Double photoionization of tribromoborazine from 25 to 138 eV

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We have measured the yield for the photoproduction of singly and doubly charged parent ions of the inorganic molecule tribromoborazine [$(BrBNH)_3$], a molecule in which three bromine atoms replace three hydrogen atoms in borazine [$(BH)_3(NH)_3$]. Borazine is isoelectronic and isostructural to benzene. We compare the ratio of doubly to singly charged parent ions as a function of the photon energy to the ratio for benzene. We find similarities but also marked differences between the two molecules. The first double-ionization threshold was found to be at 28.5(4) eV.

I. INTRODUCTION

A convenient method to investigate electron correlations in gas-phase atoms and molecules is to measure the relative probability of the simultaneous removal of two electrons from the system by absorption of photons with sufficient energy [1]. Because a single photon interacts with only one electron, the emission of a second electron is due to electron correlation [2]. Many atomic and molecular systems have been investigated in the past, and the ratio of doubly to singly charged ions has been determined as a function of the photon energy. Recently this ratio has been measured for (deuterated) benzene and other aromatic molecules [3–7].

The key findings of those investigations on aromatic molecules were as follows. (a) At low energies the photoproduction of doubly charged parent ions is well modeled by the helium ratio curve. (b) Above a certain photon energy the ratio rises almost perfectly linearly with increasing photon energy due to an as yet unknown double-photoionization mechanism. (c) Some aromatic molecules such as benzene show a resonant enhancement of the ratio, possibly due to the formation of electron pairs that act like a single particle whose de Broglie wave has a wavelength that matches the carbon-carbon distance in the molecule, resulting in a standing wave in the molecular π orbital [3,4].

Borazine [$(BH)_3(NH)_3$] is isoelectronic and isostructural to benzene but is neither aromatic nor organic as benzene is. The substitution of two carbon atoms with a boron-nitrogen compound has for a long time attracted interest in a study of BNC heterocycles [8]. The consequences of substituting carbon atoms with a combination of boron and nitrogen atoms have been investigated for acenes [9–11] and also for graphene-related BN sheets of atoms [12].

The question that we address in this paper is how the differences between these two molecules, borazine and benzene, affect electron correlation and, in particular, the ratio of doubly to singly charged parent ions.

Borazine is commercially available but it is much more expensive than the related molecule tribromoborazine [$(BrBNH)_3$], in which the three hydrogen atoms attached to the boron atoms are replaced with bromine atoms (see Fig. 1).

II. EXPERIMENT

We have measured the ratios of doubly to singly charged molecular parent ions of tribromoborazine [$(BrBNH)_3$; Fisher Scientific; 96% purity], over a wide range of incident photon energies. The photons came from the VLS-PGM (variable-linespacing plane grating monochromator) beamline [13] at the Canadian Light Source, which consists of a plane polarized undulator and monochromator with three gratings to cover the energy range.

The powder sample was frozen-pumped-thawed two times to remove gases from the vial holding the sample. The base pressure of the sample chamber was in the 10^{-9} mb range. The vial and gas line were heated to about $37\,°C$, resulting in a sample gas pressure in the chamber of about 7.0×10^{-7} mb during the experiment. This temperature is too low for tribromoborazine to decompose due to heat, which starts to happen at $70\,°C$ [14].

An ion time-of-flight (TOF) spectrometer was employed to separate photoions of different mass-to-charge ratios. The TOF spectrometer is a Wiley-McLaren-type [15] spectrometer with static electric fields, which uses the electron signal as the start and the ion signal(s) as the stop for the TOF analysis [16]. The timing is performed with a CAEN V1290N 16CH 25-ps multihit time-to-digital converter. The electron acceleration voltages are such that we do not expect any geometrical loss of collection efficiency until an electron energy of about 200 eV. We checked that the microchannel plate voltage for ion detection was sufficiently high so that there was no discrimination between singly and doubly charged ions.

The photon beam entered the chamber horizontally, which was assumed to be 100% linearly polarized, with the plane of polarization also horizontal. The electric fields were such that ions were accelerated vertically upwards and electrons were accelerated vertically downwards. One consequence of using static electric fields (as opposed to pulsed extraction)

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FIG. 1. In the ball-and-stick model of tribromoborazine the largest balls (dark red) represent bromine atoms and are bonded to the second largest balls (light red), which represent boron atoms. The smallest balls represent hydrogen atoms (gray) and are bonded to the second smallest balls (blue), which represent nitrogen atoms.

is that metastable ions with a lifetime longer than the flight time will be detected before fragmentation. The pulsed TOF spectrometer in Refs. [3–7] strongly discriminates against ions or fragments with appreciable kinetic energy.

The photon energy was calibrated using the Ar $3s \rightarrow 10p$ resonance, and photon energies of the low-energy spectra were corrected accordingly.

III. DATA ANALYSIS

In order to analyze the double-photoionization process for tribromoborazine we first convert the time scale of our TOF spectra to mass-to-charge spectra. The goal is to divide the ion yield of its doubly charged parent ions by the yield of its singly charged parent ions. With this normalization of the doubly charged ion yield one can achieve stable values over a long period of time, thereby reducing any systematical error. However, boron and bromine have more than one stable isotope that needs to be considered in the data analysis as described below.

Boron and bromine each have two stable isotopes— $^{10}B(19.9\%)$ and $^{11}B(80.1\%)$, and $^{79}Br(50.69\%)$ and $^{81}Br(49.31\%)$ [17]—leading to additional lines in the photoion TOF spectrum as shown in Fig. 2. Hydrogen and nitrogen have additional stable isotopes of little abundance, namely, 0.015% and 0.366% [17], respectively. These isotopes do not contribute visibly to the spectrum and are ignored in the analysis. However, we do have to consider the boron and bromine isotopes.

From a simple analysis we obtain a group of 10 photoion peaks for the singly charged parent ion of tribromoborazine ranging from 312 to 321 Da. Using the known isotope abundances we calculate for tribromoborazine the probabilities of having certain masses and, thus, obtain the relative intensities of these peaks. This group of 10 peaks, with each peak having a Gaussian shape with a width of 1.1 Da, serves as a fit function for the singly charged parent ions in our spectra.

FIG. 2. Ion yield spectrum of tribromoborazine taken at a photon energy of 72 eV. Singly (M^+) and doubly (M^{2+}) charged parent ions are shaded. Note that bromine as well as boron has two major isotopes. Also note that the abscissa is on a log scale.

Besides the fact that we have several peaks for the parent ion, it is also possible (likely) that the parent ion loses hydrogen atoms in the photoionization process, leading to masses that are reduced by up to 3 mass units, depending on the number of hydrogen atoms lost. The breakoff of hydrogen atoms does not depend on the particular isotope mixture of tribromoborazine and should, therefore, exhibit the same intensity distribution as the peaks in the original parent ion. Thus, we apply our fit function described above to the intact parent ion, to the parent ion that has lost one hydrogen atom shifted by 1 mass unit, to the parent ion that has lost two hydrogen atoms (shifted by 2 mass units), and to the parent ion that has lost all three hydrogen atoms (shifted by 3 mass units). In the overall fit procedure the only free parameters are the intensity-scaling factors of the fit functions for losing from zero (parent ion) to three hydrogen atoms. Since the widths of the individual peaks are only an approximation we include a convolution in the fit procedure that accounts for the actual resolution of the TOF spectrometer.

The resulting fit curves are shown in Fig. 3. The main intensity is indeed from the singly charged parent ion (without losing a hydrogen atom) as can be seen from the red lines for the 10 different isotope combinations. The black shaded area corresponds to parent ions that have lost one hydrogen atom. The contribution of parent ions that have lost more than one hydrogen atom is very small and not included in the figure. The overall fit curve, which includes the instrumental resolution, is shown as the thick black line; it fits the mass spectrum very well. The difference between the fit curve and the mass spectrum (upper panel in Fig. 3) shows only statistical scatter, indicating that all components have been correctly accounted for.

We now turn to the analysis of the doubly charged parent ion. Double photoionization is independent of the isotopes in a given molecule. We also assume that we have a certain amount of doubly charged parent ions that have lost a hydrogen atom with a similar probability as for the hydrogen loss for singly charged parent ions. Thus, we make use of the shape of the total fit curve for the *singly* charged parent ion (described above) to obtain a fit function for the *doubly* charged parent ion by dividing the mass values by 2. In other words, the
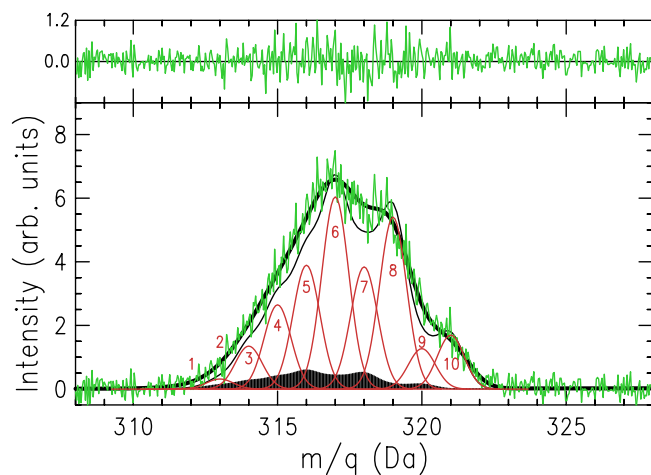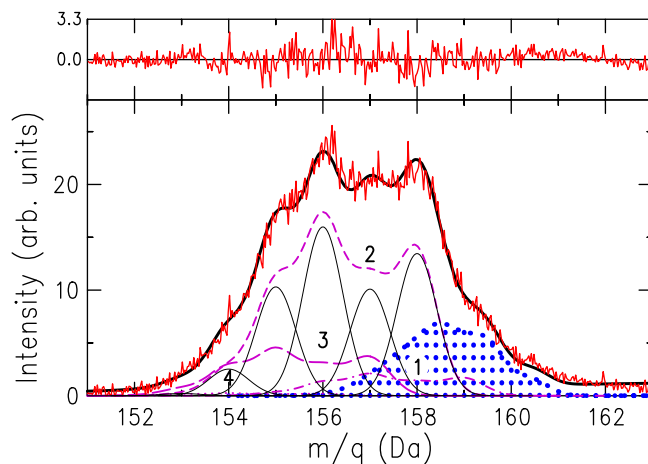
FIG. 3. Part of the ion yield spectrum of tribromoborazine showing the region of the singly charged parent ion taken at a photon energy of 72 eV. Experimental data, green line; relative intensities for a specific set of isotopes, thin red lines; intensity contribution from a parent ion that has lost one hydrogen atom, black shaded area; fit curve of the experimental data, thin black line; convoluted fit curve, thick black line. The top panel shows the difference between the fit curve and the data.

FIG. 4. Part of the ion yield spectrum of tribromoborazine showing the region of the doubly charged parent ion taken at a photon energy of 72 eV. Experimental data, red line; doubly charged parent ion, blue shaded area; fragment $BrB_3N_3H_3^+$, dotted line; fragment $BrB_3N_3H_2^+$, dashed line; fragment $BrB_3N_3H^+$, dot-dashed line; fragment $BrB_3N_3^+$, double-dot-dashed line; fit curve, solid black line. The top panel shows the difference between the fit curve and the data.

mass peaks for the singly charged parent ion that appeared between 312 and 321 Da are now between 156 and 160.5 Da, in steps of 0.5 Da. Unfortunately, there is a singly charged fragment ($BrB_3N_3H_3^+$) of similar mass-to-charge ratio overlapping partially with the doubly charged parent ion. Again, this fragment can have different sets of isotopes ranging from 154 to 159 Da, and we can calculate the relative intensity distribution in the spectrum for this fragment from the known abundances of the isotopes. As discussed above for the singly charged parent ion, this fragment may have lost up to three hydrogen atoms in the photoionization or fragmentation process, i.e., the intensity distribution for this fragment has to be applied to the spectra also for 1, 2, and 3 mass units lower than the original fragment. Fortunately, three facts help us to separate the fragment from the doubly charged parent ion. First, any intensity below 156 Da is due only to the fragment. Second, any intensity above 159 Da is due only to the doubly charged parent ion. And third, intensities at 156.5, 157.5, and 158.5 Da are due only to the doubly charged parent ion.

To summarize, in order to determine the yield of the doubly charged parent ion we perform a least-squares fit with five fit functions. One fit function has been derived from the fit curve of the singly charged parent ion. The other four fit functions are for the fragments $BrB_3N_3H_n^+$ ($n = 0-3$). Thus, we have five free fit parameters, each of them scaling the intensity of the respective fit function.

As we can see in Fig. 4 most of the $BrB_3N_3H_3^+$ fragments lose one hydrogen atom; i.e., we have mainly $BrB_3N_3H_2^+$ fragments. The separation of the different fragments in Fig. 4 is certainly difficult but not necessary in this investigation. The doubly charged parent ion, shown as the blue shaded area, can be separated reliably from the fragments as we see below.

The least-squares fits for the singly and doubly charged parent ions are performed for spectra in the photon energy

range from 25 to 138 eV. The areas of doubly and singly charged parent ions are then obtained by numerical integration of the corresponding fit curves. We note that these areas also contain parent ions that have lost a hydrogen atom. This contribution, however, is small and should be similar for the singly and doubly charged parent ion. Any attempt to correct for this systematic (small) inaccuracy would result in large error bars and increased scatter in the ratio of doubly to singly charged parent ions. Since the ratio of doubly to singly charged parent ions is rather high, compared to a few percent for atoms—as we see below—it is better to compare the yield of doubly charged parent ions (M^{2+}) to the *sum* of singly plus doubly charged parent ions ($M^+ + M^{2+}$). In the following text the term *ratio* always refers to the ratio of doubly to singly plus doubly charged parent ions unless otherwise noted.

IV. RESULTS AND DISCUSSION

The ratio for tribromoborazine is presented in Fig. 5, along with the ratio for partially deuterated benzene ($C_6H_3D_3$) for comparison. Despite the complicated data analysis the resulting ratio values show only little scatter. Using the same analysis procedure as before [18] we fit the curve of the helium double-to-total photoionization ratio [19] to our tribromoborazine ratios for photon energies up tp 98 eV (dashed line in Fig. 5). Here, the scaled He ratio curve represents the contributions from the so-called knockout and shake-off mechanisms [20,21], which describe the double photoionization ratio very well for atoms and small molecules. From this fit we determine the double-ionization threshold at 28.5(4) eV. We note that the ratios do not go down to 0 below threshold but show an offset that may be caused by second-order light or double ionization due to electron-molecule collisions. The tribromoborazine ratios follow closely the scaled He ratio curve up to about 98 eV. Above 98 eV the
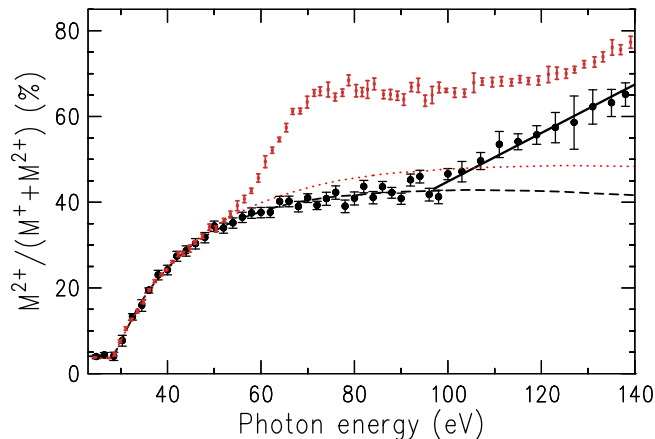
FIG. 5. Ratio of doubly (M^{2+})–to–singly plus doubly charged parent ions ($M^+ + M^{2+}$) of tribromoborazine as a function of the photon energy (filled black circles). Data above 100 eV are binned in 4-eV intervals. Red data points are for $C_6H_3D_3$ [3] multiplied by 12.3 and shifted to match the tribromoborazine ratios at lower energies. The dashed line and red dotted line are fits in the low-energy region of the He double-to-total photoionization ratios [19] to our data and the benzene data, respectively. The straight black line is a linear fit to the data in the 98- to 138-eV energy region.

ratios start rising linearly with increasing photon energy. A linear fit curve (black solid line) fits very well to the ratios at high energies. This energy dependence of the ratio—following a scaled He ratio curve at low energies, with an additional linear increase at higher energies—has been found for several aromatic molecules such as pyrrole. Here, however, we have a nonaromatic molecule, demonstrating that the linear increase in the ratio is not associated with aromaticity. Because the linear increase does not exist either for atoms [1] or for small molecules [22], the question remains what the origin of this behavior is.

The benzene ratio curve in Fig. 5 (red data points) is scaled up by a factor of 12.3 and also shifted up to account for the ratio offset in the tribromoborazine ratios. In addition, the energy scale of the benzene ratios was shifted according to the energy difference of the double-photoionization thresholds, which results in a very good overlap of the two data sets at photon energies below 50 eV. We need to mention here that the two data sets were obtained with different TOF spectrometers. Whereas the benzene ratio is based on long-lived or stable parent ions due to the pulsing technique of the TOF spectrometer in that experiment, the tribromoborazine ratios may include an appreciable amount of metastable ions whose lifetime is longer than their flight time to our detector. Therefore, the scaling factor of 12.3 between these two data sets may be affected by the difference in the experimental techniques.

A broad hump around 75 eV is clearly visible in the benzene ratios [3,23] but is not present for tribromoborazine.

The hump, which exists for several but not all aromatic molecules, is absent in the case of tribromoborazine, although the basic molecular structure of the two molecules is the same. Therefore we conclude that the hump in the ratio requires aromaticity. However, aromaticity alone is not sufficient for the existence of a hump, as some aromatic molecules, e.g., pyrrole, do not exhibit this resonant behavior of the ratio. A previous investigation indicates that aromatic molecules with a pentagonal structure do not show this feature [4].

The current interpretation for the existence of this hump is that it is possibly due to the formation of two-electron pseudoparticles, which have a de Broglie wavelength that approximately matches the bond lengths in the hexagonal ring, so that there is a standing wave. For a more detailed discussion, see Ref. [3].

V. SUMMARY

We have measured the ion yields for singly and doubly charged parent ions of tribromoborazine from the double-ionization threshold to 138 eV. We obtained an energy of 28.5(4) eV for the first double-ionization threshold. We have compared the double-photoionization results for tribromoborazine with those for benzene, which both have a very similar molecular structure.

Indeed, the ratios of both molecules are very similar to the ratio for the helium atom at lower photon energies. At high photon energies the ratio of doubly to singly plus doubly charged parent ions of tribromoborazine rises linearly with the energy, which has only been seen so far in aromatic molecules, and not in atoms or small molecules. The mechanism behind this linear rise in the ratio is still unknown.

In contrast to aromatic molecules consisting of hexagonal rings (e.g., benzene, naphthalene, pyrene, pyrimidine), tribromoborazine does not exhibit a hump in the ratio—a resonant enhancement in the ratio that is common for the molecules mentioned above. A possible interpretation of this hump is the formation of two-electron pseudoparticles, which have a de Broglie wavelength that approximately matches the bond lengths in the ring, so that a standing wave is created in the molecular π orbital. This orbital does not exist in tribromoborazine, and thus, the absence of the hump is not a surprise but supports the current interpretation of the hump.

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