce the pressure from 760 Torr (atmosphere) to 10^{-7} Torr. In the first RF octopole guide (pressure ~ 10^{-4} Torr) an inlet (connected to an external manifold held at a pressure of 10-3 Torr) allows HNO₃ vapors to be incorporated into the $Cs^{+}(H_2O)_n$ molecular beam. After bending the ion trajectory by 90° with a DC turning guadrupole where the neutral background is largely rejected, the ions are subsequently guided and stored in a home-built copper 3D Paul trap held between 12-20 K by a helium cryostat. In the trap, the ions are collisionally cooled by helium buffer gas doped with a tagging or reaction gas, such as D_2 , N_2 or CO_2 , which provides the necessary messenger adducts to evaporate during laser interaction.

The experiment described in this report utilized D_2 tagging (25% D_2 in He buffer gas). The tagged ions are then pushed out of the Paul trap into the Wiley-McLaren extraction region where they are transiently focused entering the time-of-flight (TOF) tube. Two sets of deflectors and einzel lenses are used to steer and focus the ion beam before and after the flight tube, ensuring that it travels in a linear path with a spatial focus at the laser crossings. Within the flight tube, the ions are temporally mass separated, ions of interest are mass selected with a deflector mass gate before they are sent into a laser crossing to undergo photofragmentation spectroscopy.^{1, 2}

When the frequency of the laser is in resonance with an IR active transition of the cluster, the cluster absorbs a photon and undergoes intramolecular vibrational redistribution (IVR) causing the weakly bound tag to evaporate, creating a photofragment. The photofragment enters into the two-stage reflectron for mass separation, two such reflectrons in succession separate the parent and the fragment ions using a series of parallel rings held at successively repelling voltages. These two reflectrons are perpendicular to each other, labelled R2 and R3 respectively, Fig. S1). After the ions are temporally mass-separated in R2, a DC turning quad bends the beam 90° into R3 for another round of mass separation and finally refocuses the ions to an MCP detector. The photofragment yield is monitored as a function of laser frequency in order to obtain the vibrational action spectra of the Cs⁺HNO₃(H₂O)_n)•D₂ clusters.

These studies were extended to double resonance hole burning experiments to reveal the structure of the smallest cluster, $Cs^+HNO_3(H_2O)\cdot D_2$. As illustrated in Fig. S1, the current experiment utilizes two lasers. Isomer specific spectra of the cold ion are obtained by scanning the pump laser (hv_1) and fixing the probe laser (hv_2) on a transition unique to one isomer. The sequence goes as follows: the parent beam, which is comprised of different isomers, is photofragmented by the probe laser (hv_2) fixed at a transition unique to one isomer and provides a population baseline which is isomer specific. Next, this baseline is monitored as a

function of the pump laser (hv_1) frequency. Upon vibrational resonance with transitions unique to the isomer monitored by hv_2 , hv_1 depletes the population baseline and yields isomer specific depletion spectra.

Table S1: Energetics of $Cs^+(HNO_3)(H_2O)_n$.

All calculated values with geometries at the B3LYP level of theory. The aug-cc-pVDZ basis was employed for all atoms except Cs⁺, which uses the LANL2DZ basis and corresponding pseudopotential. Single point energies are calculated at the CCSD(T) level with the same basis and pseudopotential. All values are ZPE corrected in the harmonic approximation at the B3LYP level of theory.

Х	Y	X+Y	Binding energy of X to form X+Y (kcal/mol)
H ₂ O	Cs ⁺ (HNO ₃)	Cs⁺(HNO ₃)(H ₂ O) [Isomer B1]	14.9
	Cs⁺(HNO ₃)	Cs ⁺ (HNO ₃)(H ₂ O) [Isomer B2]	11.0
	HNO ₃	(HNO ₃)(H ₂ O)	8.7
HNO ₃	$Cs^{+}(H_2O)$	Cs⁺(HNO ₃)(H ₂ O) [Isomer B2]	12.2
Cs⁺	$HNO_3(H_2O)$	Cs ⁺ (HNO ₃)(H ₂ O) [Isomer B1]	13.5

Table S2: Band Frequencies for HNO₃, HNO₃(H₂O), H₂O, Cs⁺(H₂O) and D₂.

All calculated values at the B3LYP/(H,O,N: aug-cc-pVDZ, Cs: LANL2DZ) level of theory, scaled by 0.9576.

Structure	Peak Label	Experimental frequency (cm ⁻¹) ^a	Calculated Scaled Harmonic Frequency (cm ⁻¹)	B3LYP/aug-cc-pVDZ Assignment
HNO ₃	$^{bare} \nu^{a}$	3550 ³	3555	NO-H stretch of free HNO ₃
HNO ₃ (H ₂ O)	^{neut} v ^{a-w}	~3100 ⁴ (broad peak)	3073	NO-H stretch of HNO ₃ bound to water
	^{free} v ^{w-a}	37084	3716	Free O-H stretch of H ₂ O
	${}^{donor} \nu^{w-a}$	36174	3605	Donor O-H stretch of H ₂ O
H ₂ O	$^{sym}\nu^w$	3657 ⁵	3634	Symmetric H ₂ O
	$^{asym}\nu^{w}$	37565	3740	Asymmetric H ₂ O
$Cs^+(H_2O)$	^{sym} v ^{w-Cs +}	3635 ⁶	3616	Symmetric H_2O bound to Cs^+ ion
	asymv ^{w-Cs+}	3712 ⁶	3701	Asymmetric H_2O bound to Cs^+ ion
D ₂	$^{bare} v^{D_2}$	2994 ⁷	3081	Symmetric D ₂ stretch

Table S3: Band Frequencies and Assignments for $Cs^+(HNO_3) \cdot D_2$.

All calculated values at the B3LYP/(H,O,N: aug-cc-pVDZ, Cs: LANL2DZ) level of theory, scaled by 0.9576.

Structure	Peak Label	Experimental Frequency (cm ⁻¹) ^a	Bare Calculated Scaled Harmonic Frequency (cm ⁻¹)	Tagged Calculated Scaled Harmonic Frequency (cm ⁻¹)	B3LYP/aug-cc-pVDZ Assignment
A	ν_o^a		3510		Free O-H stretch of Cs ⁺ bound HNO_3
A2	v^a	3512		3511	Cs^+ bound HNO ₃ free O-H stretch (D ₂ bound to Cs ⁺)
A1	ν ^{a-D} 2	3456		3389	Cs⁺ bound HNO₃ free O-H stretch (D₂ bound to HNO₃ O-H bond)
A1	v ^D 2 ^{-a}	2959		2924	D_2 stretch bound to HNO ₃ O-H stretch
A2	v^{D_2}			2935	D_2 stretch bound to Cs ⁺ ion

Table S4: Band Frequencies and Assignments for $Cs^+(HNO_3)(H_2O) \cdot D_2$.

All calculated values at the B3LYP/(H,O,N: aug-cc-pVDZ, Cs: LANL2DZ) level of theory, scaled 0.9576.

Structure	Peak Label	Experimental Frequency (cm ⁻¹) ^a	Bare Calculated Scaled Harmonic Frequency (cm ⁻¹)	Tagged Calculated Scaled Harmonic Frequency (cm ⁻¹)	B3LYP/aug-cc-pVDZ Assignment
B1	ν_1^w	3740	3725	3727	Asymmetric stretch of acceptor H_2O bonded to HNO_3
B2	ν_2^w	3706	3706	3710	Asymmetric stretch of Cs^+ bound H_2O
B1	v_3^w	3651	3626	3626	Symmetric stretch of acceptor H_2O bonded to HNO_3
B2	v_4^w	3604	3619	3619	Symmetric H_2O stretch of Cs ⁺ bound H_2O
B2	ν^a	3516	3513		NO-H stretch of free HNO $_3$, Cs ⁺ bound H ₂ O
	ν ^{<i>a-D</i>} 2	3461		3397	NO-H stretch of HNO $_3$ bound to D $_2$, Cs ⁺ bound H $_2$ O
B1	$\begin{array}{c} v^{a - w}_{7} \\ v^{a - w}_{6} \\ v^{a - w}_{5} \\ v^{a - w}_{4} \\ v^{a - w}_{3} \\ v^{a - w}_{2} \end{array}$	3062 2970 2949 2823 2750 2666			Soft modes of HNO_3 bound to H_2O
	$v_1^{a\cdot w}$	2641	2772	2780	NO-H stretch of HNO_3 bound to H_2O
B1	v^{D_2}			2937	D_2 stretch bound to Cs ⁺ ion
B2	v ^D 2 ^{-a}			2925	D_2 stretch bound to HNO ₃ O-H stretch

Table S5: Band Frequencies and Assignments for $Cs^{+}(HNO_3)(H_2O)_2 \cdot D_2$.

All calculated values at the B3LYP/(H,O,N: aug-cc-pVDZ, Cs: LANL2DZ) level of theory, scaled by 0.9576.

Structure	Peak Label	Experimental Frequency (cm ⁻¹) ^a	Bare Calculated Scaled Harmonic Frequency (cm ⁻¹)	Tagged Calculated Scaled Harmonic Frequency (cm ⁻¹)	B3LYP/aug-cc-pVDZ Assignment
С	v_1^w	3738	3728	3729	Asymmetric stretch of acceptor H_2O bonded to HNO_3
	$ u_2^w $ $ u_{2'}^w$	3708 3698	3695	3695	Asymmetric stretch of H ₂ O bound to Cs ⁺
	v_3^w	3649	3629	3628	Symmetric stretch of acceptor H_2O bonded to HNO_3
	v_4^w	3570	3521	3523	Symmetric stretch of H_2O bound to Cs^+
	$ \begin{array}{c} \nu^{a-w}_{7} \\ \nu^{a-w}_{6} \\ \nu^{a-w}_{5} \\ \nu^{a-w}_{4} \\ \nu^{a-w}_{3} \\ \nu^{a-w}_{2} \end{array} $	3118 2975 2867 2775 2745 2682			Soft modes of HNO_3 bound to H_2O
	v ^{<i>a-w</i>} ₁	2652	2780	2784	NO-H stretch of hydrogen-bonded HNO_3
	v^{D_2}			2939	D ₂ stretch bound to Cs ⁺ ion

Table S6: Fingerprint Region Band Frequencies for HNO₃, HNO₃(H₂O), H₂O and Cs⁺(H₂O).

All calculated values at the B3LYP/(H,O,N: aug-cc-pVDZ, Cs: LANL2DZ) level of theory, scaled by 0.9719.

Structure	Peak	Experimental	Calculated Scaled	B3LYP/aug-cc-pVDZ Assignment
	Label	frequency (cm ⁻¹) ^a	Harmonic	
			Frequency (cm ⁻¹)	
HNO ₃	$^{bare} v_4^a$	879 ³	872	HO-N stretch
	$^{bare}\nu_3^a$	1302 ³	1288	NO-H bend
	$^{bare}\nu_2^a$	1326 ³	1314	NO ₂ sym stretch
	$^{bare}\nu_1^a$	1710 ³	1712	NO ₂ asym stretch
HNO ₃ (H ₂ O)	$\nu_{HO-N}^{a-w'}$		919	HNO ₃ HO-N stretch
	^{sym} v ^{a-w'} _{NO2}		1302	HNO ₃ NO ₂ sym stretch
	$v_{bend}^{a-w'}$		1433	HNO ₃ NO-H bend
	$\nu_{bend}^{w-a'}$		1557	H ₂ O bend bound to acid O-H
	^{asym} v _{NO2} ^{a'}		1699	NO ₂ asym stretch
NO ₃ -	ν_1^{nit}	1054 ⁸	1118	NO_3 sym stretch (only in Raman)
	ν_2^{nit}	1379 ⁸	1308	NO ₂ asym stretch
H ₂ O	ν_{bend}^{w}	1595 ⁵	1573	H ₂ O bend
Cs⁺(H ₂ O)	v^{w-Cs}_{bend} +		1602	H_2O bend bound to Cs^+ ion

Table S7: Fingerprint Region Band Frequencies and Assignments for Cs⁺(HNO₃)·D₂.

All calculated values at the B3LYP/(H,O,N: aug-cc-pVDZ, Cs: LANL2DZ) level of theory, scaled by 0.9719.

Structure	Peak Label	Experimental Frequency (cm ⁻¹) ^a	Bare Calculated Scaled Harmonic Frequency (cm ⁻¹)	Tagged Calculated Scaled Harmonic Frequency (cm ⁻¹)	B3LYP/aug-cc-pVDZ Assignment
A	v ₀₁ ^a		1664		HNO ₃ NO ₂ asym stretch
	v ^a ₀₂		1330		HNO ₃ NO ₂ sym stretch
	v _{o3} ^a		1300		HNO ₃ NO-H bend
	ν^{a}_{o4}		941		HNO ₃ HO-N stretch
A1 (D ₂ on acid O-H)	asym1v _{N02}	~1665		1658	HNO ₃ NO ₂ asym stretch
	v _{bend} ^{a-D} 2	1349		1335	$HNO_3 NO-H$ bend coupled with HNO_3 NO_2 sym stretch
	^{sym1} v _{NO2} ^a	1330		1322	HNO ₃ NO ₂ sym stretch coupled with NO-H bend
	$v_{HO-N}^{a-D_2}$	946		952	HNO ₃ HO-N stretch
A2 (D ₂ on Cs ⁺)	asymv _{NO2}	~1665		1665	HNO ₃ NO ₂ asym stretch
	symvanove symvestic strain str	1330		1331	HNO ₃ NO ₂ sym stretch
	v_{bend}^{a}	1286		1301	HNO ₃ NO-H bend
	$\overline{\nu_{HO-N}^{a}}$	937		940	HNO ₃ HO-N stretch

Table S8: Fingerprint Region Band Frequencies and Assignments for $Cs^+(HNO_3)(H_2O) \cdot D_2$.

All calculated values at the B3LYP/(H,O,N: aug-cc-pVDZ, Cs: LANL2DZ) level of theory, scaled by 0.9719.

^a Experimental frequencies are accurate within ±4 cm⁻¹.

Structure	Peak Label	Experimental Frequency (cm ⁻¹) ^a	Bare Calculated Scaled Harmonic Frequency (cm ⁻¹)	Tagged Calculated Scaled Harmonic Frequency (cm ⁻¹)	B3LYP/aug-cc-pVDZ Assignment
B1 (H ₂ on acio O-H, E on Cs ⁻	$\begin{array}{c} O & asym_1 v_{NO_2}^{a-w} \\ d & 0_2 \\ \hline \end{array}$	~1675	1653	1653	$HNO_3 NO_2$ asym stretch
	v_{bend}^{w-a}	1627	1572	1572	H ₂ O bend (on HNO ₃ NO-H str)
	$v_{bend}^{a\cdot w}$	1411	1430	1429	HNO_3NO-H bend coupled with NO_2 sym stretch
	sym1v _{N02}	1331	1331	1332	$HNO_3 NO_2$ sym stretch coupled with $HNO_3 NO-H$ bend
	$\nu {a - w \over HO - N}$	990	994	994	HNO ₃ HO-N stretch
B2(D on acie O-H, H ₂ O o Cs ⁺ ,)	$v_{NO_2}^{asym}$	~1675	1669	1665	HNO₃ NO₂ asym stretch
	$Cs^+ v_{bend}^w$	1640	1598	1591	H_2O bend (on Cs^+ ion)
			1328		HNO ₃ NO ₂ sym stretch
			1301		HNO ₃ NO-H bend
	$v_{bend}^{a - D_2}$	1353		1338	$HNO_3 NO-H$ bend with $HNO_3 NO_2$ sym stretch
	^{sym} v ^{a-w} _{NO2}	1331		1322	$HNO_3 NO_2$ sym stretch coupled with $HNO_3 NO-H$ bend
	$v_{HO-N}^{a-D_2}$	946	935	946	HNO ₃ HO-N stretch

Table S9: Band Frequencies and Assignments for $Cs^+(HNO_3)(H_2O)_2 \cdot D_2$.

Structure	Peak Label	Experimental Frequency (cm ⁻¹) ^a	Bare Calculated Scaled Harmonic Frequency (cm ⁻¹)	Tagged Calculated Scaled Harmonic Frequency (cm ⁻¹)	B3LYP/aug-cc-pVDZ Assignment
С	^{asym} v ^{a-w} _{NO2}	1694	1664	1664	HNO ₃ NO ₂ asym stretch
	$v^{w-Cs}_{bend}^+$	1648	1596	1596	H_2O bend (on Cs^+ ion)
	v ^{w-a} bend	1629	1570	1570	H ₂ O bend (on HNO ₃ NO-H str)
	$v_{bend}^{a \cdot w}$	1435	1441	1441	$HNO_3 NO-H$ bend with $HNO_3 NO_2$ sym stretch
	^{sym} v ^{a-w} _{NO2}	1334	1331	1331	$HNO_3 NO_2$ sym stretch coupled with $HNO_3 NO-H$ bend
	ν_{HO-N}^{a-w}	987	991	991	HNO ₃ HO-N stretch

All calculated values at the B3LYP/(H,O,N: aug-cc-pVDZ, Cs: LANL2DZ) level of theory scaled by 0.9719.



Fig. S1: Schematic of the MS³IR² photofragmentation spectrometer used in the Johnson lab. Further details about the experimental apparatus can be found in Section S1.











Fig. S4: Effect of electric field of a Cs⁺ ion is explored on water symmetric and asymmetric stretches, leading to a redshift that is depicted from (a) to (b). The combined Cs⁺ and HNO₃ electric field leads to both redshift and blueshift of the water frequencies, as seen in trace (c). Double resonance experiment is performed to reveal the presence of two isomers (labelled B1 and B2) for Cs⁺(HNO₃)(H₂O)·D₂, represented by traces (i) and (ii). Traces (a) and (b) made using values obtained from reference 6.











Fig. S7: Taking HNO₃ as a reference, the changes in its geometry in the presence of Cs⁺ ion and H₂O molecules, are depicted here. H₂O molecule as well as Cs⁺ ion can independently contract the \angle NO₂ angle such that it becomes more NO₃⁻ like, whereas the effect of both of them together is additive, as it can be seen in (e). All calculations are computed at the B3LYP/(H,O,N: aug-cc-pVDZ, Cs: LANL2DZ) level of theory.















Fig. S11: The mid-IR spectrum of $Cs^+(HNO_3)(H_2O)_2 \cdot D_2$ is shown in trace (a). The calculated stick spectra of bare $Cs^+(HNO_3)(H_2O)_2 \cdot D_2$ (structure C) and its tagged counterpart (structure $C \cdot D_2$) are displayed in traces (b) and (c) respectively.











Fig. S14: The fingerprint region IR spectrum of $Cs^{+}(HNO_3)(H_2O)_2 \cdot D_2$ is shown in trace (a). The calculated stick spectra of bare $Cs^{+}(HNO_3)(H_2O)_2 \cdot D_2$ (C) and its tagged counterpart $(C \cdot D_2)$ are displayed in traces (b) and (c) respectively.

References:

- 1. N. Yang, C. H. Duong, P. J. Kelleher, M. A. Johnson and A. B. McCoy, *Chem. Phys. Lett.*, 2017, **690**, 159-171.
- 2. A. B. Wolk, C. M. Leavitt, E. Garand and M. A. Johnson, *Acc. Chem. Res.*, 2014, **47**, 202-210.
- 3. G. E. Mcgraw, D. L. Bernitt and I. C. Hisatsune, J. Chem. Phys., 1965, 42, 237-+.
- 4. M. H. Kuo, A. David, N. Kamelamela, M. White and M. J. Shultz, *J. Phys. Chem. C*, 2007, **111**, 8827-8831.
- 5. T. Shimanouchi, *Tables of Molecular Vibrational Frequencies Consolidated, National Bureau of Standards*, 1972, **1**, 1-160.
- 6. T. D. Vaden, B. Forinash and J. M. Lisy, J. Chem. Phys., 2002, **117**, 4628-4631.
- 7. G. D. Dickenson, M. L. Niu, E. J. Salumbides, J. Komasa, K. S. E. Eikema, K. Pachucki and W. Ubachs, *Phys. Rev. Lett.*, 2013, **110**, 193601.
- 8. A. Weaver, D. W. Arnold, S. E. Bradforth and D. M. Neumark, J. Chem. Phys., 1991, 94, 1740.
- 9. E. D. Glendening, C. R. Landis and F. Weinhold, J. Comput. Chem., 2019, 40, 2234-2241.