SUPPORTING INFORMATION FOR:

Measuring H-Bonding in Supramolecular Complexes by Gas Phase Ion-Molecule Reactions

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Experimental

Mass spectrometry experiments were performed with the BioApex 47e Fourier transform ion cyclotron resonance mass spectrometer equipped with an Infinity™ cell, a passively shielded 4.7 tesla 160 mm bore superconducting magnet, and an external Apollo™ electrospray ionization source manufactured by Bruker Daltonics (Billerica, MA, USA). The required $1 \cdot 10^{-9}$ torr vacuum was maintained by rotary vacuum pumps and turbomolecular pumps supplied by Edwards (Edwards High Vacuum International, Crawley, UK). The sample was introduced to a 70° off-axis sprayer (stainless steel metal capillary) through a syringe infusion pump (Cole-Parmer 74900 series, Cole-Parmer Instrument Company, Vernon Hills, IL) at a flow rate of 1.5 $\mu L\ min^{-1}$. Room temperature nitrogen (N_2) was used as a nebulizing and counter-current drying gas.

Experimental parameters were kept as constant as possible to maintain comparable conditions. Generated ions were collected at the end-plate electrode (-3.8 to -4.0 kV) and passed through a dielectric glass capillary (entrance and exit potentials -4.0 to -4.4 kV and 250 to 375 V, respectively). After this, ions were focused with a skimmer 1 (40 V), pre-hexapole, skimmer 2 (15 V) to a (rf) hexapole (5.2 MHz, 550-600 $V_{p\text{-}p}$), which was used to accumulate the ions for a predefined time (1 s). From the hexapole, ions were extracted from the ion source and transferred to an ICR cell by electrostatic focusing of transfer optics. In the ICR cell, ions were trapped with the use of the Sidekick™ technique before conventional frequency sweep excitation and broadband detection. Data sets of 256 k, consisting of 16 or 32 summed scans, were generally used. The measurements and data handling were accomplished with Bruker XMASS software, version 6.0.2.

The reagents for the ion–molecule reactions were chosen for their volatility, appropriate proton affinities, and *m/z* ratio of their complexes with cavitands. In the ion–molecule reactions, the reagents were introduced to the cell via a variable leak inlet valve and the pressure was allowed to rise to $5 \cdot 10^{-8}$ torr, where it was kept constant. Ions were isolated with the use of CHEF procedure,[1] and allowed to react with a neutral reagent with delay times from 0.001 up to 300 s. In the *n*-propylamine reactions monoisotopic isolations were not pursued, but in the case of H/D exchange reactions with ND_3, single frequency excitation shots were used to achieve monoisotopic isolations. The spectra consisted of 2, 4, 8, or 16 scans. The number of scans was varied according to the reaction delay needed, while keeping the time of the experiment convenient. Variation in the number of scans did not influence the relative intensities (r.I.) in the resulting spectra. All the spectra were background corrected. The decay of the relative abundance of the reactant ion as a function of time was used to deduce the reaction rate constant (k_{obs}). The pressure readings for the neutral reagent were corrected with the measured geometrical correction factors.

Cavitands **1-4** have been prepared following the published procedures.[2-4] Cavitands were dissolved in toluene and the cavitand concentration in the final samples was 2.0–4.0 µM. The alkyl ammonium ions were commercially available and were used as their chlorides. Alkyl ammonium chlorides were dissolved in methanol and then diluted in acetonitrile. 1:1 or in the case of reactions 1:3 cavitand-alkylammonium ion ratios were used and acetonitrile was used as a solvent in the samples.

(1) L. J. de Koning, N. M. M. Nibbering and S. L. Van Orden, F. H. Laukien, *Int. J. Mass Spectrom. Ion Proc.* 1997, **165/166**, 209-219.
(2) R. Pinalli, F. F. Nachtigall, F. Ugozzoli and E. Dalcanale, *Angew. Chem. Int. Ed. Engl.* 1999, **38**, 2377-2380.
(3) M. Suman, M. Freddi, C. Massera, F. Ugozzoli and E. Dalcanale, *J. Am. Chem. Soc.* 2003, **125**, 12068-12069.
(4) P. Delangle, J.-C. Mulatier, B. Tinant, J.-P. Declercq and J.-P. Dutasta, *Eur. J. Org. Chem.* 2001, 3695-3704.

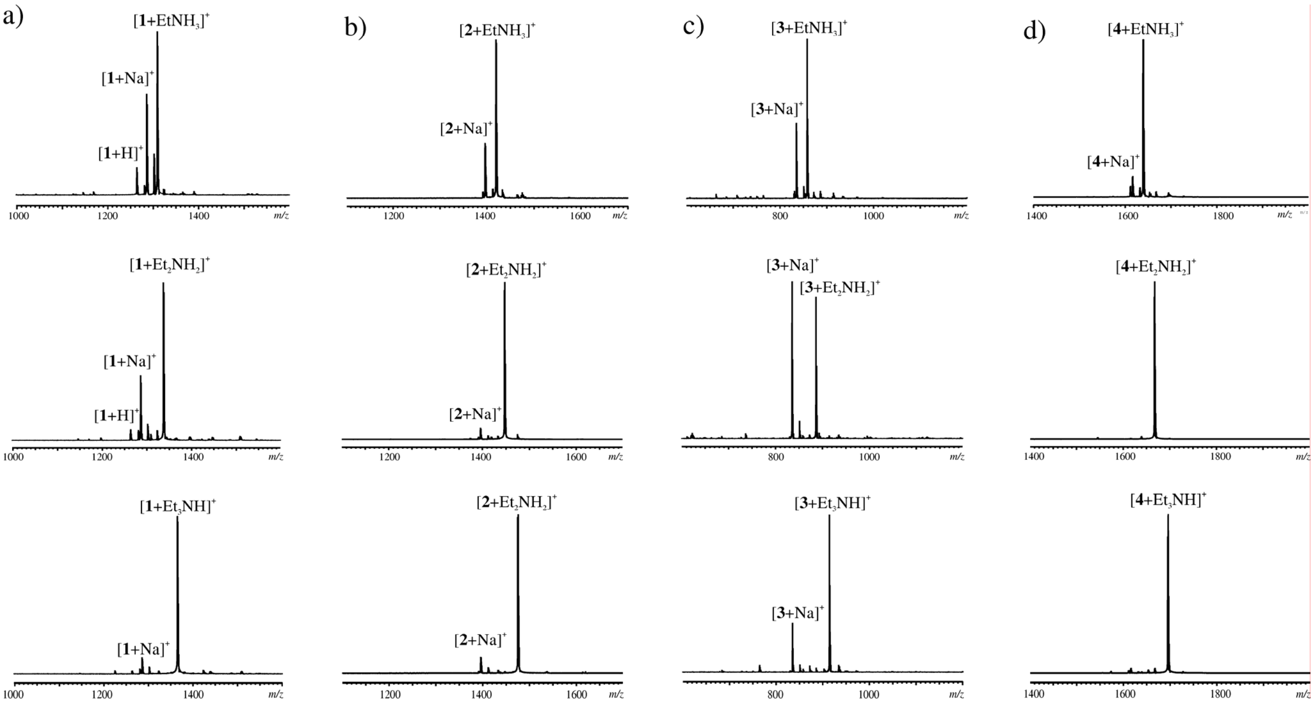

Figure S1. ESI-spectra measured from solutions containing ethyl substituted ammonium ions and cavitands (a) **1**, (b) **2**, (c) **3**, and (d) **4**.

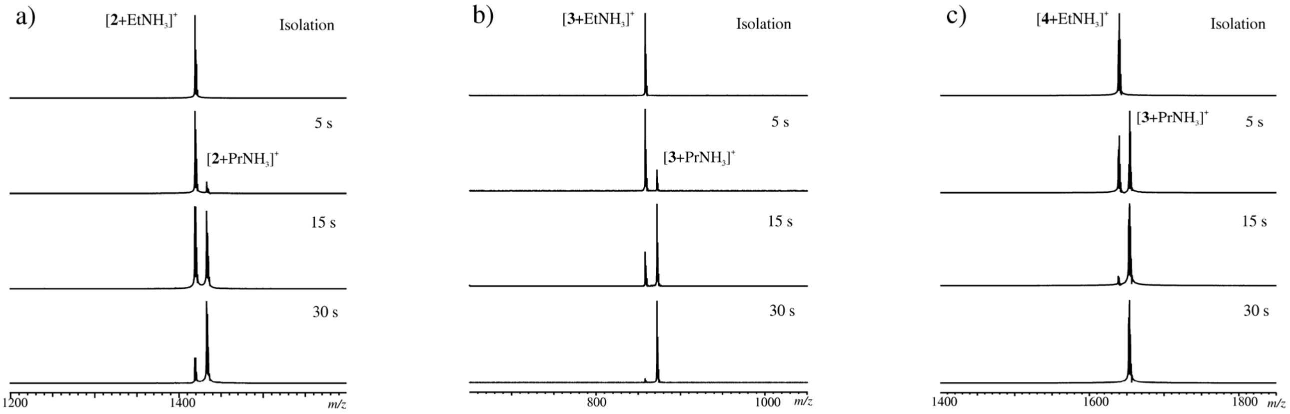

Figure S2. Reaction with $PrNH_2$: isolation spectra and spectra measured at 5 s, 15 s, and 30s delays. (a) [**2**+$EtNH_3$]$^+$, (b) [**3**+$EtNH_3$]$^+$, and (c) [**4**+$EtNH_3$]$^+$.

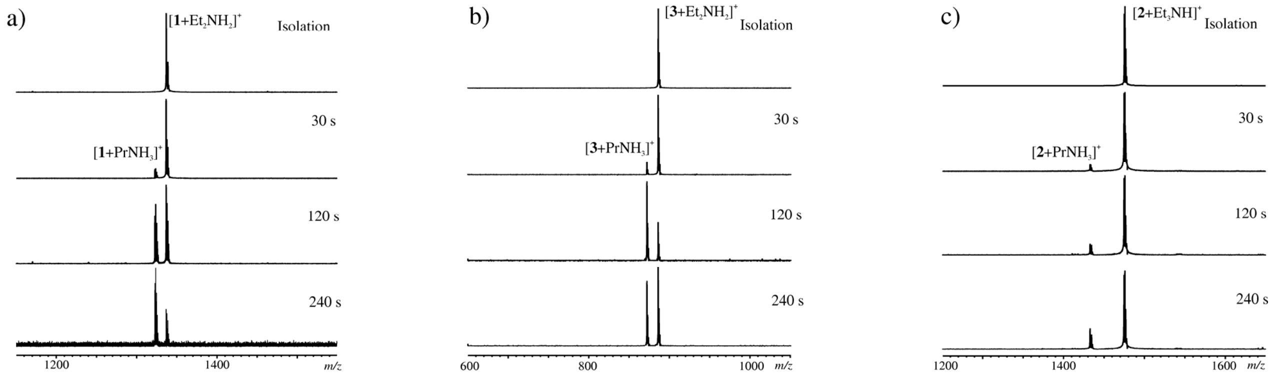

Figure S3. Reaction with $PrNH_2$: isolation spectra and spectra measured at 30s, 120s, and 240s delays. (a) [**1**+Et_2NH_2]$^+$, (b) [**3**+Et_2NH_2]$^+$, and (c) [**2**+Et_3NH]$^+$.

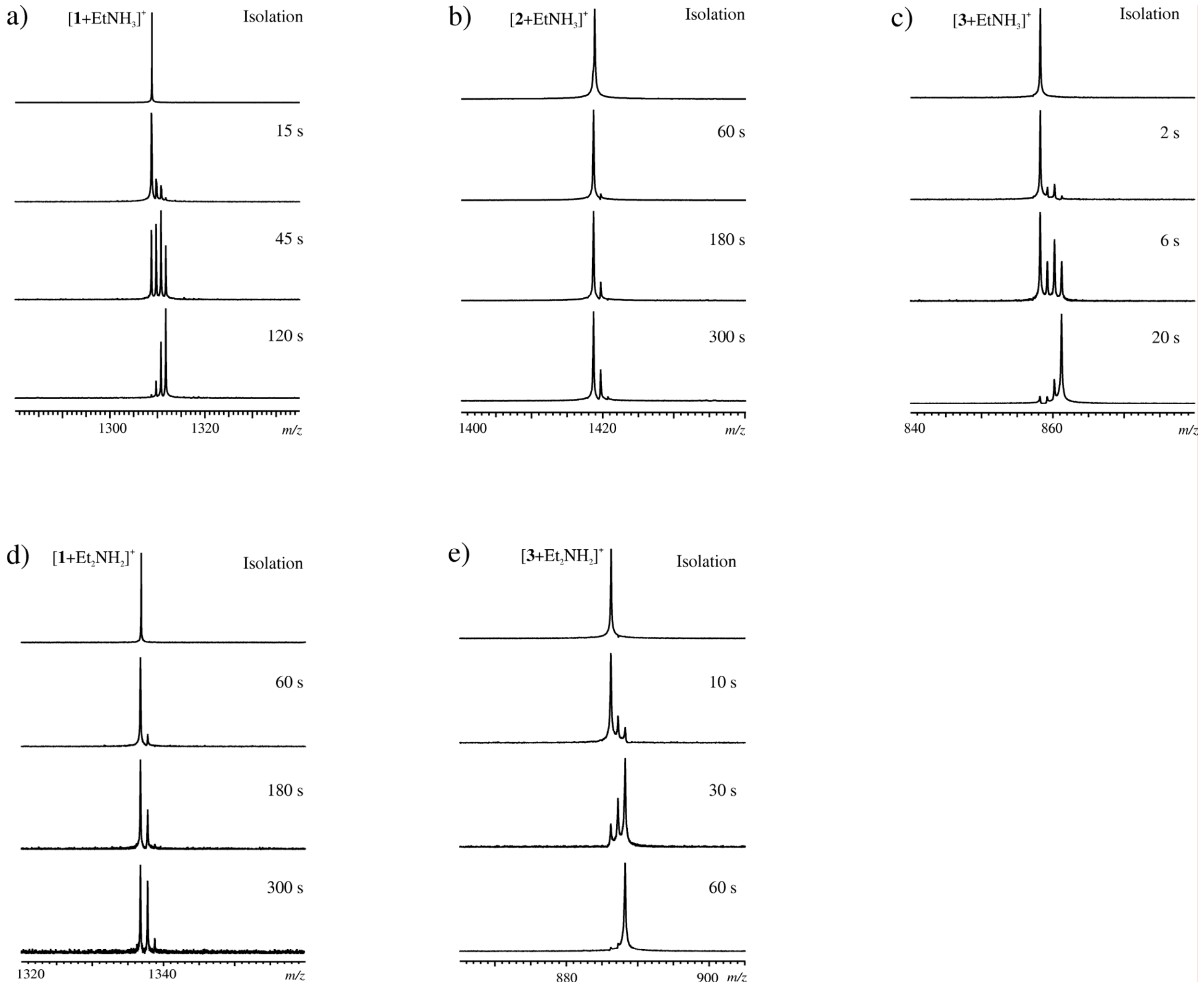

Figure S4. Reaction with ND_3: isolation spectra and selected reaction spectra (a) [**1**+$EtNH_3$]$^+$, (b) [**2**+$EtNH_3$]$^+$, and (c) [**3**+$EtNH_3$]$^+$, (d) [**1**+Et_2NH_2]$^+$, and (e)[**3**+Et_2NH_2]$^+$