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Gas phase infrared spectroscopy of cluster anions as a function of size: The effect of solvation on hydrogen-bonding in Br\(^-\)-(HBr)\(_{1,2,3}\) clusters

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The gas phase vibrational spectroscopy of Br\(^-\)-(HBr)\(_{1,2,3}\) clusters has been studied between 6 and 16 \(\mu\m\) (625 and 1700 cm\(^{-1}\)) by multiphoton infrared photodissociation spectroscopy using the output of the free electron laser for infrared experiments. Infrared (IR) spectra were recorded by monitoring the mass-selected ion yield. In all three systems neutral HBr loss is found to be the dominant photofragmentation channel. BrHBr\(^-\) exhibits a weak absorption band at 1558 cm\(^{-1}\) which is assigned to the overtone of the antisymmetric stretching mode \(\nu_3\). A series of strong absorption bands was observed for Br\(^-\)-(HBr)\(_2\) at energies in the 950–1450 cm\(^{-1}\) range. The Br\(^-\)-(HBr)\(_3\) spectra reveal two absorption bands at 884 and 979 cm\(^{-1}\), which are assigned to two H-atom stretching modes. Evidence for the localization of the H atom and destruction of the symmetric BrHBr\(^-\) hydrogen bond in the larger clusters is presented. Standard electronic structure calculations fail to reproduce the experimental IR spectra, indicating a breakdown of the harmonic approximation. © 2002 American Institute of Physics. [DOI: 10.1063/1.1506308]

I. INTRODUCTION

The hydrogen bond is one of the most important interactions in chemistry, governing diverse phenomena from the properties of liquids to the structure of proteins and DNA.\(^1\) Hydrogen bonds are particularly appealing from the perspective of cluster spectroscopy, which can probe how the properties of a collection of molecules held together by hydrogen bonds evolve with size.\(^2\) Such studies have shown, for example, how many of the properties of liquid water can be understood in terms of fundamental interactions between water molecules.\(^3\)

Some of the strongest known hydrogen bonds are the symmetric bihalide anions XHX\(^-\) (X=F, Cl, Br, I), with dissociation energies ranging from 1.93 eV for FHF\(^-\) to 0.73 eV for IHI\(^-\).\(^4\) Experiments and calculations indicate these anions to be symmetric, \(D_{\text{sh}}\) species with two equal H–X bond lengths.\(^5\)–\(^6\) These anions and their asymmetric counterparts, such as BrHI\(^-\), are also of interest as transition state precursors in negative ion photoelectron spectroscopy experiments.\(^7\)–\(^8\) However, the very factor that causes these hydrogen bonds to be so strong, namely the extensive sharing of the H atom between two halogen atoms, also makes these bonds highly susceptible to solvent perturbation that can, for example, destroy the symmetry of the bonds in symmetric XHX\(^-\) anions. In this paper, we use the tunable infrared (IR) radiation from a free electron laser to obtain the first gas phase spectrum of BrHBr\(^-\) and probe the effect of solvation on the hydrogen-bonding in this anion via IR spectroscopy of size-selected Br\(^-\)-(HBr)\(_n\) clusters.

Considerable recent progress has been made in the IR spectroscopy of hydrogen-bonded anion clusters, primarily...
through IR predissociation experiments in which size-selected clusters are vibrationally excited with one or more IR photons, and then predissociate to daughter ions that can be detected with near-unit efficiency. This type of IR action spectroscopy is extremely sensitive and can be applied to mass-selected ion beams where number densities are as low as $10^3$--$10^4$/cm$^3$. These experiments require intense, tunable laser sources, and have thus been largely restricted to vibrational frequencies above 2350 cm$^{-1}$. However, for strongly hydrogen-bonded anions such as symmetric bihalides, the antisymmetric stretch ($v_3$) fundamental is considerably lower than this; gas phase IR spectroscopy of HBF and ClHCl$^-$ yields $v_3$ frequencies of 1331 and 723 cm$^{-1}$, respectively, while matrix isolation spectroscopy of BrHBr$^-$ yields $v_3$ frequencies ranging from 728 to 753 cm$^{-1}$. Hence, the systematic study of the IR spectroscopy of bare and clustered bihalides requires a very different type of light source.

A novel approach to study the vibrational spectroscopy of cations in the spectral region below 2000 cm$^{-1}$ using infrared photodissociation (IRPD) spectroscopy has recently been demonstrated by Meijer and co-workers using the free electron laser for infrared experiments (FELIX) at the FOM-Institute Rijnhuizen. Multiphoton excitation IRPD spectra of selected polycyclic aromatic hydrocarbons were measured using excimer laser ionization followed with multiphoton excitation with a pulsed free electron laser (FEL) in the 400–1700 cm$^{-1}$ region. Asmis et al. extended the technique to study mass-selected parent ions by coupling a tandem-mass spectrometer to the FEL source. In the present study, we apply this technique for the first time to investigate the vibrational spectroscopy of gas phase cluster anions. Our results indicate that the addition of one or more HBr solvent molecules to the BrHBr$^-$ cluster destroys the symmetry of the BrHBr$^-$ bond, with the resulting system resembling two or three HBr ligands bound to a Br$^-$ core.

### II. EXPERIMENT

Br$^-$·(HBr)$_n$ clusters are produced at the intersection of a pulsed supersonic molecular beam and a 1 keV, 300 $\mu$A electron beam using an arrangement similar to that used in previous photoelectron spectroscopy studies of BrHBr$^-$.

The molecular beam is formed from a gas mixture of 4% HBr in Ar, which is expanded through a pulsed valve (General Valve) with a 780 $\mu$m diameter orifice. The pulsed valve is operated at 20 Hz with a stagnation pressure of 2–5 bar. Br$^-$ ions are formed through dissociative electron attachment to HBr and are clustered and internally cooled as the supersonic expansion progresses. Anion clusters generated in the supersonic expansion pass a 2 mm skimmer into a previously described guided ion beam tandem mass spectrometer, where they are mass-selected and subsequently trapped in a temperature-adjustable, helium filled radio frequency (RF) hexadecapole ion trap. The ion trap is kept at a constant temperature of $\sim$50 K and He buffer gas pressure of $\sim$80 $\mu$bar.

Infrared excitation is performed with the output of FELIX. The FELIX output is composed of 5 $\mu$s long macro-pulses at 5 Hz, with each macro-pulse containing a series of $\sim$1 ps micropulses separated by a nanosecond. The FELIX bandwidth is transform limited to $\sim$0.8% of the central frequency and pulse energies of 50 and 25 mJ per macro-pulse (measured before the ZnSe optics) were employed in these experiments. The FELIX beam is directed through two ZnSe windows and focused within the ion trap by a 600 mm focal length ZnSe lens. The scan range for these experiments was limited by the IR transmission function of the ZnSe windows and lenses which was $>85\%$ between 8 and 14 $\mu$m and dropped to <10% below 6 $\mu$m and above 17 $\mu$m. When FELIX is in resonance with an infrared transition of the trapped anion, multiple photon absorption and dissociation can occur, leading to production of ionic photofragments, as follows:

$$AB^-(\nu = 0) \rightarrow h\nu AB^-(\nu = 1) \rightarrow A^- + B.$$  

During a measurement cycle, the ion trap is allowed to fill for a period of 290 ms and the ions are then stored until a trigger signal from the FEL is received. During this time either two or three FELIX macro-pulses interact with the trapped ions, producing photofragment ions if multiphoton dissociation occurs. The trap is partially emptied over a period of 100 ms and the mass-selected ion yield is recorded as a function of the FEL wavelength. Depending on the signal intensity, this process is repeated over 5–20 fill/extraction cycles and for each fragment ion monitored. The stability of the parent ion production is checked by measuring the parent ion yield once at the beginning and once at the end of each wavelength step. The ion trap is completely emptied after

<table>
<thead>
<tr>
<th>Parent ion</th>
<th>Fragment ion</th>
<th>Position (cm$^{-1}$) and normalized intensity</th>
</tr>
</thead>
</table>
| BrHBr$^-$  | Br$^-$       | 1558
|            | BrHBr$^-$    | $\sim$875 (0.05), $\sim$940 (0.06), 992 (1.00), 1012 (0.74), 1048 (0.73), 1104 (0.75), 1147 (0.56), 1205 (0.16), 1222 (0.10), 1269 (0.10), 1289 (0.10), 1359 (0.66), 1420 (0.27) |
| Br$^-$·(HBr)$_2$ | BrHBr$^-$ | 888 (1.00), 979 (0.16), 884 (0.07), 934 (0.08), 984 (1.00), 1052 (0.11), 1098 (0.08), 1142 (0.06), 1203 (0.03), 1225 (0.01), 1264 (0.01), 1289 (0.01), 1359 (0.06), 1416 (0.04) |
each wavelength step. A typical spectrum is measured in steps of 20–100 nm and takes roughly 30–60 min to record. Peak positions are summarized in Table I.

III. RESULTS

A. BrHBr$^-$

The IRPD spectrum of BrHBr$^-$ in the range from 1460 to 1700 cm$^{-1}$ is shown in Fig. 1. Both parent ion (open dots) and Br$^-$ fragment ion (solid dots) intensities are plotted. The parent ion signal, which was measured with less signal averaging than the fragment ion signal, varies by $<$10% over the acquisition time. A single broad, weak absorption band is observed in the Br$^-$ fragment ion yield (HBr loss channel) at 1558 cm$^{-1}$ with a full width at half maximum of 60 cm$^{-1}$. Depletion of the parent ion signal is not resolved, because it is three orders of magnitude smaller than the parent ion signal itself. Coarser scans extending from 625 to 1700 cm$^{-1}$ showed no additional features, nor did finer scans from 700–800 cm$^{-1}$, where the $\nu_3$ antisymmetric stretch fundamental is expected. A constant Br$^-$ background signal resulting from collision induced dissociation of the BrHBr$^-$ parent ions is observed. The Br$^-$ background is on the order of 0.03% of the parent ion signal, and photofragmentation at 1558 cm$^{-1}$ yields approximately three times the background signal. The transmission of the ZnSe optics (inset of Fig. 1) strongly decreases below 8 $\mu$m and varies by a factor of $\sim$3 in the shown spectral region. As a result of this the band shape may be distorted due to the decreasing pulse energy at the interaction region.

B. Br$^-$-(HBr)$_2$

Figure 2 shows IRPD spectra of Br$^-$-(HBr)$_2$. The dominant photofragment channel is production of HBr+BrHBr$^-$ (solid dots). The parent ion depletion spectrum is also shown (top right corner). In contrast to BrHBr$^-$, the parent depletion is quite pronounced. At 992 cm$^{-1}$, the largest absorption band, roughly 85% of the parent ions are depleted, indicating that photofragmentation does not exclusively occur at the focus of IR beam, but extends over the complete irradiated region of the 23 cm long ion trap. Collisional fragmentation of Br$^-$-(HBr)$_2$ within the ion trap gave a small baseline BrHBr$^-$ signal of $\sim$70 c/s over the entire scan range. The depletion and fragment ion spectra exhibit a strong correlation, with six distinct, strong absorption peaks appearing at 992, 1048, 1104, 1147, 1359, and 1420 cm$^{-1}$. The 992 cm$^{-1}$ feature exhibits a shoulder at 1012 cm$^{-1}$, hinting at an addi-
tional, overlapping absorption band. Lorentzian fits of these peaks yield widths (FWHM) of 15–21 cm\(^{-1}\), save the peak at 992 cm\(^{-1}\), which is 40 cm\(^{-1}\) wide. Lower intensity absorption bands appear in the BrHBr\(^{-}\) fragment ion spectrum at 875, 940, 1205, 1222, 1269, and 1289 cm\(^{-1}\). The fragment ion yield is not equivalent to the depletion signal, mainly due to the optimization of the mass spectrometer for parent ion detection. All observed peak widths are well in excess of the 8–11 cm\(^{-1}\) FELIX bandwidth. A background free Br\(^{-}\) fragment ion spectrum (not shown) was also acquired over the same wavelength range, but <0.2% of the total photoproducts appear as Br\(^{-}\) and no distinct features were observed.

C. Br\(^{-}\)-(HBr)\(_3\)

The IRPD spectroscopy of Br\(^{-}\)-(HBr)\(_3\) was studied in the spectral range from 6 to 16 \(\mu\)m with macropulse energies of 50 mJ and 25 mJ (50% attenuation). At the lower laser power (Fig. 3) the dominant fragmentation products are Br\(^{-}\)-(HBr)\(_2\)+HBr. Loss of two HBr units leading to the formation of BrHBr\(^{-}\) is also observed, but with considerably less efficiency (<1% at 888 cm\(^{-1}\)). The photofragment yield spectrum for Br\(^{-}\)-(HBr)\(_2\) production (solid dots) shows two absorption bands at 888 and 979 cm\(^{-1}\). At 888 cm\(^{-1}\) more than 80% of the parent ion signal is depleted (inset of Fig. 3). The width of the intense absorption band is >30 cm\(^{-1}\) and may be broadened in part from saturation effects. A constant background of Br\(^{-}\)-(HBr)\(_2\) formed by He atom collision induced dissociation in the ion trap is also observed and amounts to <10% of the fragment ion intensity at the maximum of the main absorption band.

IRPD spectra of Br\(^{-}\)-(HBr)\(_3\) taken at a FELIX power of 50 mJ/macropulse are shown in Fig. 4. The parent depletion spectrum differs considerably from the spectrum measured at lower laser power, exhibiting an additional, pronounced minimum at 979 cm\(^{-1}\). Complete saturation of the 884 cm\(^{-1}\) transition is effected, with no residual parent ions observed. The single HBr loss spectrum (not shown) looks similar to the one measured at lower laser power (see Fig. 3), but saturation effects significantly broaden the absorption peaks. However, the intensity of the BrHBr\(^{-}\)+2HBr channel (solid dots, Fig. 4) increases significantly at higher power and looks quite different from the single HBr loss channel in Fig. 3. In particular, the BrHBr\(^{-}\) channel is much more intense at 984 cm\(^{-1}\) than at 884 cm\(^{-1}\), totally opposite to the intensity distribution in Fig. 3. In addition, a series of much smaller peaks at higher frequency are observed that do not appear in Fig. 3 nor in the parent depletion spectrum in Fig. 4.

The differences between Figs. 3 and 4 arise from two effects. The peak at 984 cm\(^{-1}\) nearly coincides with the peak at 992 cm\(^{-1}\) in the IRPD spectrum of Br\(^{-}\)-(HBr)\(_2\) in Fig. 2. We therefore attribute the 984 cm\(^{-1}\) peak in Fig. 4 to a sequential process producing BrHBr\(^{-}\),

\[
\text{Br}^{-}(\text{HBr})_{3} \xrightarrow{n \cdot h\nu} \text{Br}^{-}(\text{HBr})_{2} \xrightarrow{n' \cdot h\nu} \text{BrHBr}^{-},
\]

where \(h\nu\) is resonant with a vibrational fundamental in both the \(n=2\) and \(n=3\) clusters. The small peaks seen in the 1000–1500 cm\(^{-1}\) region of the spectrum in Fig. 4 appear at the same locations as peaks in the Br\(^{-}\)-(HBr)\(_2\) IRPD spectrum (Fig. 2 and also shown in the gray shaded area of Fig. 4) discussed in the previous section, and these are attributed exclusively to the IRPD of Br\(^{-}\)-(HBr)\(_2\) produced by collisional fragmentation of Br\(^{-}\)-(HBr)\(_3\) in the ion trap. The intensity of the gray shaded peaks is consistent with the magnitude of Br\(^{-}\)-(HBr)\(_2\) fragments observed in the trap in the absence of FELIX excitation, and the absorption cross section of Br\(^{-}\)-(HBr)\(_2\).

D. Electronic structure calculations

A sophisticated theoretical treatment of BrHBr\(^{-}\) has been reported recently, in which vibrational energy levels on a multidimensional potential energy surface were
determined. However, no calculations of any sort have been done for the larger clusters. Therefore, optimized geometries and vibrational frequencies were calculated for the \( \text{Br}^-\cdot(\text{HBr})_2 \) clusters at the B3LYP (Ref. 31) level of theory, employing the Dunning correlation consistent split valence triple zeta basis set with diffuse functions (aug-cc-pVTZ) (Refs. 32–34) as packed in GAUSSIAN 98.35 Calculated harmonic vibrational frequencies, IR intensities, and approximate mode descriptions for both clusters are listed in Tables II and III. The minimum energy structures found are shown in Fig. 5. \( \text{Br}^-\cdot(\text{HBr})_2 \) exhibits a \( C_{2v} \) minimum energy structure with two HBr ligands complexed to a central \( \text{Br}^- \). Addition of a third HBr ligand yields a \( C_{3v} \) minimum energy structure for \( \text{Br}^-\cdot(\text{HBr})_3 \).

The inner HBr bond lengths for the \( n = 2 \) and 3 clusters were found to be 2.03 and 2.16 Å and the terminal HBr bond lengths were calculated to be 1.53 and 1.49 Å. The terminal HBr bond lengths in the \( n = 2 \) and 3 clusters are nearer the unperturbed HBr bond length of 1.4144 Å (Ref. 36) than the previously calculated16 HBr bond lengths of 1.73 Å in \( \text{BrHBr}^- \). The Br–Br distances increase by ~0.1 Å per additional HBr ligand. The calculations predict that the addition of even a single HBr to BrHBr– destroys the symmetrical hydrogen bond in the bihalide; the two larger cluster ions are better represented as HBr ligands complexed to a central bromide ion. The effect of solvation on binary hydrogen bonds in negatively charged species was recently probed by Robertson et al. in an IR study of \( \text{Cl}^-\cdot(\text{H}_2\text{O})(\text{CCl}_4)_n \) clusters, where addition of a single \( \text{CCl}_4^- \) molecule was shown to perturb the Cl–H–O bond length.37

These trends are reflected in the calculated frequencies and intensities in Tables II and III, according to which the IR spectroscopy of the \( n = 2 \) and \( n = 3 \) clusters should be dominated by two modes representing symmetric and antisymmetric linear combinations of HBr stretches. The calculated frequencies for these modes lie between the \( \text{BrHBr}^- \) antisymmetric stretch, 753 cm\(^{-1} \), and the HBr fundamental at 2559 cm\(^{-1} \), indicating significant and increasing perturbation of the hydrogen bond in \( \text{BrHBr}^- \) by the additional HBr molecules.

The zero point corrected binding energies of a single HBr ligand to \( \text{Br}^-\cdot(\text{HBr})_2 \) and \( \text{Br}^-\cdot(\text{HBr})_3 \) were calculated to be 2963 and 3918 cm\(^{-1} \). The HBr binding energy of \( \text{BrHBr}^- \) calculated by the same method was 7582 cm\(^{-1} \), which agrees reasonably well with the experimental binding energy of 7480 cm\(^{-1} \) reported by Caldwell et al.4

The \( C_{2v} \) structure calculated for \( \text{Br}^-\cdot(\text{HBr})_2 \) is consistent with past experimental and theoretical work on \( \text{Cl}^-\cdot(\text{HCl})_2 \) and \( F^-\cdot(\text{HF})_2 \) which showed similar structures for these clusters.38–44 Likewise, the \( C_{3v} \) structure calculated for \( \text{Br}^-\cdot(\text{HBr})_3 \) confirms the trend observed in previously calculated structures for \( F^-\cdot(\text{HF})_2 \) and \( \text{Cl}^-\cdot(\text{HCl})_2 \) which predicted a geometry change from \( D_{3h} \) to \( C_{3v} \) in the transition from fluorine to chlorine.38,39,42

### IV. DISCUSSION

The observed absorption band of \( \text{BrHBr}^- \) at 1558 cm\(^{-1} \) is assigned to the overtone of the \( \nu_3 \) absorption band previ-
ously observed at 728 and 753 cm\(^{-1}\) in matrix IR studies\(^8,12\). The high negative anharmonicity implied by this assignment is consistent with the calculations by Del Bene and Jordan\(^,16\) who find a substantial negative anharmonicity for the \(v_3\) mode in FHF\(^-\), CHCl\(^+\), and BrHBr\(^-\).

For Br\(^-\)·(HBr)\(_2\), using the calculated results in Table II as a guide, the experimental peaks at 1359 and 1420 cm\(^{-1}\) are closest in frequency to the calculated harmonic frequencies of 1453 and 1662 cm\(^{-1}\) for the \(b_2\) and \(\alpha_1\) antisymmetric and symmetric HBr stretches, and the experimental and calculated relative intensities of the two peaks agree reasonably well. The calculated frequencies for the corresponding modes in Br\(^-\)·(HBr)\(_2\) are higher and would be out of range of the instrument due to the ZnSe windows. One would then assign the peaks around 1000 cm\(^{-1}\) for the two clusters to combination bands of the various bending modes for which the calculated fundamentals lie between 500–600 cm\(^{-1}\). However, this assignment is problematic because the calculated harmonic intensity for the bend fundamentals are several orders of magnitude lower than for the HBr stretches, and the experimental and calculated relative intensities of the two peaks agree reasonably well. The calculated frequencies for the corresponding modes in Br\(^-\)·(HBr)\(_2\) are higher and would be out of range of the instrument due to the ZnSe windows. One would then assign the peaks around 1000 cm\(^{-1}\) for the two clusters to combination bands of the various bending modes for which the calculated fundamentals lie between 500–600 cm\(^{-1}\). However, this assignment is problematic because the calculated harmonic intensity for the bend fundamentals are several orders of magnitude lower than for the HBr stretches, and the experimental and calculated relative intensities of the two peaks agree reasonably well. The calculated frequencies for the corresponding modes in Br\(^-\)·(HBr)\(_2\) are higher and would be out of range of the instrument due to the ZnSe windows. One would then assign the peaks around 1000 cm\(^{-1}\) for the two clusters to combination bands of the various bending modes for which the calculated fundamentals lie between 500–600 cm\(^{-1}\). However, this assignment is problematic because the calculated harmonic intensity for the bend fundamentals are several orders of magnitude lower than for the HBr stretches, and the experimental and calculated relative intensities of the two peaks agree reasonably well. The calculated frequencies for the corresponding modes in Br\(^-\)·(HBr)\(_2\) are higher and would be out of range of the instrument due to the ZnSe windows. One would then assign the peaks around 1000 cm\(^{-1}\) for the two clusters to combination bands of the various bending modes for which the calculated fundamentals lie between 500–600 cm\(^{-1}\). However, this assignment is problematic because the calculated harmonic intensity for the bend fundamentals are several orders of magnitude lower than for the HBr stretches, and the experimental and calculated relative intensities of the two peaks agree reasonably well. The calculated frequencies for the corresponding modes in Br\(^-\)·(HBr)\(_2\) are higher and would be out of range of the instrument due to the ZnSe windows.

These considerations lead one to question the reliability of the calculated harmonic frequencies for the asymmetric hydrogen bonds in these clusters. Indeed, in a theoretical study BrHI\(^-\), a prototypical asymmetric bihalide, by Morokuma and co-workers\(^,45\) the harmonic frequency of the \(v_3\) mode obtained was found to be 1779 cm\(^{-1}\), substantially higher than the 1267 cm\(^{-1}\) frequency obtained by constructing a full three-dimensional surface for BrHII\(^-\) and calculating the eigenvalues, and higher still than either of the two reported matrix IR spectroscopy values, 666 and 920 cm\(^{-1}\). Additionally, the harmonic antisymmetric H-atom stretch of the asymmetric F\(^-\)·(HF)\(_2\) complex was calculated at 2364 cm\(^{-1}\)\(^,40\) while experimental work placed the frequency at 1815 cm\(^{-1}\).\(^,44\) As an alternate assignment, the bands at 992 and 1048 cm\(^{-1}\) for Br\(^-\)·(HBr)\(_2\) and 888 and 979 cm\(^{-1}\) for Br\(^-\)·(HBr)\(_3\) could be the fundamentals of the two H-atom stretch vibrations. The higher frequency peaks in the Br\(^-\)·(HBr)\(_2\) spectrum then result from combination bands; comparison with Table II suggests the likeliest candidates are the \(b_2\) H-atom wag and antisymmetric Br–Br stretch modes, with calculated frequencies of 568 and 98 cm\(^{-1}\), respectively, and small but nonzero IR intensities. While neither set of assignments is wholly satisfactory, both place the antisymmetric HBr stretch at a considerably higher frequency than the \(v_3\) fundamental in BrHBr\(^-\), providing experimental evidence for destruction of the symmetric hydrogen bond and localization of the H atom in the larger clusters.

Comparison of the three ions studied here suggests that BrHBr\(^-\) lies in a different regime with respect to multiphoton absorption and dissociation than the two larger clusters. In the generally accepted picture of multiphoton absorption and dissociation within the low field approximation (the maximum photon flux at the interaction region is on the order of 10\(^{11}\) W/cm\(^2\))\(^,46,47\) absorption of the first few photons occurs within the “discrete” regime, in which the photons resonantly excite a particular vibrational mode of a molecule.

Higher excitation accesses the “quasicontinuum” regime in which the density of states is so high that the vibrational energy is rapidly randomized among all vibrational modes of the molecule; the transition between the two regimes depends on the vibrational density of states and the strengths of the interactions between vibrational modes. The molecule continues to absorb photons until the dissociation rate exceeds the up-pumping rate.

In BrHBr\(^-\), the \(v_3\) mode exhibits significant negative anharmonicity; the fundamental frequency is 730–750 cm\(^{-1}\), but the first overtone is centered at 1558 cm\(^{-1}\). Hence, the absence of the fundamental and low dissociation yield for BrHBr\(^-\) for the overtone indicates that the discrete regime acts as an anharmonic bottleneck, with one-color excitation unable to resonantly excite both the 1–0 and 2–1 transitions. On the other hand, observation of the overtone transition suggests the density of states near 3000 cm\(^{-1}\) is sufficiently high for absorption of the second (and subsequent) photon to occur under the conditions of our experiment. In addition, ~10 collisions with the He buffer gas occur during the 5 μs duration of each macropulse, resulting in additional state mixing that can facilitate multiphoton absorption.

In the Br\(^-\)·(HBr)\(_{2,3}\) clusters, the additional HBr ligands raises the vibrational density of states relative to BrHBr\(^-\), and based on the calculations in Sec. III, the dissociation energies are lower. The breakdown of the harmonic approximation for the description of the H-atom stretch modes also hints at a considerable coupling of the vibrational modes. All three effects favor multiphoton absorption and dissociation, consistent with the much higher signals seen for the two larger clusters. Hence, these clusters behave more like the cation clusters previously studied with FELIX\(^,28,48\).

The results presented here show that IRPD studies with FELIX can access the vibrational spectroscopy of anions spanning a wide size range, and in particular can be applied to anions with as few as three atoms. It is therefore an ideal method for observing the size-dependence of the vibrational spectroscopy of anion clusters over an extended frequency range that has previously been inaccessible. In the case of the hydrogen bonded clusters studied here, the inclusion of anharmonic effects is a prerequisite for an adequate theoretical description of the IR spectra of these species.

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