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SPECIAL
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The Ionic Hydrogen/Deuterium Bonds between Diammoniumalkane Dications and Halide Anions

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Halide-anion binding to 1,12-dodecanediammonium, tetramethyl-1,12-dodecanediammonium, and tetramethyl-1,7-heptanediammonium has been investigated with infrared multiple-photon dissociation (IRMPD) spectroscopy in the 1000–2250 cm⁻¹ spectral region and with theory. Both charged ammonium groups in these diammonium compounds interact with the halide anion resulting in an ionic hydrogen bond (IHB) stretching frequency outside of the spectral frequency range that can be measured with the free-electron laser (FEL). This frequency is shifted into the spectral range upon exchanging all of the labile hydrogen atoms with deuterium atoms, thus making measurement of the ionic deuterium bond (IDB) stretching frequency possible. The IDB stretching frequency

shifts to higher values with increasing halide-anion size, methylation of the ammonium groups, and alkane chain length, consistent with the halide-anion–deuterium bond strength decreasing with decreasing gas-phase basicity of the halide anion and the increasing gas-phase basicity of the ammonium groups. The IDB stretching frequency also depends on the alkane chain length owing to constraints on the angle of the bonds between the halide anion and the two ammonium groups. There are additional bands in the IDB stretching feature in the IRMPD spectra, which are attributed to Fermi resonances and arise from coupling with overtone or combination bands that can be identified from theory and depend on the halide-anion identity and alkane chain length.

Introduction


Ionic hydrogen bonds (IHBs) affect the physical properties and reactivities of many molecular species, and these strong interactions play an important role in ion solvation, nucleation, acid–base chemistry, enzyme catalysis, and many other chemical and biological processes.^[1] Understanding the nature of these interactions is of fundamental importance, but IHBs can be difficult to study in complex systems owing to many competing effects. By investigating simple systems without competing interactions in the gas phase, the IHBs can be probed directly without interference from solvent molecules. Such studies provide valuable information on the strengths, geometries, and character of the IHBs, thereby giving insight into the role of these interactions in more complex environments.^[1,2]

IHBs in various isolated complexes have been investigated extensively using both experimental and theoretical methods.^[1,2] Thermochemical techniques, such as high-pressure mass spectrometry and equilibrium measurements,^[3] guided-ion-beam mass spectrometry,^[4] and blackbody infrared radiative dissociation,^[5] have played an important role in determining the factors that influence the strength and nature of IHBs from the measured dissociation enthalpies and entropies of hydrogen bonding in various gas-phase complexes. From these experiments, the trends in binding energies have been correlated with gas-phase basicities of the hydrogen-bond donor or acceptor in the complexes and have been used to obtain information on whether multiple hydrogen bonding, partial charge transfer, and/or steric hindrance occurs in the complexes. Infrared photodissociation (IRPD) spectroscopy^[6] has emerged as a powerful and sensitive technique for directly probing the structures of various gaseous ion complexes.^[7] These spectroscopic studies can provide both detailed structural information as well as information about the potential surface of the proton bond and coupling with other modes that may occur. In an elegant and systematic vibrational predissociation spectroscopic study of proton-bound homo- and heterodimers, Johnson and co-workers showed that the frequency of the shared proton depends on the proton-affinity difference between the two molecules, with higher frequencies resulting from larger proton-affinity differences.^[7a] This effect was explained by a simple one-dimensional potential for the shared proton motion, with homodimers that share the proton equally having relatively flat potentials resulting in lower vibra-

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tional frequencies. As the proton-affinity difference between the molecules increases, the proton becomes increasingly localized on one side of the complex resulting in a narrower potential and a stronger bond with a higher frequency. The spectral band for the shared proton is sharp for complexes with frequencies above 2000 cm^{-1} , whereas the peaks are broader and contain multiplets when this band is at lower frequencies owing to coupling with other modes in these complexes.^[7a]

The properties of IHBs have been extensively investigated in complexes in which nitrogen or oxygen serve as proton acceptors, but there are fewer studies of IHBs in halide-anion complexes in which the halide anion is the proton acceptor.^[2b] Halide anions are important in biology, and recent results indicate that they may be involved in stabilizing biomolecular structures by forming halogen-ionic bridges.^[8] Halide-anion binding to ammonia^[7g,h,9] or water^[7c-f,10] molecules has been investigated. These systems can serve as simple models for investigating the interactions between amine- or hydroxyl-group hydrogen atoms in biomolecules and halide anions. The binding energies of water^[10] and ammonia^[9] molecules to F^- , Cl^- , Br^- , and I^- decrease with increasing halide-anion size, which is consistent with weakening of the IHB as the gas-phase basicity of the anion decreases with increasing anion size.^[9,10] IRPD spectroscopy of halide anions bound to water^[7c-f] or NH_3 ^[7g,h] show that the IHB stretching frequency increases with increasing halide-anion size, which is consistent with a decrease in gas-phase basicity of the halide anion reported from the earlier binding-energy studies.^[9,10] The IRPD spectroscopy experiments also indicate that coupling between the IHB stretches and bending overtones occurs in the halide-anion-bound water and ammonia complexes owing to the anharmonic nature of the IHB, which results in Fermi resonances and the appearance of additional spectral bands.^[7f-h]

In addition to the gas-phase basicity of the proton donor, IHBs in halide complexes are affected by the presence of a charge and by the solvent. In isolation, a hydrogen bond is formed in ammonium chloride, that is, $\text{H}_3\text{N}\cdots\text{H}-\text{Cl}$, whereas the ionic species are formed in water, that is, NH_4^+ and Cl^- .^[11] Calculations indicate that only one water molecule is required to induce the ionic rather than the hydrogen-bonded ammonium chloride complex.^[12] Similarly, experiments show that adding an extra electron results in proton transfer and formation of the negatively charged $[\text{NH}_4^+\text{Cl}^-]$ ionic species.^[13] The ionic gaseous complex becomes more favorable with increasing halide-anion size and increasing proton affinity of the ammonium group by methylation.^[11,14]

Diammoniumalkanes complexed with halide anions are similar to the neutral ammonium halide species, but can be readily investigated by IRPD spectroscopy because there is a net positive charge. Herein, halide-anion binding to 1,12-dodecanediammonium, tetramethyl-1,12-dodecanediammonium, and tetramethyl-1,7-heptanediammonium is studied using infrared multiple-photon dissociation (IRMPD) spectroscopy and theory. Changes in the IHB stretching frequency as a function of halide-anion size, methylation of the ammonium groups, and alkane chain length are investigated. These results show that the IHB stretching frequency increases with increasing halide-

anion size, methylation of the ammonium groups, and with increasing alkane chain length. Additional bands appearing in the stretching feature arise from Fermi resonances, owing to coupling of this stretch with overtone or combination bands, assigned from calculated and experimental spectra. These Fermi resonances are sensitive to the specific composition of the halide-anion-bound diammonium complexes, and can be effectively tuned in or out of resonance by changing the halide anion or the length of the alkane chain.

Results and Discussion

IRMPD spectra of halide-anion-bound diprotonated diamine complexes

IRMPD spectra of diprotonated 1,12-dodecanediamine complexed with I^- , and tetramethyl-1,12-dodecanediamine complexed with Cl^- or I^- were measured in the spectral frequency range of approximately $500\text{--}2250\text{ cm}^{-1}$ (Figure 1, top) and compared with their deuterated forms (Figure 1, bottom). The IRMPD spectrum of diprotonated 1,12-dodecanediamine complexed with Br^- is essentially identical to that of the iodide-bound complex and is therefore not shown. In the IRMPD spectrum of diprotonated 1,12-dodecanediamine complexed with I^- (Figure 1a), there are two relatively narrow and intense bands at approximately 1470 and approximately 1585 cm^{-1} and a broad and weak feature at approximately 940 cm^{-1} . The band at approximately 1470 cm^{-1} is attributed to CH_2 bending modes, an assignment that is consistent with previous IRMPD results for protonated tetramethylputrescine and tetramethyl-1,3-propanediamine.^[7] The band at approximately 1585 cm^{-1} is assigned to $\text{N}-\text{H}$ bending modes, consistent with the absence of this band in the IRMPD spectrum of deuterated 1,12-dodecanediammonium complexed with I^- , in which all amine hydrogen atoms have been exchanged for deuterium atoms (Figure 1a, bottom). A new band corresponding to the $\text{N}-\text{D}$ bend appears at lower frequency ($\approx 1130\text{ cm}^{-1}$) as a result of the heavier deuterium isotope (Figure 1a, bottom). The broad weaker feature at approximately 940 cm^{-1} (Figure 1a, top) is assigned to $\text{N}-\text{H}$ wagging modes, and this assignment is supported by the absence of intensity in this same spectral region for the deuterated complex (Figure 1a, bottom).

The IRMPD spectra of diprotonated tetramethyl-1,12-dodecanediamine with Cl^- or I^- attached (Figure 1b,c, top, respectively) are similar to each other. The most intense band corresponding to CH_2 bending modes in these spectra is also at approximately 1470 cm^{-1} . However, the sharp bending $\text{N}-\text{H}$ band at approximately 1585 cm^{-1} in the spectrum of 1,12-dodecanediammonium with I^- attached is absent from these spectra and instead there is a broader shoulder band at lower frequency around 1380 cm^{-1} . This 1380 cm^{-1} shoulder band is absent in the spectra of the deuterated complexes (Figure 1b,c, bottom, respectively), which indicates that this band corresponds to the $\text{N}-\text{H}$ bending mode. There are two sharp peaks at approximately 945 and 1000 cm^{-1} in the IRMPD spectra of the chloride- and iodide-bound tetramethyl-1,12-dodecanediammonium complexes. These bands are also observed in

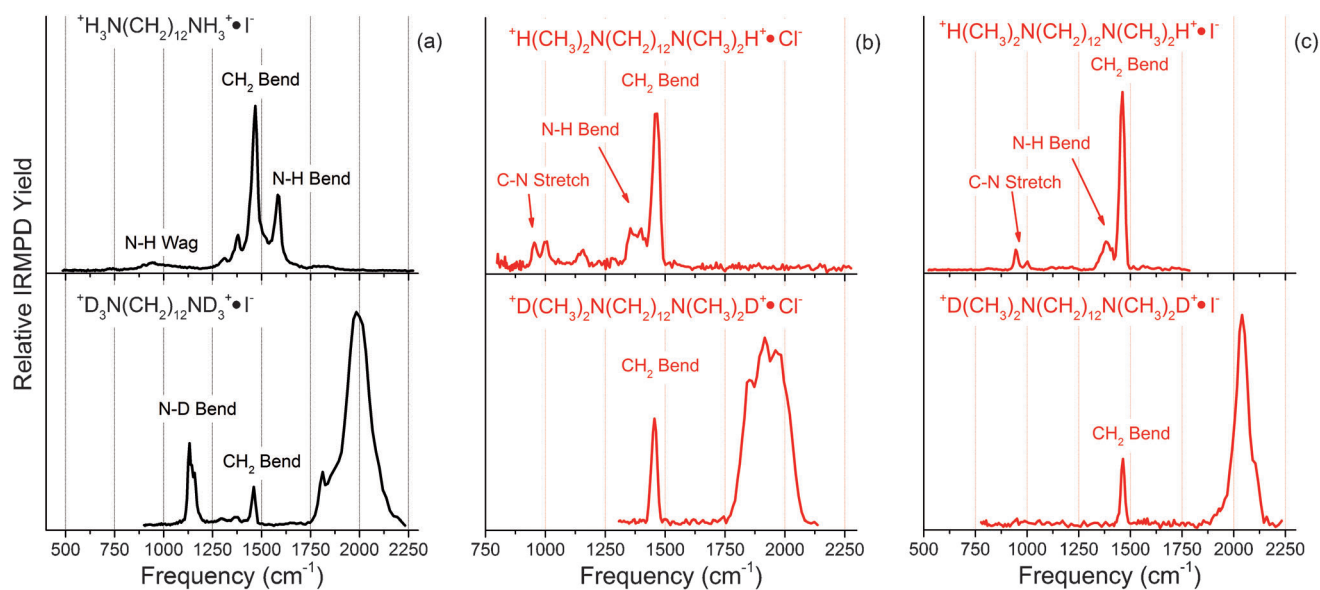


Figure 1. IRMPD spectra at 298 K of doubly charged protonated (top) or deuterated (bottom) (a) 1,12-dodecanediamine complexed with I⁻, (b) tetramethyl-1,12-dodecanediamine complexed with Cl⁻, and (c) tetramethyl-1,12-dodecanediamine complexed with I⁻.

the spectra of protonated tetramethylputrescine and tetramethyl-1,3-propanediamine^[7] and correspond to C–N stretches between the nitrogen and the methyl groups. This assignment is consistent with the absence of these sharp features in the IRMPD spectrum of the diprotonated 1,12-dodecanediamine iodide complex (Figure 1a, top). Both of these bands should be in the IRMPD spectrum of deuterated tetramethyl-1,12-dodecanediammonium complexed with I⁻ (Figure 1c, bottom). The absence of the C–N stretches, which are calculated to be approximately 1000 cm⁻¹ (see below), can be attributed to low laser power. The bands at approximately 945 and 1000 cm⁻¹ in Figure 1b,c (top) were observed only after increasing the laser power by a factor of two in this frequency range. This indicates that absorption of multiple IR photons is required to produce measurable fragmentation at these frequencies.^[6b] The average number of absorbed photons can be estimated from the measured dissociation extent by master equation modeling, which takes into account the initial ion internal-energy distribution and the microcanonical rate constants for radiative absorption and emission, as well as dissociation.^[15]

The ionic hydrogen bond (IHB) stretching frequency between the halide anion and the protonated amine groups is outside of the spectral frequency range in which IRMPD can be obtained with the free-electron laser (FEL) and is absent in the spectra of the iodide-bound diprotonated 1,12-dodecanediamine and the chloride-bound diprotonated tetramethyl-1,12-dodecanediamine complexes in Figure 1a,b (top), respectively. However, this stretching frequency is shifted down into the spectral range for the deuterated complexes and corresponds to the broad feature that appears around 1750 to 2250 cm⁻¹ in Figure 1a,b (bottom). The corresponding IHB stretching features for the protonated complexes are expected to appear around 2350 to 2700 cm⁻¹, based on IRMPD results for diprotonated tetramethyl-1,7-heptanediamine complexed

with I⁻, as shown in the Supporting Information. The IHB stretching frequency for this diprotonated complex appears around 2630 cm⁻¹ and upon deuteration this frequency shifts down to approximately 2030 cm⁻¹.

IRMPD spectra of halide-anion-bound deuterated diammonium complexes

Deuteration shifts the frequencies of the halide-anion-bound amine-hydrogen stretches into the spectral range of the FEL, thus allowing direct observation of the ionic deuterium bond (IDB) stretching frequency between the halide anions and the ammonium groups. Therefore, IRMPD spectra of the deuterated forms of 1,12-dodecanediammonium, tetramethyl-1,12-dodecanediammonium, and tetramethyl-1,7-heptanediammonium complexed with Cl⁻, Br⁻, or I⁻ were measured and are shown in Figure 2. The broad feature that appears in the frequency range 1600–2200 cm⁻¹ in all spectra corresponds to the IDB stretches. There are clear differences in the frequency, width, and number of identifiable peaks in the IDB stretching features for these spectra. For ${}^+\text{D}_3\text{N}(\text{CH}_2)_{12}\text{ND}_3^+$ with Cl⁻ attached (Figure 2a, top), there are three bands in the IDB feature. The most intense band is at approximately 1790 cm⁻¹ with shoulder peaks at approximately 1680 and 1900 cm⁻¹. For the bromide-bound complex (Figure 2a, middle), the IDB feature consists of two well-resolved bands at approximately 1810 and 1930 cm⁻¹ and an unresolved shoulder at approximately 1870 cm⁻¹. There is also a peak at approximately 1810 cm⁻¹ for the iodide-bound complex (Figure 2a, bottom), but it has significantly lower intensity than the band at approximately 2000 cm⁻¹.

The IRMPD spectra of the halide-anion bound ${}^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_{12}\text{N}(\text{CH}_3)_2\text{D}^+$ and ${}^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_7\text{N}(\text{CH}_3)_2\text{D}^+$ complexes shown in Figure 2b,c are similar for a given anion with respect

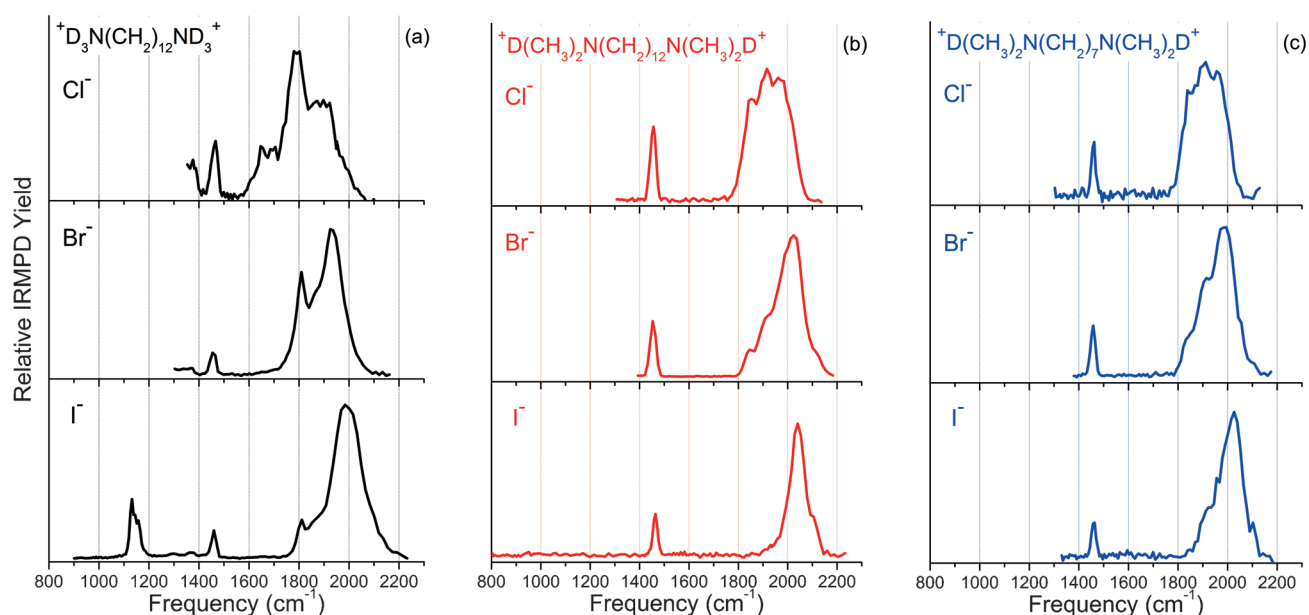


Figure 2. IRMPD spectra at 298 K of deuterated (a) 1,12-dodecanediammonium (b) tetramethyl-1,12-dodecanediammonium, and (c) tetramethyl-1,7-heptanediammonium complexed with halide anion Cl⁻ (top), Br⁻ (middle), or I⁻ (bottom).

to width and the number of distinct bands in the IDB stretching feature. For example, the spectra for the chloride-bound complexes have three distinct peaks in this broad feature at about the same frequencies of approximately 1850, 1910, and 1970 cm⁻¹. For the bromide-bound complexes (Figure 2b,c, middle), the IDB stretching feature has an intense band around 2000 cm⁻¹ and two shoulder peaks at approximately 1850 and 1910 cm⁻¹. However, these spectra differ in the intensities of the two shoulder peaks relative to the most intense band. There is a more significant difference in the IRMPD spectra between the iodide-containing complexes. The IDB stretching feature at approximately 2040 cm⁻¹ in the IRMPD spectrum of the iodide-bound ⁺D(CH₃)₂N(CH₂)₁₂N(CH₃)₂D⁺ complex (Figure 2b, bottom) is relatively narrow. This band does not have any lower frequency shoulder peaks but it does have a higher frequency shoulder. This contrasts with the same feature for the iodide-bound ⁺D(CH₃)₂N(CH₂)₇N(CH₃)₂D⁺ complex (Figure 2c, bottom), which has a band at approximately 2020 cm⁻¹ with a higher frequency shoulder and a lower-intensity shoulder band at approximately 1910 cm⁻¹.

Fermi resonance

To determine whether the multiplets in the IDB stretching frequencies might arise from different conformers of similar energy, quantum mechanical geometry optimization and frequency calculations on tetramethyl-1,7-heptanediammonium complexed with Cl⁻ were performed by systematically varying the halide-anion bond lengths and binding angles (see the Supporting Information). Results from these calculations indicate that structures with halide-anion deuterium bond lengths between 1.9 and 2.0 Å and halide-anion binding angles between 120 and 140° have relative Gibbs free energies at 298 K that are within 1.5 kcal mol⁻¹ of the lowest-energy structure.

These calculations show that increasing the binding angle by 20° and the bond lengths by 0.1 Å results in an approximately 40 and 100 cm⁻¹ increase in the IDB stretching frequency, respectively. This spread in binding angles and bond lengths is consistent with that found for the structures obtained from initial Monte Carlo conformational searches for Cl⁻ and Br⁻ bound diammoniumalkane complexes, which have standard deviations less than 8° and 0.09 Å for the binding angle and bond lengths, respectively. Thus, a distribution of structures with a small continuous range of binding angles and bond lengths are likely present in the experiments. Contributions of these structures to the IRMPD spectra should result in a broadening of the IDB band as observed. However, because these structures have a continuum of bond lengths and angles, they should not cause the multiple peaks in this feature that occur in many of these spectra. Thus, these distinct IDB peaks are most likely the result of Fermi resonances. The effects of the binding angle and bond lengths on the IDB stretching frequency and on likely conformers are discussed further in the Supporting Information.

High-intensity IHB stretches can couple with weaker overtone and combination bands of similar energy to and the same symmetry as the IHB stretch and result in Fermi resonances.^[16] For example, Fermi resonances in IRPD spectra were reported for the IHB stretch between H₂O and Br⁻,^[7f] and between NH₃ and I⁻, and 3NH₃ and Br⁻.^[7g] The IHB stretch in these complexes couples with a weaker bending overtone mode and “lends” intensity to the weaker band, which results in a doublet with peaks of similar intensity.^[7f] In our experiments, the IRMPD spectrum of ⁺D₃N(CH₂)₁₂ND₃⁺ complexed with Br⁻ (Figure 2a, middle) contains a splitting in the IDB stretching feature into mainly two bands with comparable intensities at approximately 1810 and 1930 cm⁻¹, which suggests that a Fermi resonance occurs from coupling with a combina-

tion or overtone band. In contrast, the IDB stretching feature for ${}^+D(CH_3)_2N(CH_2)_{12}N(CH_3)_2D^+$ complexed with I^- (Figure 2b, bottom) has no lower frequency shoulder bands, which indicates that the IDB stretch in this complex does not couple with other bands. The differences in the experimental IRMPD spectra between methylated and nonmethylated diammonium compounds complexed with halide anions can be attributed to differences in the types of weak bands that couple with the IDB stretch.

Nonmethylated diammonium halide-anion complexes

Electronic structure calculations were used to obtain harmonic frequencies and IR intensities to aid in identifying the combination or overtone bands (calculated as the sum of the scaled harmonic frequencies) responsible for the Fermi resonances observed in the experimental IRMPD spectra of the halide-anion-bound diammonium complexes. Experimental IRMPD spectra along with calculated IR spectra are shown in Figure 3a–c for ${}^+D_3N(CH_2)_{12}ND_3^+$ complexed with Cl^- , Br^- , and I^- , respectively. The two distinct bands in the IDB stretching feature for the Br^- and I^- complexes indicate that only one combination or overtone band couples appreciably with the IDB stretch. However, the IDB feature for the chlorinated complex contains three bands, which indicates that coupling occurs with an additional weaker overtone or combination band. The calculated IR spectra for ${}^+D_3N(CH_2)_{12}ND_3^+$ complexed with Cl^- , Br^- , or I^- are very similar. The most notable difference is the IDB stretch, which shifts from approximately 1900 cm^{-1} for the chloride-bound complex to approximately 2000 cm^{-1} for the iodide-bound complex. The bands at approximately 720 and 1150 cm^{-1} are the N–D wagging and bending modes, respectively. The frequencies for these bands are insensitive to the

halide-anion identity. The N–D bending mode at approximately 1150 cm^{-1} in the calculated spectra is consistent with the assignment made for the band at approximately 1130 cm^{-1} in the experimental spectrum of the deuterated iodide-bound complex in Figure 1. The N–H wagging modes in the experimental IRMPD spectrum for the nondeuterated iodide-bound complex occur around 940 cm^{-1} . Deuterium exchange results in the corresponding N–D wagging frequencies appearing at lower frequencies. These N–D wagging modes were not observed in the experimental spectra of the deuterated complexes, likely a result of the bands appearing at frequencies below 800 cm^{-1} .

The results from calculations and experimental data suggest two possibilities for weak overtone or combination bands that could couple with the IDB stretches in the halide-anion-bound ${}^+D_3N(CH_2)_{12}ND_3^+$ complexes. The first possibility is an overtone from the N–D wagging modes that is calculated to be between approximately 1360 and 1560 cm^{-1} (calculated as the sum of the scaled harmonic frequencies). The second possibility is a combination band that results from the N–D wagging and N–D bending modes with a frequency of approximately 1870 cm^{-1} . Thus, the peak observed at approximately 1650 cm^{-1} for the chloride-bound complex could arise from coupling between the IDB stretch and the overtone of the N–D wagging modes. The band at approximately 1900 cm^{-1} corresponds to the IDB stretch and the most intense band at approximately 1790 cm^{-1} could be the result of coupling between the IDB stretch and the N–D wagging and bending combination band. Because the IDB stretch for the bromide- and iodide-bound complexes at approximately 1930 and 2000 cm^{-1} , respectively, shifts to higher frequencies as a function of the halide-anion size, coupling with the higher-frequency combination band is observed mainly in the IRMPD spectra

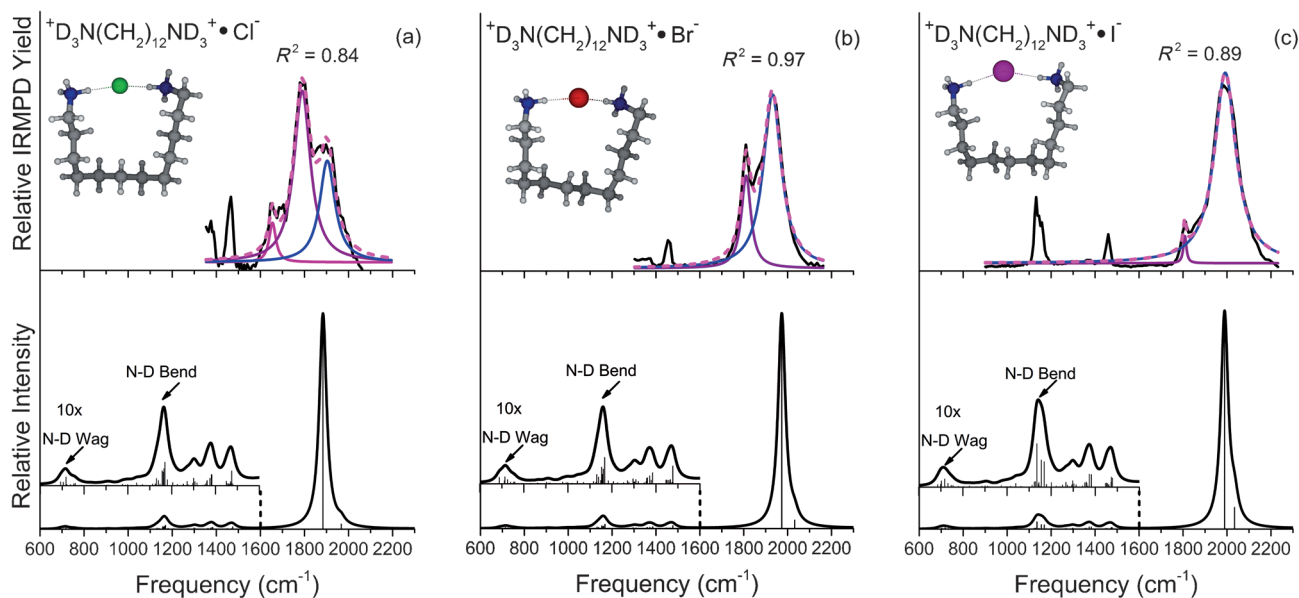


Figure 3. Experimental IRMPD spectra (top) and calculated IR spectra (bottom) of deuterated 1,12-dodecanediammonium complexed with (a) Cl^- , (b) Br^- , or (c) I^- . The ionic deuterium bond stretching feature in the experimental spectra is deconvolved by Lorentzian peak functions. The number of Lorentzian functions used depends on the number of well-resolved bands contributing to this feature and the quality of the fits is given by the R^2 values.

of these complexes. In addition to these identified combination and overtone bands, there are likely other modes that could couple and contribute to the broadness and complexities in this feature as well.

Methylated diammonium halide-anion complexes

The IDB stretching features in the experimental IRMPD spectra of the halide-anion-bound ${}^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_{12}\text{N}(\text{CH}_3)_2\text{D}^+$ and ${}^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_7\text{N}(\text{CH}_3)_2\text{D}^+$ complexes differ from those of ${}^+\text{D}_3\text{N}(\text{CH}_2)_{12}\text{ND}_3^+$. Methylation of the amine groups alters the N–D wagging and bending frequencies, which are likely responsible for the Fermi resonances observed for ${}^+\text{D}_3\text{N}(\text{CH}_2)_{12}\text{ND}_3^+$ complexed with Cl^- , Br^- , or I^- . Possible overtone or combination bands for the methylated diammonium halide-anion complexes that might be responsible for the multiple bands in the IDB stretch are identified from computations. Calculated and experimental IRMPD spectra are shown in Figures 4 and 5 for halide-anion-bound ${}^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_{12}\text{N}(\text{CH}_3)_2\text{D}^+$ and ${}^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_7\text{N}(\text{CH}_3)_2\text{D}^+$ complexes, respectively. Calculated harmonic frequencies at approximately 930 and 1000 cm^{-1} correspond to C–N stretches between the methyl groups and the amine nitrogen with contributions from N–D bending modes and are consistent with the assignment of C–N stretches for the two sharp bands at approximately 945 and 1000 cm^{-1} in the experimental IRMPD spectra of the chloride- and iodide-bound diprotonated tetramethyl-1,12-dodecanediamine complexes in Figure 1b,c, respectively. The broader shoulder at 1380 cm^{-1} from N–H bending modes in the IRMPD spectra of the chloride- and iodide-bound diprotonated tetramethyl-1,12-dodecanediamine complexes (Figure 1b,c, top) is expected to shift to lower frequency upon deuteration owing to the heavier isotope and is calculated to

be approximately 1000 cm^{-1} . Both the C–N stretches and N–D bends are missing from the experimental spectrum of the deuterated iodide complex in Figure 4c (top) likely because of insufficient laser power to dissociate the complex. Nonetheless, the complexities in the IDB stretching features observed for the Cl^- - and Br^- -bound ${}^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_{12}\text{N}(\text{CH}_3)_2\text{D}^+$ and ${}^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_7\text{N}(\text{CH}_3)_2\text{D}^+$ complexes can be explained by coupling between the IDB stretch and the overtones of the C–N stretches and N–D bends that result in Fermi resonances, which give rise to the two shoulder bands at approximately 1850 and 1900 cm^{-1} .

IDB stretching frequency

The IRMPD spectra indicate that the IDB stretching frequency depends on the halide anion, chain length, and methylation of the amine groups. The IDB stretching frequencies were obtained from the experimental IRMPD spectra by deconvolving the IDB stretching feature into the minimum number of Lorentzian functions necessary to obtain a good fit with an R^2 value of at least 0.84. These Lorentzian fits were overlaid with the experimental IRMPD spectra in Figures 3–5 for halide-anion-bound ${}^+\text{D}_3\text{N}(\text{CH}_2)_{12}\text{ND}_3^+$, ${}^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_{12}\text{N}(\text{CH}_3)_2\text{D}^+$, and ${}^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_7\text{N}(\text{CH}_3)_2\text{D}^+$ complexes, respectively. Coupling with overtone and combination bands will perturb the frequency of the IDB stretch and shift it from the unperturbed frequency value.^[7e,g,17] Thus, the observed IDB stretching frequencies obtained from the deconvolution will likely deviate somewhat from the unperturbed frequencies in the absence of these resonances.

The IDB stretching frequencies obtained from the Lorentzian fits as a function of gas-phase basicity of the halide anion for ${}^+\text{D}_3\text{N}(\text{CH}_2)_{12}\text{ND}_3^+$, ${}^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_{12}\text{N}(\text{CH}_3)_2\text{D}^+$, and ${}^+\text{D}(\text{CH}_3)_2\text{N}$

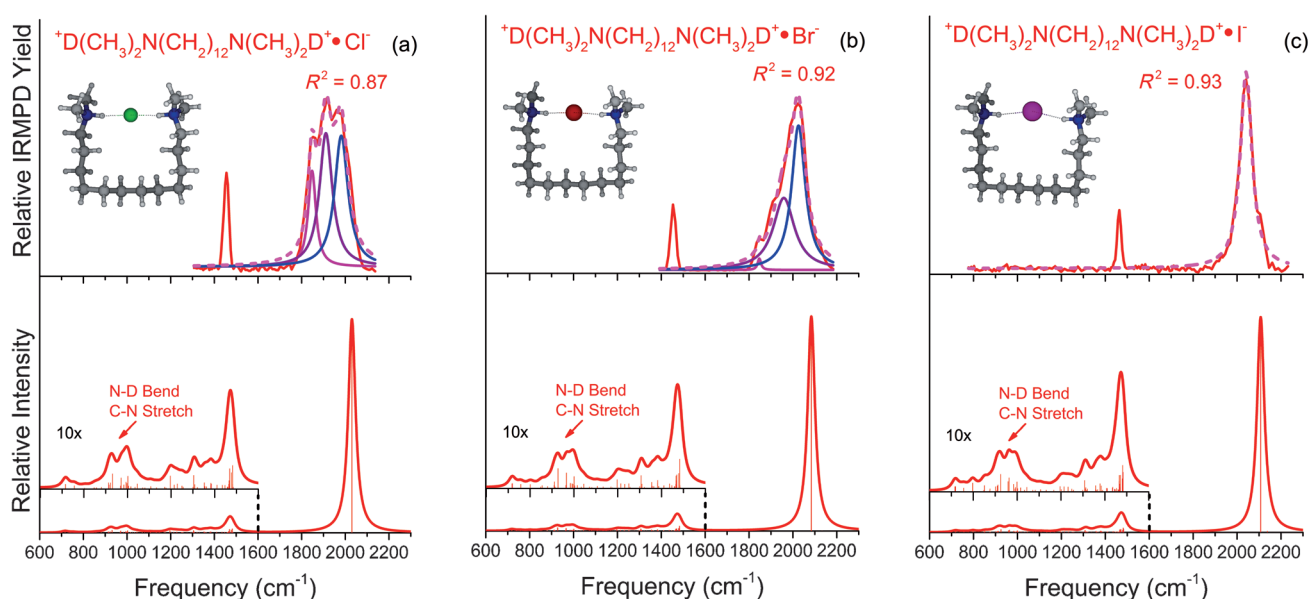


Figure 4. Experimental IRMPD spectra (top) and calculated IR spectra (bottom) of deuterated tetramethyl-1,12-dodecanediammonium complexed with (a) Cl^- , (b) Br^- , or (c) I^- . The ionic deuterium bond stretching feature in the experimental spectra is deconvolved by Lorentzian peak functions. The number of Lorentzian functions used depends on the number of well-resolved bands contributing to the feature and the quality of the fits is given by the R^2 values.

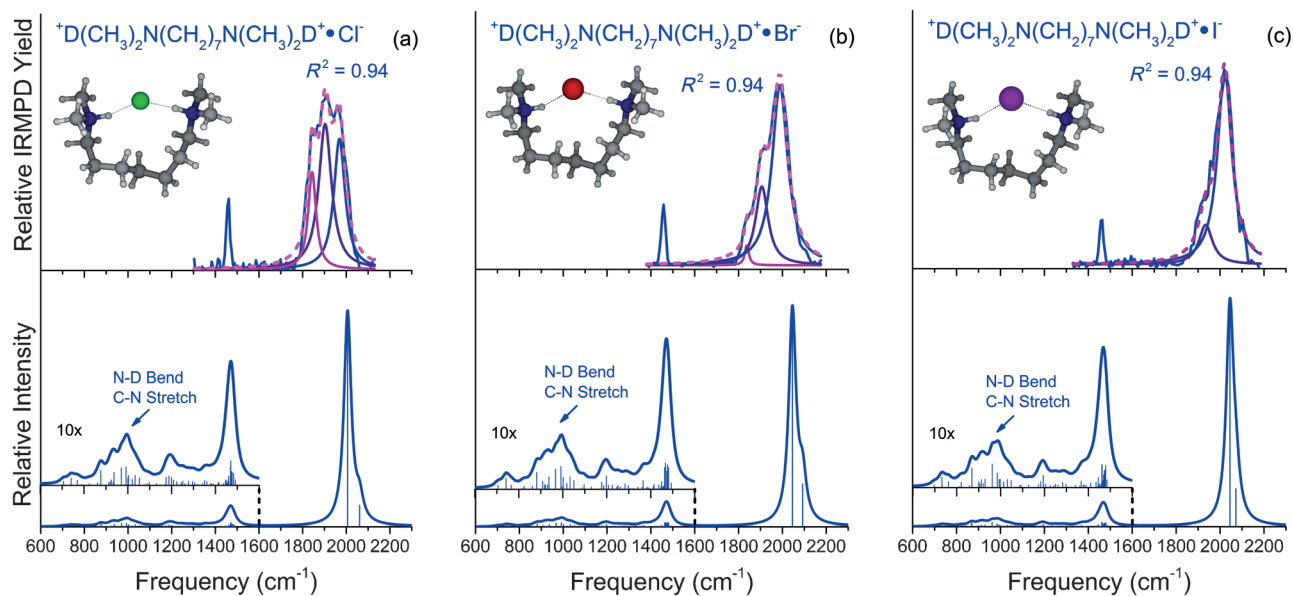


Figure 5. Experimental IRMPD spectra (top) and calculated IR spectra (bottom) of deuterated tetramethyl-1,7-heptanediammonium complexed with (a) Cl^- , (b) Br^- , or (c) I^- . The ionic deuterium bond stretching feature in the experimental spectra is deconvolved by Lorentzian peak functions. The number of Lorentzian functions used depends on the number of well-resolved bands contributing to this feature and the quality of the fits is given by the R^2 values.

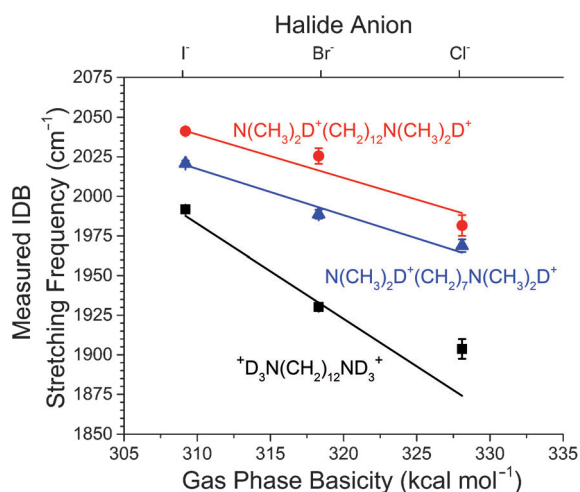


Figure 6. The measured IDB stretching frequency obtained by deconvolving the experimental spectra with Lorentzian functions (see Figures 3–5) for deuterated 1,12-dodecenediammonium (squares), tetramethyl-1,12-dodecenediammonium (circles), and tetramethyl-1,7-heptanediammonium (triangles) as a function of gas-phase basicity of the halide anion. Error bars indicate the standard error in the IDB stretching frequency from the Lorentzian fit. Data are fit with lines as a guide.

$(\text{CH}_2)_7\text{N}(\text{CH}_3)_2\text{D}^+$ are shown in Figure 6. For $^+\text{D}_3\text{N}(\text{CH}_2)_{12}\text{ND}_3^+$, the IDB stretching frequency shifts from 1904 cm^{-1} for Cl^- to 1992 cm^{-1} for I^- . The blueshift in the frequency of the IDB stretch with increasing halide-anion size is about 50 cm^{-1} per halogen from Cl^- to I^- , which is similar to results for halide-anion-bound NH_3 complexes,^[7g] but less than the blueshift ($\approx 130\text{ cm}^{-1}$) observed in the IHB stretching frequency per halogen for halide-anion-bound H_2O complexes.^[7e] A decrease in the gas-phase basicity of the halide anion results in a decrease in the strength of the bond^[7e,g,9,10] between the halide anion

and the deuterium atoms on the amine groups, thus shifting the IDB stretching frequency to higher values.

There is also a blueshift in the IDB stretching frequency as a function of halide-anion size for the methylated diammonium compounds, $^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_{12}\text{N}(\text{CH}_3)_2\text{D}^+$ and $^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_7\text{N}(\text{CH}_3)_2\text{D}^+$. However, the shift ($\approx 25\text{ cm}^{-1}$) to higher frequencies per halogen is lower than for the nonmethylated $^+\text{D}_3\text{N}(\text{CH}_2)_{12}\text{ND}_3^+$ complexes. This is due to the higher gas-phase basicity of the amine group as a result of methylation, which decreases the bond strength between the halide anion and the deuterium atoms, and thereby reduces the effect of halide-anion gas-phase basicity on the IDB stretching frequency. This is also consistent with the overall higher IDB stretching frequencies observed for the methylated versus the nonmethylated diammonium halide-anion-bound complexes. Results for $^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_{12}\text{N}(\text{CH}_3)_2\text{D}^+$ and $^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_7\text{N}(\text{CH}_3)_2\text{D}^+$ show that the IDB stretching frequency also depends on the chain length separating the two charged amine groups. The IDB stretching frequencies of the halide-anion-bound complexes with the shorter (seven carbon) alkane chain are lower than those for the complexes with the longer (twelve carbon) alkane chain. This likely results from differences in the $\text{D}^+\text{-X}^-\text{-D}^+$ angle, which is more constrained for $^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_7\text{N}(\text{CH}_3)_2\text{D}^+$ than $^+\text{D}(\text{CH}_3)_2\text{N}(\text{CH}_2)_{12}\text{N}(\text{CH}_3)_2\text{D}^+$ because of the shorter alkane chain separating the two charged amine groups. The flexible longer alkane chain allows for a nearly linear binding angle between the halide anion and the amine deuterium atoms, which maximizes the distance between the two positively charged amine groups and results in stronger amine–deuterium bonds and a higher IDB stretching frequency. This is supported by calculations (see the Supporting Information), which indicate that structures obtained with Monte Carlo conformational searching for tetramethyl-1,12-dodecane-

diammonium halide-anion complexes have a binding angle of approximately 160° compared with approximately 125° for tetramethyl-1,7-heptanediammonium halide-anion complexes.

Effects of the halide anion and chain length on the Fermi resonance

A large halide-anion size results in reduced coupling between the IDB stretch and the weaker overtone or combination bands as shown for the iodide-bound $^+D_3N(CH_2)_{12}ND_3^+$ (Figure 3c) and $^+D(CH_3)_2N(CH_2)_7N(CH_3)_2D^+$ (Figure 5c) complexes, and this Fermi resonance is eliminated for the iodide-bound $^+D(CH_3)_2N(CH_2)_{12}N(CH_3)_2D^+$ complex as indicated by the relatively narrow IDB stretching feature in the experimental IRMPD spectrum. These results indicate that the increase in the IDB stretching frequency with increasing halide-anion size can effectively "tune" the IDB stretching frequency out of resonance with the weaker overtone or combination bands in these complexes. This effect has been demonstrated previously for the Cl^- -bound water complex by the sequential addition of CCl_4 , which shifted the IHB stretch to higher frequencies and "tuned" this stretch through a Fermi resonance interaction with the bending overtone.^[17] Because the IDB stretching frequency depends on the alkane chain length between the two ammonium groups in these complexes, Fermi resonances can also be effectively "tuned" in and out by changing the alkane chain length. This is indicated for the iodide $^+D(CH_3)_2N(CH_2)_7N(CH_3)_2D^+$ and $^+D(CH_3)_2N(CH_2)_{12}N(CH_3)_2D^+$ complexes, where there is still some coupling observed between the IDB stretch and the weak overtone in the diammonium complex with the shorter alkane chain, but there is no Fermi resonance observed for the complex with the longer alkane chain.

Conclusion

IRMPD spectra in the $1000\text{--}2250\text{ cm}^{-1}$ region were measured for 1,12-dodecanediammonium, tetramethyl-1,12-dodecanediammonium, and tetramethyl-1,7-heptanediammonium complexed with Cl^- , Br^- , or I^- . The IDB stretching frequency shifts with halide-anion size, methylation of the ammonium groups, and alkane chain length, a result related to the gas-phase basicities of the halide anions and the ammonium groups, and the constraints in the binding angle between the halide anion and the two ammonium groups. The IDB stretching frequencies in these complexes couple with weaker overtone or combination bands that give rise to Fermi resonances, which can be tuned in or out of resonance by changing the halide anion or the alkane chain length. The results obtained for the deuterated halide-anion-bound diammonium complexes should apply to the corresponding nondeuterated complexes as well.

In gaseous ammonium chloride complexes, the proton resides closer to the halide anion, that is, forming $H-Cl$ rather than to the NH_3 group to form NH_4^+ , even though the ionic species are formed in aqueous solution.^[11] Our IRMPD results indicate that binding of two ammonium groups to a halide anion in the gas phase favors formation of the ionic com-

plexes, in which the protons reside closer to the amine groups rather than the halide anion. This is consistent with results showing that addition of an extra electron to gaseous ammonium chloride induces proton transfer to the NH_3 group, $[NH_4^+ Cl^-]^-$. Unlike the neutral ammonium chloride complex, diammonium compounds, such as those investigated here, contain two protonated amine groups and form a singly charged species when complexed to a halide anion, which makes them amenable for study with IRMPD spectroscopy. Thus, diammonium compounds for which the two ammonium groups are separated by a rigid linker that prevents these groups from both interacting with the halide anion could be used in future IR(M)PD experiments to characterize the hydrogen bond expected to form in neutral ammonium chloride complexes in the gas phase.

Recent studies indicate that halide anions are involved in stabilizing the structures of biomolecules by forming halogen-ionic bridges.^[8] Thus, these diammonium compounds, in which the alkane chain length is varied, can serve as simple models for studying and providing insight into the interactions between halide anions and positively charged functional groups in biomolecules, such as the basic residues in proteins.

Experimental Section

Experiments

IRMPD experiments were performed using a 4.7 T Fourier-transform ion cyclotron resonance mass spectrometer coupled to a free-electron laser (FEL) that produces intense tunable IR radiation. Both the experimental procedures^[18] and apparatus^[19] have been described in detail elsewhere. Ions were formed by electrospray ionization from 70:30 methanol/water or 60:40 deuterated water/methanol containing approximately 2 mM diamino compound with approximately 2 mM of the corresponding HX acid, in which $X=Cl, Br, \text{ or } I$. The precursor-ion complexes of interest were isolated by ejecting all other ions from the cell using stored wave-form inverse Fourier-transform excitation^[20] and were subsequently irradiated for 2–5 s with tunable radiation from the FEL. An IRMPD spectrum for diprotonated tetramethyl-1,7-heptanediamine complexed with I^- in the frequency range between 2500 and 3100 cm^{-1} was measured using a tunable optical parametric oscillator/amplifier (OPO/OPA) system (LaserVision, Bellevue, WA) with this same mass spectrometer and irradiation time of 4.5 s. The major dissociation pathway observed in the IRMPD experiments was the loss of HX. The IRMPD intensities in the spectra were obtained from the IRMPD yield determined from the precursor- and product-ion abundances, and were corrected for the frequency-dependent laser power.^[18,21]

All reagents were obtained from Sigma–Aldrich (Zwijndrecht, Netherlands) and were used without further purification. Methylation of 1,7-heptanediamine and 1,12-dodecanediamine to produce tetramethyl-1,7-heptanediamine and tetramethyl-1,12-dodecanediamine, respectively, was accomplished using a previously reported procedure.^[22] Briefly, the methylated diamines ($\approx 0.5\text{ g}$) were prepared by mixing the diamine (0.5 g), 3 M sulfuric acid (1.4 mL), 40% aqueous formaldehyde (2.5 mL), and slow addition of sodium borohydride ($\approx 0.6\text{ g}$) to a glass flask placed in an ice bath. The mixture was allowed to react for 5–10 min, after which concentrated sulfuric acid was carefully added. Impurities were extracted three

times with diethyl ether (2 mL), and the aqueous layer was subsequently made basic with an excess amount of KOH. Three more extractions with diethyl ether (2 mL) followed, after which the methylated diamines remained in the ether.

Computations

Initial structures for diprotonated 1,12-dodecanediamine, tetramethyl-1,12-dodecanediamine, and tetramethyl-1,7-heptanediamine complexed with halide anions Cl^- or Br^- were generated from Monte Carlo conformational searching using the Merck molecular force fields (MMFFs) as implemented in MacroModel 9.9 (Schrödinger, LLC, Portland, OR). About 2200, 1350, and 50 different structures that were within 12 kcal mol^{-1} of each other were found for these respective ions. For a given diammoniumalkane and halide anion, the structures differ mainly in the conformation of the alkane chain rather than the binding of the halide anion to the two charged amine groups (see the Supporting Information for a more detailed discussion). Starting structures for complexes with I^- attached were obtained by halide-anion substitution into the brominated structures. Quantum mechanical geometry optimization of selected low-energy structures from the conformational search was carried out in Q-Chem^[23] 3.2 at the B3LYP/6-31++G** level of theory using the CRENLB basis set and effective core potential for Br^- and I^- .^[24]

Vibrational frequencies and intensities were calculated by using the double-harmonic approximation and the analytical Hessian of the energy-minimized structures in Q-Chem 3.2. Frequencies for complexes with the amine hydrogen atoms exchanged for deuterium atoms were calculated by replacing the mass of the corresponding hydrogen atom with the mass of its heavier isotope. All optimized structures had no imaginary harmonic frequencies, which indicated that they were local minima on the potential-energy surface. Vibrational frequencies were scaled by 0.975 to provide reasonable agreement with the experimental spectra, and the line shapes were approximated with Lorentzian functions using 40 cm^{-1} for the full width at half-maximum.^[6]

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