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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(Received 24 May 2002; accepted 22 July 2002)

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 \(v_3\). 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, \(D_{\infty h}\) species with two equal H–X bond lengths.\(^5\) 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.19–23 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 \(10^3 - 10^4 \text{cm}^{-3}\). 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 FHF\(^-\) and ClHCl\(^-\) yields \(v_3\) frequencies of 1331 and 723 cm\(^{-1}\), respectively,\(^{10,11}\) while matrix isolation spectroscopy of BrHBr\(^-\) yields \(v_3\) frequencies ranging from 728 to 753 cm\(^{-1}\).\(^{6,12}\) 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.\(^{24–27}\) Multiphoton excitation IRPD spectra of selected polycyclic aromatic hydrocarbons were measured using excimer laser ionization followed with multiphoton excitation with a pulsed electron laser (FEL) in the 400–1700 cm\(^{-1}\) region. Asmis \textit{et al.}\(^{28}\) 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\(^-\).\(^{18}\) 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,\(^{28}\) 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 \(\approx\)50 K and He buffer gas pressure of \(\approx\)80 \(\mu\)bar.

Infrared excitation is performed with the output of FELIX.\(^{29}\) The FELIX output is composed of 5 \(\mu\)s long macropulses at 5 Hz, with each macropulse containing a series of \(\approx\)1 ps micropulses separated by a nanosecond. The FELIX bandwidth is transform limited to \(\approx 0.8\%\) of the central frequency and pulse energies of 50 and 25 mJ per macropulse (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:

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

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 macropulses 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 I. Experimental infrared band positions and intensities.

<table>
<thead>
<tr>
<th>Parent ion</th>
<th>Fragment ion</th>
<th>Position (cm(^{-1})) and normalized intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrHBr(^-)</td>
<td>Br(^-)</td>
<td>1558</td>
</tr>
<tr>
<td>Br(^-)•(HBr)(_2)</td>
<td>BrHBr(^-)</td>
<td>(-875 (0.05, -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))</td>
</tr>
<tr>
<td>Br(^-)•(HBr)(_3)</td>
<td>Br(^-)•(HBr)(_2), BrHBr(^-)</td>
<td>888 (1.00), 979 (0.16)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>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)</td>
</tr>
</tbody>
</table>
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 $v_3$ antisymmetric stretch fundamental is expected. 7,8,12,15,16,30 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 $\sim3$ 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 $\sim70$ 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-
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.

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$^-$.

\[
\text{Br}^-(\text{HBr})_3 + h\nu \rightarrow \text{Br}^-(\text{HBr})_2 + \text{HBr}^-, \quad (2)
\]

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
TABLE II. Normal modes, harmonic vibrational frequencies, and oscillator strengths for the $C_{3v}$ ground state of Br$^-$·(HBr)$_3$ calculated at the B3LYP/aug-cc-pVTZ level of theory.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Intensity (km/mol)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>1662</td>
<td>1776</td>
<td>symmetric H-atom stretch</td>
</tr>
<tr>
<td>$b_2$</td>
<td>1453</td>
<td>7285</td>
<td>antisymmetric H-atom stretch</td>
</tr>
<tr>
<td>$a_1$</td>
<td>632</td>
<td>&lt;1</td>
<td>in-plane synchronous H-atom wag</td>
</tr>
<tr>
<td>$a_2$</td>
<td>585</td>
<td>0</td>
<td>out-of-plane asynchronous H-atom wag</td>
</tr>
<tr>
<td>$b_2$</td>
<td>568</td>
<td>33</td>
<td>in-plane asynchronous H-atom wag</td>
</tr>
<tr>
<td>$b_1$</td>
<td>567</td>
<td>2</td>
<td>out-of-plane synchronous H-atom wag</td>
</tr>
<tr>
<td>$a_1$</td>
<td>106</td>
<td>13</td>
<td>symmetric Br–Br stretch</td>
</tr>
<tr>
<td>$b_2$</td>
<td>98</td>
<td>123</td>
<td>antisymmetric Br–Br stretch</td>
</tr>
<tr>
<td>$a_1$</td>
<td>11</td>
<td>&lt;1</td>
<td>Br–Br bond stretch</td>
</tr>
</tbody>
</table>

TABLE III. Normal modes, harmonic vibrational frequencies, and oscillator strengths for the $C_{3v}$ ground state of Br$^-$·(HBr)$_2$ calculated at the B3LYP/aug-cc-pVTZ level of theory.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Intensity (km/mol)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>1981</td>
<td>480</td>
<td>symmetric H-atom stretch</td>
</tr>
<tr>
<td>$e$</td>
<td>1807</td>
<td>4669</td>
<td>antisymmetric H-atom stretch</td>
</tr>
<tr>
<td>$e$</td>
<td>559</td>
<td>&lt;1</td>
<td>H atom wag</td>
</tr>
<tr>
<td>$a_1$</td>
<td>527</td>
<td>2</td>
<td>H atom wag</td>
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<tr>
<td>$a_2$</td>
<td>514</td>
<td>0</td>
<td>H atom wag</td>
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<tr>
<td>$e$</td>
<td>512</td>
<td>1</td>
<td>H atom wag</td>
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<tr>
<td>$e$</td>
<td>101</td>
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<td>2</td>
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<td>HBr wag</td>
</tr>
<tr>
<td>$a_1$</td>
<td>11</td>
<td>&lt;1</td>
<td>intramolecular umbrella</td>
</tr>
</tbody>
</table>

FIG. 5. Structures of Br$^-$·(HBr)$_3$ (above) and Br$^-$·(HBr)$_2$ (below) calculated at the B3LYP/aug-cc-pVTZ level of theory. Upper panel shows bond lengths and angles for the $C_{3v}$ Br$^-$·(HBr)$_3$ complex. Lower panel shows top and side views of the $C_{3v}$ Br$^-$·(HBr)$_2$ complex. H–Br–H and Br–Br–Br bond angles are indicated in the top view, along with inner and outer H–Br bond lengths (Å). Side view shows slight deviation from linearity in the Br–H–Br bond, and also illustrates the 120° dihedral of the third HBr ligand.

![Image](https://via.placeholder.com/150)

**IV. DISCUSSION**

The observed absorption band of 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.\textsuperscript{8,12} The high negative anharmonicity implied by this assignment is consistent with the calculations by Del Bene and Jordan,\textsuperscript{16} who find a substantial negative anharmonicity for the $\nu_3$ 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 $a_1$ 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)$_3$ 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 IR intensities for the bend fundamentals are several orders of magnitude lower than for the HBr stretches, whereas in the experimental spectrum for Br$^-$·(HBr)$_2$, the peaks around 1000 cm$^{-1}$ are more intense than the 1359/1416 cm$^{-1}$ doublet.

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 BrH$^-$, a prototypical asymmetric bihalide, by Morokuma and co-workers,\textsuperscript{45} the harmonic frequency of the $\nu_3$ 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 BrH$^-$ and calculating the eigenvalues, and higher still than either of the two reported matrix IR spectroscopy values, 666 and 920 cm$^{-1}$.\textsuperscript{46} Additionally, the harmonic antisymmetric H-atom stretch of the asymmetric F$^-$·(HF)$_2$ complex was calculated at 2364 cm$^{-1}$,\textsuperscript{40} while experimental work placed the frequency at 1815 cm$^{-1}$.\textsuperscript{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 $\nu_3$ 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$^2$),\textsuperscript{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 $\nu_3$ 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 $\mu$s 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.\textsuperscript{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.

ACKNOWLEDGMENTS

This work is funded by the Sonderforschungsbereich 546 and the Ph.D. Graduate Study Program 788 of the Deutsche Forschungsgemeinschaft. United States Air Force Office of Scientific Research Grant No. F49620-00-1-0018 provided support for N.L.P. The authors gratefully acknowledge the support of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) in providing the required beam time on FELIX and highly appreciate the skillful assistance of the FELIX staff, in particular Dr. A. F. G. van der Meer. This work was supported in part under the “Access to research infrastructure action of the Improving Human Potential Program” of the European Community. The authors would like to thank Professor Dr. W. J. Buma of the University of Amsterdam for the loan of HBr gas.


