

COMMUNICATIONS

**Probing a strong hydrogen bond with infrared spectroscopy:
Vibrational predissociation of $\text{BrHBr}^- \cdot \text{Ar}$**

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The gas phase vibrational spectroscopy of BrHBr^- , a prototypical strongly hydrogen-bonded species, has been studied between 6 and 17 μm (590 and 1670 cm^{-1}) by infrared vibrational predissociation of the $\text{BrHBr}^- \cdot \text{Ar}$ ion. Infrared excitation was accomplished using the output of the free electron laser for infrared experiments (FELIX). Predissociation spectra were recorded by monitoring depletion of mass-selected $\text{BrHBr}^- \cdot \text{Ar}$ ions as a function of excitation wavelength. Four prominent absorption bands are observed at 733, 890, 1048, and 1201 cm^{-1} . They are assigned to the fundamental of the hydrogenic stretching mode ν_3 and a sequence of $\nu_3 + n\nu_1$ combinations ($n=1-3$). Additional features to the blue of these bands spaced by $\sim 21 \text{ cm}^{-1}$ are attributed to combination bands involving motion of the Ar messenger atom. Differences in the relative intensities of the $\nu_3 + n\nu_1$ combinations bands in comparison to previous matrix experiments are rationalized on the basis of the underlying dissociation dynamics. © 2003 American Institute of Physics. [DOI: 10.1063/1.1559478]

Hydrogen bonding governs a number of diverse and important chemical interactions, ranging from the solvent properties of water and other liquids to the structure of proteins and nucleic acids.¹ An important classification used in this context is based on the strength of the hydrogen bond, which is reflected in the distance between the heteroatoms sharing the hydrogen atom. As the bond strength increases, the distance between the heteroatoms as well as the hydrogen exchange barrier decreases. In the limit of strong or low-barrier hydrogen bonds, the barrier to hydrogen exchange has dropped below the zero point vibration, and the hydrogen assumes a symmetric position between the heteroatoms. These types of hydrogen bonds play an important role in both enzyme catalysis^{2,3} and proton exchange phenomena in acidic and basic aqueous solutions (e.g., H_3O_2^- and H_5O_2^+).^{4,5}

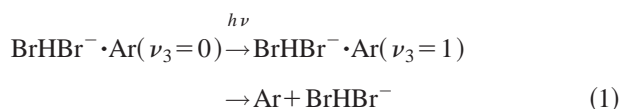
The simplest strongly hydrogen-bonded species are the triatomic bihalide anions XHX^- and XHY^- . The vibrational spectroscopy of these anions has been studied extensively in cryogenic matrices.⁶ This work showed that the hydrogenic stretching frequencies were extremely low, ranging from 1330 cm^{-1} in FHF^- to 645 cm^{-1} in IHI^- , in contrast to the uncomplexed HX frequencies of 4138 cm^{-1} in HF and 2309 cm^{-1} in HI .^{7,8} This frequency shift is a direct consequence of extensive sharing of the central hydrogen between the two halogen atoms. However, these studies indicated that the effects of the matrix on the vibrational frequencies could be significant, providing strong motivation to measure the unperturbed gas phase infrared (IR) spectra of these bihalide anions. High resolution gas phase IR spectra over narrow frequency ranges have been measured for FHF^- and ClHCl^- using diode laser absorption.⁹⁻¹² In this paper, we report a

different and more general approach to gas phase ion vibrational spectroscopy, combining excitation by means of a tunable infrared free electron laser [free electron laser for infrared experiments (FELIX)] with vibrational predissociation spectroscopy.^{13–15} The result is the first broadband infrared spectrum (from 590–1670 cm^{-1}) of a gas phase bihalide anion, BrHBr^- , measured by vibrational predissociation of $\text{BrHBr}^- \cdot \text{Ar}$.

The bihalide anion BrHBr^- is believed to be symmetric ($D_{\infty h}$),⁶ and its high dissociation energy of 0.93 eV makes it a model strong hydrogen bonding system.¹⁶ Inorganic salt and solution phase experiments yielded the first IR absorptions attributed to the BrHBr^- complex in the region between 500 and 1300 cm^{-1} .¹⁷ Further IR absorption experiments performed by several groups in rare gas matrices assigned asymmetric stretch absorptions between 646 and 753 cm^{-1} .^{18–21} These experiments also yielded $\nu_3 + n\nu_1$ combination bands, with $(\nu_3 + \nu_1) - \nu_3$ values near 160 cm^{-1} .

Evaluation of the BrHBr^- infrared spectrum through electronic structure calculations is complicated by the strong coupling between the vibrational modes. Del Bene and Jordan²² have shown that vibrational frequencies determined by one-dimensional harmonic analysis are inadequate, regardless of the level of theory used in the calculation, and that it is instead necessary to construct a two-dimensional potential energy surface upon which energy levels involving symmetric and asymmetric stretch excitation can be computed accurately. Their calculated frequencies agree well with the earliest sets of Ar matrix results.^{18–20}

For many years, the photoelectron spectrum of BrHBr^- has represented the only gas phase data on this anion.^{23,24} However, as part of a recent study of larger clusters, we performed tunable infrared multiphoton dissociation (IRMPD) experiments on BrHBr^- using a free electron laser and observed a single broad peak near 1550 cm^{-1} ; this feature was tentatively assigned to the overtone of the ν_3 vibrational mode.²⁵ The IRMPD approach, which relies on a high density of states to overcome the anharmonic bottleneck in the multiphoton dissociation process, was less than ideal for bare BrHBr^- with its relatively high HBr binding energy (7480 cm^{-1}) and low number of vibrational degrees of freedom.¹⁶ Drawing on previous cation and anion spectroscopy experiments by Lee¹³ and Johnson,^{14,15} we present results here on the vibrational predissociation of $\text{BrHBr}^- \cdot \text{Ar}$. The Ar atom acts as a “messenger” or “spy” atom, and its expected low binding energy allows detection of the absorption of a *single* IR photon via vibrational predissociation:



By monitoring depletion of the $\text{BrHBr}^- \cdot \text{Ar}$ complex or production of BrHBr^- as a function of excitation energy, the vibrational spectrum of BrHBr^- can be obtained.

The present experiments were carried out on a previously described tandem mass spectrometer ion trap system.²⁶ Briefly, $\text{BrHBr}^- \cdot \text{Ar}$ cluster anions are created by crossing a

pulsed supersonic expansion of $\sim 0.1\%$ HBr in Ar with a 300 μA , 1 keV electron beam. The supersonic expansion is generated by a pulsed valve operating at 100 Hz with a backing pressure of 5 bar. The anions pass through a 2 mm skimmer, are collimated by a linear radio frequency (RF) ion guide, then mass-selected by a quadrupole mass spectrometer. Subsequently the mass-selected ions are collected in a He filled linear RF hexadecapole ion trap which is connected to a helium cryostat and kept at a temperature of < 70 K. Collisions with the He buffer gas (~ 0.03 mbar) slow the ions and cool them to the ambient temperature. Roughly 80% of the (“fast”) $\text{BrHBr}^- \cdot \text{Ar}$ ions entering the ion trap fragment through collisions with the He atoms, forming BrHBr^- . Because of this wavelength independent BrHBr^- background signal, a better signal-to-noise ratio is achieved by monitoring $\text{BrHBr}^- \cdot \text{Ar}$ depletion rather than the BrHBr^- formation.

The ion trap is continuously filled for 160 ms. Trapped ions interact with a single macropulse of the 5 Hz output of FELIX, composed of 5 μs long macropulses, with each macropulse comprising a series of ~ 1 ps micropulses separated by a nanosecond.²⁷ Pulse energies used in these experiments were on the order of 15 mJ/macropulse, with a Gaussian bandwidth of $\sim 0.8\%$ of the central energy (FWHM). The output of FELIX was introduced into the ion trap region through a KBr lens (focal length 478 mm) and a 5 mm thick KBr window. Focusing of the FELIX beam is required to avoid light scattering off the ion trap exit and entrance lenses. One millisecond after irradiation, the ion trap is emptied, and the $\text{BrHBr}^- \cdot \text{Ar}$ signal is mass-selectively monitored using a (second) quadrupole mass spectrometer. The ion trap is then refilled again and the cycle repeated multiple times at each wavelength step in order to assure sufficient signal averaging.

Infrared predissociation spectra of $^{81}\text{BrH}^{81}\text{Br}^- \cdot \text{Ar}$ are shown in Fig. 1. Observed peak positions and assignments are listed in Table 1. Overview scans (main spectrum) were measured from 6 to 17 μm with a step size of 0.1 μm . Higher resolution spectra (step size: 0.01–0.02 μm) were measured with an increased number of shots per data point in selected regions and are shown in the inset. Four prominent depletion features are readily identifiable at 733, 890, 1048 and 1201 cm^{-1} . Gaussian peak widths (FWHM) were found to be 15, 13, 11, and 10 cm^{-1} and are chiefly limited by the bandwidth of FELIX. An assignment of these features based on the previous matrix experiments is straightforward (see Tables 1 and 2). The peak at 733 cm^{-1} is assigned to the fundamental of the $\text{BrHBr}^- \nu_3$ mode and the sequence observed at shorter wavelengths to $\nu_3 + n\nu_1$ ($n = 1–3$) combinations bands involving the symmetric stretch vibration. Weaker features are observed in the (smoothed) higher resolution spectra at 754, 775, 911, 929 and 1070 cm^{-1} , which we attribute to combination bands involving excitation of the Ar motion with a characteristic fundamental frequency of 21 cm^{-1} . There is also suggestion of a weak depletion feature near 650 cm^{-1} , in the anticipated region of the ν_2 fundamental, but further study will be necessary to confirm this observation.

In the overview spectra, depletion of the parent ion signal is as high as $\sim 75\%$, with baseline fluctuations on the

TABLE I. Observed depletion features, bandwidths and assignments.

Frequency (cm ⁻¹)	Width (cm ⁻¹)	Assignment
733	15	1 ν_3
754		1 $\nu_3 + 1 \nu_{Ar}$
775		1 $\nu_3 + 2 \nu_{Ar}$
890	13	1 $\nu_3 + 1 \nu_1$
911		1 $\nu_3 + 1 \nu_1 + 1 \nu_{Ar}$
929		1 $\nu_3 + 1 \nu_1 + 2 \nu_{Ar}$
1048	11	1 $\nu_3 + 2 \nu_1$
1070		1 $\nu_3 + 2 \nu_1 + 1 \nu_{Ar}$
1202	10	1 $\nu_3 + 3 \nu_1$

order of 5%–10%. The fluctuations are mainly a result of variations in source conditions. No Br⁻ ions were observed over the entire scan region, indicating (a) no collisionally induced rupture of the hydrogen bond and (b) no IRMPD processes resulting in BrHBr⁻ breakdown. No features are found at the location of the previously assigned overtone near 1550 cm⁻¹, calling that assignment into question.²⁵

A comparison of the experimental peak energies and those calculated by Del Bene and Jordan²² for the $\nu_3 + n\nu_1$ series ($n=0-3$) is shown in Table 2. The calculated and experimental ν_3 fundamentals (731 and 733 cm⁻¹) are in excellent agreement. The absolute deviations across the series are small (≤ 10 cm⁻¹), so the assignment of the experimental peaks to this series is straightforward. The experimental peak spacings between adjacent peaks are 157, 158 and 154 cm⁻¹ for $n=0-1$, 1-2, and 2-3, i.e., decreasing slightly with increasing n . These spacings are 4–6 cm⁻¹ less than the corresponding spacings between the calculated peak positions in Table 2. One of the more striking features of the calculation by Del Bene and Jordan was that the spacing between the peaks of the $\nu_3 + n\nu_1$ series was 20–30 cm⁻¹ less than the calculated energy of the ν_1 fundamental, 189 cm⁻¹, indicating that antisymmetric stretch excitation reduces the symmetric stretch frequency, and the overall agreement between experiment and theory in Table 2 supports this conclusion. The very presence of the $\nu_3 + n\nu_1$ sequence further demonstrates the breakdown of the harmonic approximation in the presence of a strong hydrogen bond such as this one, and emphasizes the need for explicit consideration of intermode coupling when calculating the properties of strongly hydrogen bonded systems.^{28,29}

TABLE II. Comparison of experimental and calculated vibrational frequencies for the BrHBr-complex ion.

Assignment	Gas phase	Matrix Ne ^a	Matrix Ar ^b	Matrix Kr ^c	Matrix Xe ^c	Calculated ^d
ν_3	733	741	728	687	646	731
$(\nu_3 + 1\nu_1) - \nu_3$	+157	+163	+164	+158	+152	+162
$(\nu_3 + 2\nu_1) - \nu_3$	+315		+325	+313	+300	+323
$(\nu_3 + 3\nu_1) - \nu_3$	+469			+466	+446	+481

^aReference 16.

^bReference 17.

^cReference 18.

^dReference 19.

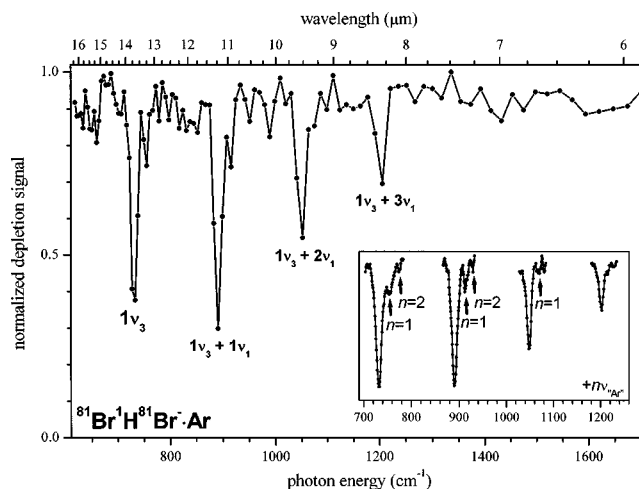


FIG. 1. Infrared predissociation overview spectrum of ⁸¹BrH⁸¹Br⁻·Ar measured by monitoring the depletion of the parent ion. Inset shows smoothed (3-point average) spectra measured with smaller step size (see text).

The depletion peak intensities in Fig. 1 differ significantly from the intensities previously observed in matrix IR absorption experiments, in which the absorption decreased by a factor of two from ν_3 to $\nu_3 + \nu_1$ and a factor of ten from ν_3 to $\nu_3 + 2\nu_1$.¹⁸⁻²¹ The depletion intensities observed in the present experiment cannot be directly compared to the absorption intensities reported in the previous matrix studies, since the depletion signal reflects not only the oscillator strengths of the IR transitions, but also (a) the variation in FELIX power and bandwidth over the scan range and (b) the cluster predissociation rate. FELIX characteristics were optimized such that power and bandwidth change as little as possible in the energy range of interest. It is more likely that the dissociation rate of the vibrationally excited clusters influences the intensity distribution, with a lower dissociation rate for less vibrationally excited anions resulting in a smaller than expected relative depletion signal.

In order for the dissociation rate to effect peak intensities, the dissociation lifetime must be at least a few microseconds, since this is the time scale for collisions between the trapped ions and the He buffer gas inside the trap. The ions are extracted 1 ms after the irradiation pulse, so it can be assumed that all photoexcited ions have either dissociated or been collisionally quenched before the extraction pulse is applied to the ion trap exit lens. It thus appears that the cluster predissociation rate increases with excitation of the symmetric stretch of the BrHBr⁻ chromophore. This could be a “total energy” effect, in which the total excess energy above the dissociation threshold (estimated³⁰⁻³² to be 300–400 cm⁻¹) determines the dissociation rate. Alternatively, the predissociation rate may be mode-specific, with ν_1 excitation promoting dissociation more efficiently than ν_3 excitation.

The combination of vibrational predissociation spectroscopy with FELIX excitation opens up a new frontier in the study of hydrogen bonded ions. The effect of solvation upon the hydrogen bond is of particular interest. Simulations based on pairwise sums of empirical potentials carried out by McCoy and co-workers predict a ν_3 shift of only -1 cm⁻¹ upon addition of an Ar atom to ClHCl⁻.³³ Vibrational predissocia-

tion experiments by Kelley *et al.*³⁴ on $\text{Cl}^- \cdot \text{H}_2\text{O} \cdot \text{Ar}_n$ found a sequential shift in the hydrogen bonded OH stretch of less than 3 cm^{-1} upon addition of 1–5 Ar atoms. Hence, the addition of a single Ar atom is expected to result in a negligible shift of the BrHBr^- frequency from its gas phase value. On the other hand, vibrational²⁵ and photoelectron³⁵ spectroscopy have shown that the addition of a single HBr to BrHBr^- profoundly alters the anionic hydrogen bond, resulting in a structure more akin to $\text{Br}^-(\text{HBr})_2$. The photoelectron spectrum of $\text{BrHBr}^-(\text{H}_2\text{O})$ suggests an intermediate degree of hydrogen bond perturbation by the water molecule.³⁵ This inference can be tested more directly through measurement of the IR spectrum of this species, an experiment planned for the very near future. The determination of vibrational frequencies in bihalide anions can also be exploited in transition state spectroscopy experiments in which the photoelectron spectrum of a vibrationally excited state is measured, because photodetachment of vibrationally excited anions will allow for Franck–Condon overlap with a larger region of the neutral $\text{X}+\text{HY}$ hydrogen exchange transition state region than can be accessed by photodetachment of ground state anions.^{36,37}

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