Supplementary Information

for

Accessing Different Binding Sites of a Multifunctional Molecule: IR Spectroscopy of Propargyl alcohol···water Complexes in Helium Droplets.

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I. Mass spectra

Mass spectra of the undoped helium droplets after electron impact ionization are shown in Figure S1. The presence of mass fragments at multiples of 4 (He_n^+, $n \geq 1$) is a signature of the helium droplet formation. The peak at m/z = 18 is due to the residual water present in the QMS chamber.

The droplets were seeded with the molecules of propargyl alcohol (PA) by leaking vapors of PA (partial pressure 2.5×10^{-6} mbar) into the first pickup chamber, using a fine controlled dosing valve. The resulting mass spectra are shown in Figure S1, where prominent peaks at m/z = 26, 27, 28, 29, 39, 53, 55 and 56 correspond to the fragments originating from PA molecule/clusters. The strong peak at m/z = 39 corresponds to the resonance-stabilized propargyl cation ($C_3H_3^+$) and the IR spectroscopic measurements were recorded at this, propargyl alcohol specific, mass channel (m/z = 39).

In the second step, vapors of D_2O (partial pressure 2.7×10^{-6} mbar) were introduced in the second pickup chamber. This leads to the pickup of D_2O by the droplets already containing PA, leading to the formation of intermolecular complexes between PA and D_2O molecules inside the droplets. The intensity of the peaks corresponding to PA fragments decreases upon the pickup of D_2O molecules. New peaks appear at m/z = 20 and 22, that correspond to the D_2O^+ and D_3O^+ fragments, respectively. The D_2O^+ fragment might have originated from D_2O clusters, formed by pickup of D_2O molecules by empty helium droplets and/or from the $PA\cdots D_2O$ clusters formed because of pickup of D_2O molecules by droplets containing PA molecule(s). Similarly, D_3O^+ fragments might have contributions from the D_2O dimer or $PA(D_2O)_2$, assuming the $PA(D_2O)_2$ follows similar fragmentation pattern as $(D_2O)_2$.

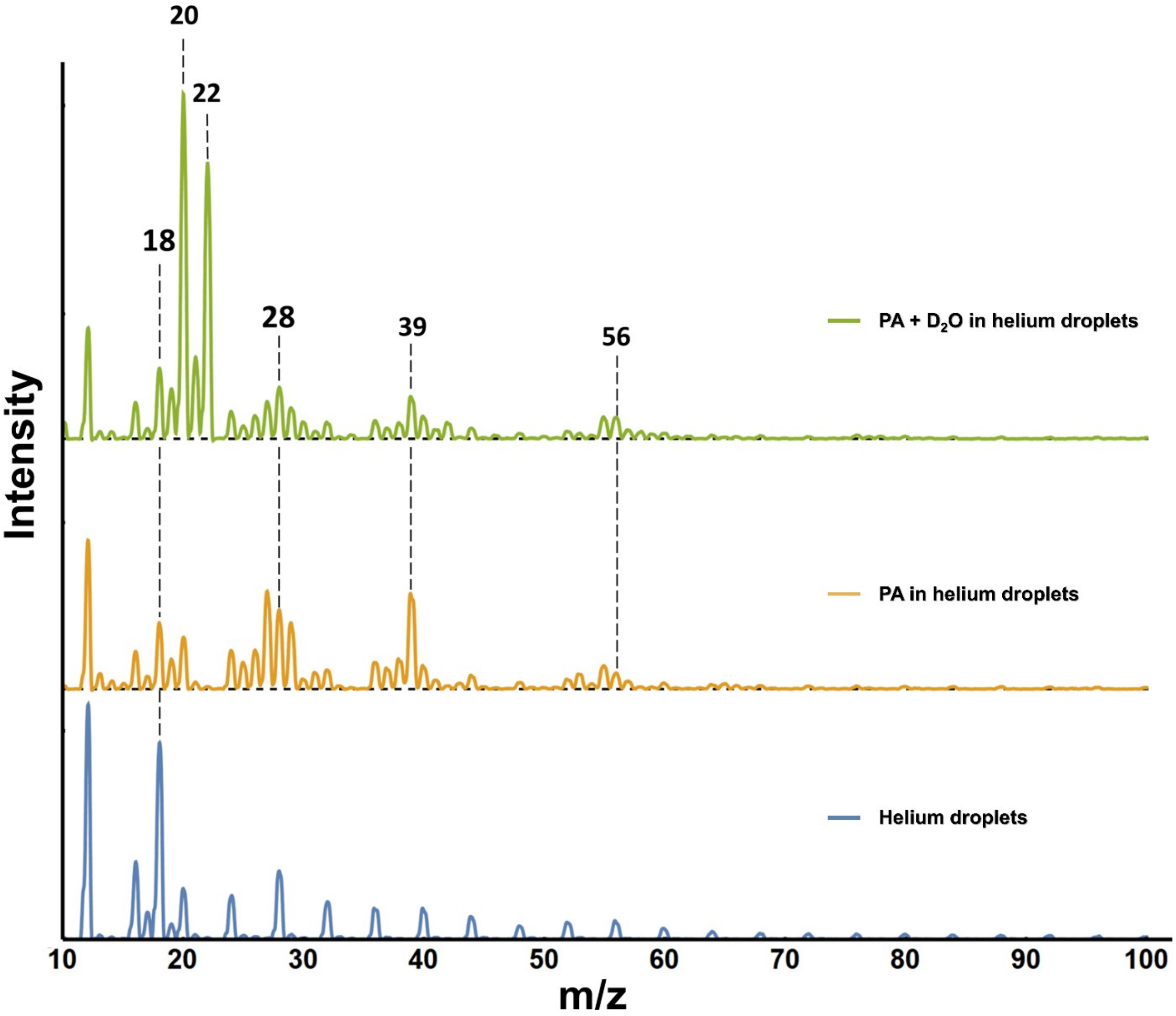

Figure S 1: Mass spectra of a) Helium cluster beam, b) Helium cluster beam doped with PA and c) helium cluster beam doped with PA and D_2O. The PA partial pressure was 2.5×10^{-6} mbar and D_2O partial pressure was 2.7×10^{-6} mbar.

II. Cluster size determination: Pickup curves

The pickup of molecules by helium droplets follows Poisson statistics[1]. The probability of the capture of 'k' molecules is:

$$P_n = \frac{(\rho\sigma l)^k}{k!} exp(- \rho\sigma l) \tag{1}$$

where, σ is the capture cross-section, l is the length of the pickup region and $\rho = \frac{p}{k_B T}$ is the number density of the dopant molecules in the pickup region, p, k_B and T being the partial pressure of the dopant, Boltzmann constant and absolute temperature, respectively.

Thus, variation of the band intensities as a function of dopant partial pressures, resulting in so-called pickup curves, can be used to determine the cluster size.

At a given resonance frequency, there might also be contribution from clusters of more than one size. In such cases, the variation of intensity with ion current of dopant (or partial pressure of dopant) is given by a sum of Poisson distributions for different sizes.

To record the PA pickup curves, D_2O pressure was kept constant at 2.7×10^{-6} mbars, while PA pressure was varied. A residual gas analyzer (RGA) was connected to the PA pickup chamber, which recorded the ion current at m/z = 55 ($C_3H_3O^+$). The laser was fixed at the resonance frequency of the particular observed band. The variation of the band intensity as a function of ion current at mass 55, which is directly proportional to the partial pressure of PA in the pickup chamber, is shown in Figure S2. Since, pickup curves were recorded as a function of the ion current of the dopants, the following equation was used for fitting

$$P_n = \frac{(bI)^k}{k!} exp(-bI)$$

(2)

with b, being the effective cross-section, is a product of σ, l and a proportionality factor for the dopant partial pressure to ion current conversion, I is the dopant ion current measured at a specific mass channel.

The band at 2761.5 cm^{-1} peaks at ion current of ~1×10^{-12} Amp, Figure S2(a). The variation of the intensity with ion current for this band is best fitted to a Poisson distribution of $k_{(PA)} = 1$, equation 2. This pickup curve was used as a reference. The pickup cross-section 'b' deduced from this fit was used as a constant to fit the pickup curves for other bands. The pickup curves at 2789.6, 2619.9 and 2613.5 cm^{-1} also peak at ~ 1×10^{-12} amp and are best described by a $k_{(PA)}$= 1 Poisson distribution. The pickup curves at 2751.6 and 2670.2 cm^{-1} are attributed to a summation of Poisson distributions for $k_{(PA)} = 1$ and $k_{(PA)} = 3$, Figure S2. (c and e).

In addition, we recorded pickup curves for variation of D_2O partial pressure, as displayed in Figure S3. Now, the PA pressure was maintained constant at 2.5×10^{-6} mbar. The RGA was connected to the second pickup chamber, which was used for the pickup of D_2O. The laser was fixed at a particular band frequency and the change in band intensity as a function of ion current at m/z = 20 (D_2O^+ fragment) (which is directly proportional to the partial pressure of D_2O) was recorded.

The band at 2761.5 cm^{-1} peaks at ion current of ~ 4.5×10^{-13} Amp; and was fitted to a Poisson distribution of $k_{(D2O)} = 1$, Figure S3(a). Further, the pickup cross-section 'b'– deduced from this fit –was used as a constant in the following fits. The pickup curves at 2789.6, 2619.9 and 2670.2 cm^{-1} are found to be best described by $k_{(D2O)}$ =1 Poisson distribution. The pickup curves at 2613.5

cm^{-1} could be fitted to n = 2 Poisson distribution. The pickup curve at 2751.6 cm^{-1} does not follow a clear Poisson distribution and is speculated to be originating from $k_{(D2O)} = 2$ and higher clusters.

Thus, we conclude that the bands at 2761.5, 2689.6, 2619.9 and 2670.2 originate from 1:1 PA:D2O clusters. The band at 2670.2 also show contribution from $k_{(PA)} = 3$ at higher partial pressures of D_2O, indicating an underlying band which originates from clusters consists of 3 PA molecules. The band at 2613.4 is assigned to $PA(D_2O)_2$ cluster. The band at 2751.6 cm^{-1} is assigned to PA

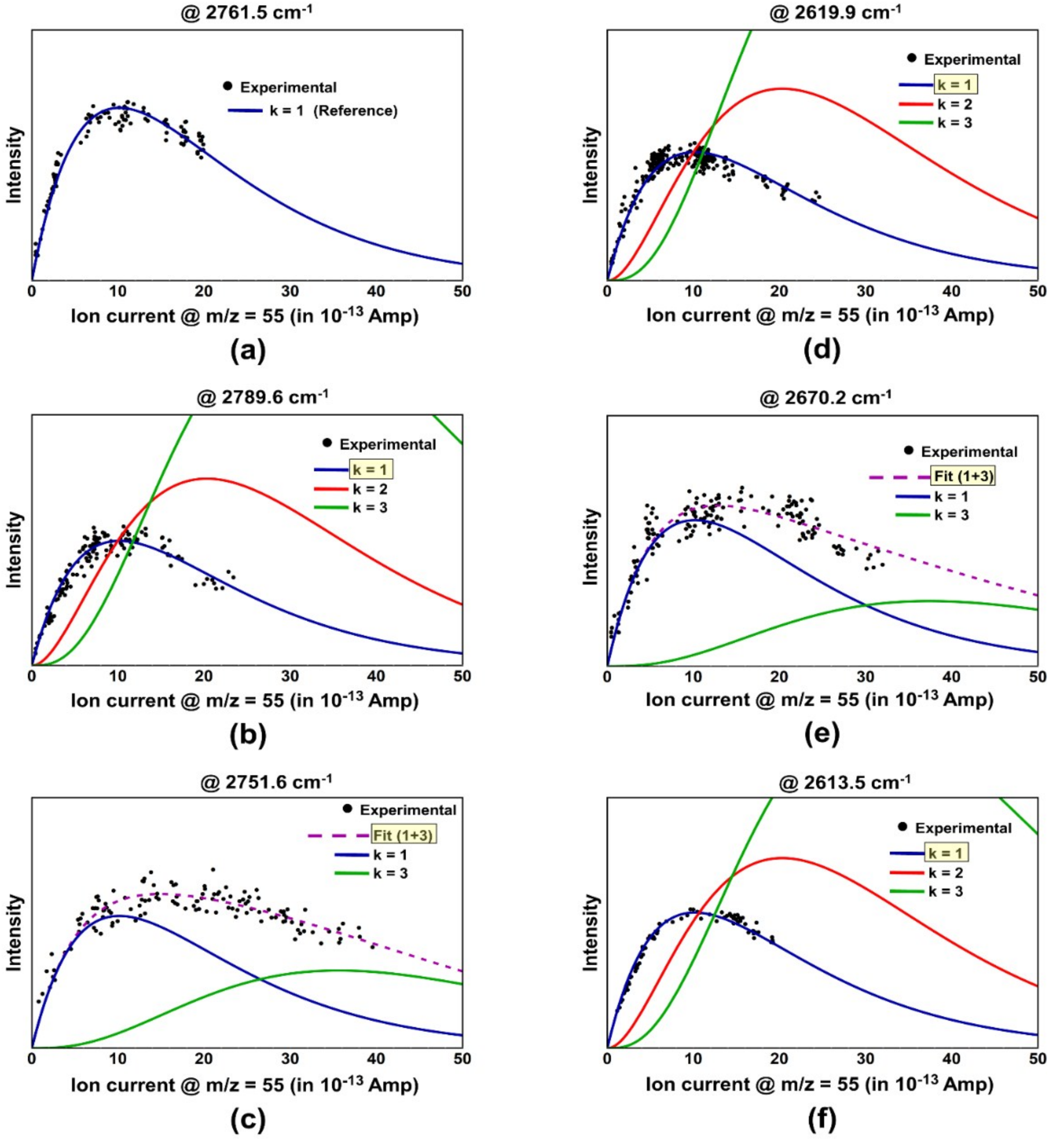

Figure S 2: Pickup curves for variation of PA pressures for the different observed bands. Laser was fixed at a particular resonant frequency. D_2O partial pressure was maintained constant at 2.7×10^{-6} mbar. Measurements were performed at m/z = 39.

$\cdots D_2O)_2$ clusters. It also has an underlying band originating from clusters with 3 PA molecules.

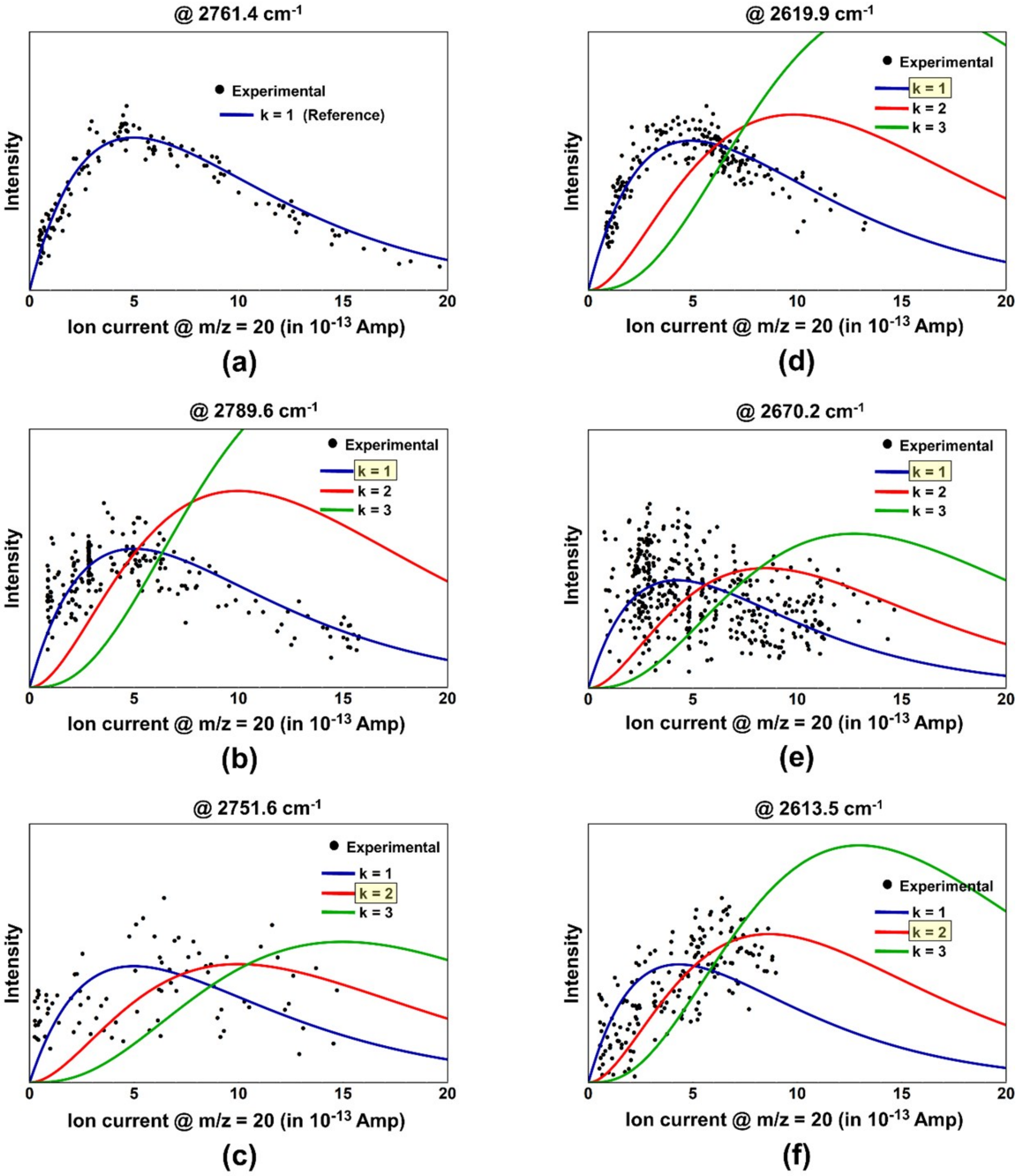

Figure S 3: Pickup curves for variation of D_2O pressures for the different observed bands. Laser was fixed at a particular resonant frequency. PA partial pressure was maintained constant at 2.5×10^{-6} mbar. Measurements were performed at m/z = 39.

III. Cartesian coordinates of the different structures of propargyl alcohol....water complex, obtained at MP2/6-311++G(d,p) level of theory.

Structure 1

Atoms	x (Å)	y (Å)	z (Å)
C	-1.49847	1.43564	-0.17989
C	-1.11665	0.301234	0.061399
H	-1.84733	2.417179	-0.40371
C	-0.66817	-1.07032	0.366317
O	0.399476	-1.50249	-0.45443
H	-1.49813	-1.7595	0.19244
H	-0.40391	-1.12303	1.430794
H	1.11408	-0.86293	-0.32176
O	1.911042	0.830098	0.177511
H	2.671563	1.26595	-0.21473
H	1.179345	1.442179	0.045399

Structure 2

Atoms	x (Å)	y (Å)	z (Å)
C	-2.93571	-0.06788	-0.05053
C	-1.72806	-0.22723	-0.0046
H	-3.99107	0.071043	-0.09043
C	-0.27429	-0.39982	0.058878
O	0.425652	0.844197	-0.06552
H	0.072413	-1.01884	-0.7702
H	-5.2E-05	-0.90247	0.993117
H	0.040304	1.452929	0.572773
O	3.018999	-0.31573	0.047278
H	2.270088	0.289564	-0.0377
H	3.679528	0.049598	-0.54412

Structure 3

Atoms	x (Å)	y (Å)	z (Å)
C	-2.46839	-0.82543	-0.20245
C	-1.50182	-0.17421	0.155225
H	-3.30245	-1.4036	-0.52609
C	-0.35706	0.630689	0.592356
O	0.484099	1.016328	-0.49942
H	0.280107	0.048102	1.260667
H	-0.71147	1.515454	1.132902
H	-0.07617	1.406522	-1.17715
O	2.633979	-0.73707	0.113322
H	2.778384	-1.4534	-0.50778
H	2.050634	-0.13338	-0.36459

Structure 4

Atoms	x (Å)	y (Å)	z (Å)
C	0.618417	-0.21845	-0.01614
C	-0.59413	-0.35478	0.003558
H	1.680187	-0.08409	-0.03443
C	-2.05155	-0.52244	0.015086
O	-2.75074	0.718571	0.066222
H	-2.35797	-1.0746	0.906165
H	-2.35475	-1.10501	-0.86406
H	-2.36887	1.27898	-0.61578
O	3.855772	0.200871	-0.05208
H	4.454978	-0.5446	-0.1404
H	4.26974	0.747805	0.620342

Structure 5

Atoms	x (Å)	y (Å)	z (Å)
C	-0.16713	1.919353	-0.01118
C	0.236604	0.767393	-0.01608
H	-0.48572	2.936025	0.000988
C	0.72058	-0.62216	-0.0191
O	2.141029	-0.7005	-0.07179
H	0.350168	-1.13813	-0.90565
H	0.318538	-1.14214	0.857237
H	2.47938	-0.17911	0.66204
O	-2.39259	-0.80938	0.081567
H	-3.23787	-0.89744	-0.36433
H	-2.15233	0.112369	-0.05039

REFERENCES

1 M. Lewerenz, B. Schilling and J. P. Toennies, Successive capture and coagulation of atoms and molecules to small clusters in large liquid helium clusters, *J. Chem. Phys.*, 1995, **102**, 8191–8207.