Photoabsorption of the molecular IH cation at the iodine 3d absorption edge

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I. INTRODUCTION

Molecular ions are of high interest due to the role they generally play in chemistry, e.g., in batteries [1] or enzymatic reactions [2]. Molecular ions can also occur as transients in dynamic molecular processes, as investigated by transient inner-shell photoabsorption spectroscopy (e.g., [3]). Moreover, molecular ions have been identified in space, where they are created by the impact of cosmic rays or by ultraviolet radiation from nearby stars or other cosmic radiation sources.

The number of laboratory studies on the photoionization of ions is limited because the production of ionic targets with sufficient densities for meaningful photoionization and photofragmentation experiments is challenging. Experiments with atomic ions which employed the photon-ion merged-beams technique have been reviewed repeatedly [5–7]. Experimental inner-shell studies with molecular ions are even more scarce. Previous work has been carried out on the photoionization and photofragmentation of cluster ions (e.g., [8]), endohedral fullerene ions [9], biomolecular ions (e.g., [10,11]), and polycyclic aromatic hydrocarbons [12].

Recently, inner-shell studies have been reported also on small molecular ions containing hydrogen, i.e., on the molecular cations CH+2, OH+2, and SiH+2 [13]. Here we investigate the photoabsorption of a similar diatomic ion, IH+2, via excitation or ionization of the iodine 3d shell. In x-ray studies on dynamic processes, iodine-containing molecules have attracted considerable interest since the massive iodine atom slows down the fragmentation process, bringing the time-dependent dynamics onto time scales accessible by free-electron laser sources [14]. Furthermore, iodine-containing molecules can be efficiently excited by soft x-rays via the strong iodine 3d and 4d resonances (e.g., [15,16]). Therefore, we have chosen the IH+ ion as a model system to utilize the iodine 3d-electron excitation for probing the molecular valence orbitals.

Previous work involving photoexcitation of the iodine 3d shell has been carried out by Hashmall et al. [17], who examined the chemical shift in photoelectron emission from the 3d orbital in dependence of the type of ligand of the iodine atom. Hitchcock and Brion [18] measured the absorption cross section of CHI around the 3d ionization threshold using electron energy-loss spectroscopy. Aksela et al. [19] measured the Auger electron spectra resulting from 3d excitation of I and I2. Most recently, photofragmentation and photoionization of neutral I2 molecules was studied by Boo and Saito [20].

For the comparison with the IH+2 (q = 2–7) ion yields resulting from photofragmentation of molecular IH+ ions, we have also measured relative cross sections for multiple photoionization of atomic I+ ions leading to the production of IH+ ions with q = 2–8. This greatly aids in disentangling atomic and molecular effects in the IH+ spectra. For the furtherinterpretation of the molecular spectra, we have performed corresponding theoretical calculations. The present paper is
organized as follows. In Sec. II the experimental procedures are briefly described. The results are presented and discussed in Sec. III. A closing summary is given in Sec. IV.

II. EXPERIMENT

The present experiments on IH$^+$ and I$^+$ ions were carried out by employing the photon-ion merged-beams method (e.g., [7]) at the photon-ion spectrometer at PETRA III (PIPE). PIPE is a permanently installed end-station at beamline P04 [21] of the PETRA III synchrotron radiation facility at DESY in Hamburg, Germany. Detailed descriptions of the PIPE setup can be found in Refs. [22] and [23]. Here only specific procedures related to the present experiment are described.

The I$^+$ and IH$^+$ ions were produced from evaporated liquid CH$_3$I in a 10-GHz electron cyclotron-resonance ion source which was kept on a potential of 6000 V. Upon extraction, the ions were accelerated towards the ion beamline, which is on ground potential. A dipole magnet was used for selecting the desired mass-to-charge ratio for further transport to the photon-ion interaction region. The mass-resolving power of our mass spectrometer can be selected by adjusting entrance and exit slits. In the present experiment the mass-resolving power was $m/(\Delta m) \approx 710$. This was sufficient for separating IH$^+$ and I$^+$, as shown in Fig. 1.

In the photon-ion interaction region the ion beam was directed onto the photon beam such that the ions propagated on the photon-beam axis along a merging section of about 1.7 m length. The ions were excited with monochromatized synchrotron radiation with photon energies $E$ ranging from 610 to 680 eV. This range comprises the iodine 3$d_{5/2}$ and 3$d_{3/2}$ ionization thresholds. For neutral iodine these thresholds are located at 619.3 and 630.8 eV, respectively [24]. In the P04 monochromator, a 400-lines/mm variable line spacing (VLS) grating was used to disperse the photons from the P04 undulator. The exit slit of the monochromator was set to a width of 1500 $\mu$m, resulting in a resolving power $E/(\Delta E) \approx 600$. The absolute energy scale of the monochromator was calibrated using Ne 1$s \rightarrow 3p/4p$ and Xe 3$d_{5/2} \rightarrow 6p$ transitions and taking the Doppler shift due to the ion motion into account. The resulting uncertainty of the experimental photon-energy scale is estimated to be approximately 1 eV.

Ionic fragments I$^q^+$ ($q \geq 2$) emerging from the photon-ion interaction region were charge separated by a second dipole magnet, and I$^q^+$ product ions with the selected charge state $q$ were counted with a channeltron-based single-particle detector. The light I$^q^+$ fragments could not be directed efficiently into the detector because they received too much transverse momentum upon molecular breakup, as will be discussed below. Neutral fragments were not detected either, since these cannot be deflected by the second magnet and, thus, continue to propagate on the photon-beam axis.

III. RESULTS AND DISCUSSION

Figure 2 shows ion-yield curves for the parent ions I$^+$ [red, panel (a)] and IH$^+$ [blue, panel (b)] summed over all measured fragment channels producing I$^q^+$ ions ($q = 2$–8 for I$^+$ and $q = 2$–7 for IH$^+$). Here, only these sum spectra are

![FIG. 1. Mass spectrum of ions produced from CH$_3$I obtained by scanning the magnetic field of the dipole magnet. The singly charged atomic iodine ion $^{127}$I$^+$ is clearly separated from the $^{127}$IH$^+$ molecular ion. The solid (red) line results from a fit of seven Gaussian functions to the experimental data. From the fit the mass-resolving power was determined to be $m/(\Delta m) \approx 710$ in this measurement.](033401-3)

![FIG. 2. Ion-yield curves for the primary target ions I$^+$ (red, panel a) and IH$^+$ (blue, panel b) summed over all measured fragment channels I$^q^+$ ($q = 2$–8 for I$^+$ and $q = 2$–7 for IH$^+$). According to a Hartree-Fock (HF) calculation [31] for I$^+$ (vertical solid lines), the narrow resonances can be assigned to the 3d$_j \rightarrow np$ ($j = 3/2, 5/2, n = 5, 6, 7$) excitations and the two broad resonance features are due to the 3d$_j \rightarrow ef$ shape resonances. The energy axis of the HF calculation was shifted to match the energetically lowest resonance of the experimental I$^+$ ion-yield curve.](033401-4)
discussed. The IH\textsuperscript{+} curve is normalized to the I\textsuperscript{+} yield at 680 eV. The overall shape of both curves resembles the 3d absorption spectra of Xe [25], Xe\textsuperscript{+} [22], I\textsubscript{2} [20], and CH\textsubscript{3}I [18]. Small narrow resonance features are found at energies below approximately 635 eV. Above this energy the onset of a strong quasicontinuum of absorption is observed, which is mainly due to the direct photoionization of the 3d subshell and the two well-known 3d\textsubscript{j} \to \epsilon f shape resonances producing either a 3d\textsubscript{3/2} or a 3d\textsubscript{5/2} vacancy. The spin-orbit splitting of the 3d\textsubscript{j} hole states is \(\sim 11\) eV, and because of their large widths of the order of 10 eV, the 3d ionization edge is smeared out.

The atomic iodine curve features several narrow resonance peaks above the 3d ionization threshold, while the IH\textsuperscript{+} curve is relatively smooth in this energy range. When normalized to the ion current of the primary ion beam, the count rate for the photoabsorption of the IH\textsuperscript{+} is lower compared to the I\textsuperscript{+} count rate by a factor of about 3. This is due to a reduced transmission of the IH\textsuperscript{+} (\(q \geq 2\)) products caused by the kinetic energy release (KER) upon fragmentation of the IH\textsuperscript{+} molecular ions. Assuming one localized charge each on the iodine and the hydrogen after photoionization and assuming an IH\textsuperscript{+} bond length of 1.65 Å [26,27], the repulsive energy due to the Coulomb interaction is 8.6 eV. Due to the associated KER, the charged fragments acquire an additional momentum which, in the worst case, can be in transversal direction. Hence, a considerable fraction of the fragment ions is cut off by the narrow acceptance of the second dipole magnet. According to a more quantitative geometric estimation, the H\textsuperscript{+} fragments will be almost completely lost at the entrance aperture and only a part of the iodine fragments IH\textsuperscript{+} can pass it and reach the detector. This is a common issue in experiments employing molecular-ion beams [13,28], where, in principle, can be overcome by choosing a detection system with a sufficiently large angular acceptance [29,30].

To identify the resonances observed in the absorption spectrum of the atomic target ion I\textsuperscript{+}, Hartree-Fock (HF) calculations [31] have been performed (vertical lines in Fig. 2). These calculations suggest that the narrow features in the spectrum can be assigned to the core-to-valence excitation 3d\textsubscript{j} \to 5p and the Rydberg resonances 3d\textsubscript{j} \to np (j = 5/2, 3/2; n = 6, 7) with a 3d spin-orbit splitting (indicated with vertical lines also in Fig. 2) of 10.8 ± 0.3 eV. This value agrees within the error bars with the 11 eV, and because of their large widths of the order of 10 eV, the 3d ionization edge is smeared out.

In Fig. 3, the calculated I\textsuperscript{+} spectra in the pre-edge region are depicted for the atomic 1\textsuperscript{1}I\textsuperscript{+}(5p\textsuperscript{4}3P\textsubscript{2,1,0}) initial levels which are populated in the I\textsuperscript{+} beam with their statistical weights. The excitation from these three initial levels results in a broadening of the 3d\textsubscript{5/2} \to 5p resonance A. For the 3d\textsubscript{3/2} \to 5p resonance B, the spin-orbit splitting of the initial \(^3P\) term causes the observed asymmetry. Rydberg levels with \(n > 7\) could not be identified experimentally, because the higher \(n\) members of the Rydberg series are superimposed by the 3d ionization threshold and the 3d \(\to \epsilon f\) resonances.

A first assignment of the resonances observed in the IH\textsuperscript{+} molecular ion can be made by comparison with the spectrum of the atomic I\textsuperscript{+} ion. The ground state of the IH molecule has been assigned [32,33] to the term

\[ KLMN (5s\sigma)^2 (5p\sigma)^2 (5p\pi)^4 \Sigma\textsuperscript{+}_b. \]

from which the following levels [34] can be derived for the IH\textsuperscript{+} molecule with a (5p \(\pi\)) electron removed:

\[ KLMN (5s\sigma)^2 (5p\sigma)^2 (5p\pi)^3 \Pi_{3/2,1/2}. \]

The \(^2\Pi_{3/2}\) level is the ionic ground level. Hence, the first peak marked A in Fig. 3 can be assigned to a transition from

<table>
<thead>
<tr>
<th>Peak label</th>
<th>Assignment</th>
<th>Chemical shift (eV)</th>
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<tbody>
<tr>
<td>A</td>
<td>3d\textsubscript{3/2} \to (5p (\pi))</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>B</td>
<td>3d\textsubscript{3/2} \to (5p (\pi))</td>
<td>0.2 ± 0.3</td>
</tr>
<tr>
<td>C</td>
<td>3d\textsubscript{3/2} \to (6p (\pi))</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>D</td>
<td>3d\textsubscript{3/2} \to (7p (\pi))</td>
<td>1.1 ± 0.4</td>
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</table>

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the inner-shell atomic iodine 3d_{5/2} orbital into the molecular (5\,p\,\pi) valence orbital, which is analogous to the 5\,p resonance in I\(^+\). Peak B is the corresponding spin-orbit split line. The next accessible molecular orbital of IH above the (5\,p\,\pi) orbital is a \(\sigma^*\) orbital [35], which we observe as a feature at 624 eV in the ion-yield curve of IH\(^+\) (peak E in Fig. 3). Peak E is not present in the absorption spectrum of atomic I\(^+\). The valence \(\sigma^*\) orbital arises from the hybridization of the iodine and hydrogen valence orbitals. In analogy to the designations for the atomic I\(^+\) ion we assign peaks C and D tentatively to molecular np states. Several exchange correlation functionals were tested, including pure Hartree-Fock, local the iodine 6\,p\,\pi and 7\,p\,\pi orbitals. The iodine has a higher electronegativity than the hydrogen. The valence \(\sigma^*\) orbital matches its 5\,p orbital with a 1.0 eV (FWHM) Gaussian.

Figure 4 shows the molecular orbital diagram for the neutral IH molecule. Iodine is a halogen atom so it attracts the electron from the hydrogen when the chemical bond is formed, filling its 5\,p shell completely. However, as shown in Fig. 4 for the \(\sigma\) molecular orbital, the effective size of the 5\,p orbital matches the I-H bond length. The real charge transfer from H to I is thus small. This fact is confirmed by the 3d_{5/2} core-level energy shift shown in Table II. For IH the energy-level shift is only 0.2 eV relative to I, while for the charged I\(^+\) and IH\(^+\) it is \(-9.6\) eV and \(-9.0\) eV, respectively. Hence, the shift of IH\(^+\) relative to I\(^+\) is 0.6 eV. The larger chemical shift in the ionized species can be explained by the contracted size of the 5\,p orbitals, which increase the charge transfer from the hydrogen to the iodine upon filling the iodine 5\,p shell.

Figure 5 shows the comparison of the experimental data (dots) with the calculated x-ray absorption spectra (solid lines) and Fig. 6 the molecular orbital isosurfaces responsible for the transitions.

From the DFT calculations the peaks A and B can be assigned to the 3d_{5/2} \(\rightarrow\) (5\,p\,\pi) and 3d_{5/2} \(\rightarrow\) (5\,p\,\pi) transitions involving the iodine 5\,p\(_x\) and 5\,p\(_z\) orbitals. The iodine 5\,p\(_x\) orbital is hybridized with the hydrogen 1s orbital and forms an antibonding \(\sigma^*\) orbital responsible for transitions E in the absorption spectrum (see Figs. 4 and 6). Peak C can be attributed to the transition 3d_{5/2} \(\rightarrow\) (6\,p\,\pi) hybridized of

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>IH</th>
<th>I(^+)</th>
<th>IH(^+)</th>
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<tbody>
<tr>
<td>0</td>
<td>0.2 eV</td>
<td>-9.6 eV</td>
<td>-9.0 eV</td>
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FIG. 5. Results of the DFT simulation with the KMLYP functional (see text). (a) I⁺: Measured ion yield (red open dots) and calculated spectrum (solid orange line). (b) IH⁺: Measured ion yield (blue open dots) and calculated spectrum (solid green line). (c) Comparison of the calculated spectra for I⁺ (orange solid line) and IH⁺ (solid green line) from (a) and (b). The gray dashed vertical lines mark the peaks calculated by DFT of the I⁺ and IH⁺ spectrum. The light blue, dashed line is the simulated IH⁺ spectrum but convoluted with a 0.5 eV Gaussian function. An additional line (peak F) becomes visible which is not resolved in the experiment. Line assignment according to the DFT calculations for IH⁺: (A) 3d^5/2 → (5p_π), (B) 3d^3/2 → (5p_π), (C) 3d^5/2 → (6p_π), (D) 3d^5/2 → (7p_π), (E) 3d^5/2 → σ*, and (F) 3d^5/2 → σ*.

The iodine (5p_x + 5d_{xz}), (6p_y + 5d_{yz}) orbitals, and of the hydrogen 2p_x and 2p_y orbitals, while peak D can be attributed to 3d^5/2 → (7p_π) weakly hybridized by the interaction of the iodine 7p_x and 7p_y and the hydrogen 2p_x and 2p_y orbitals. Peak F, consisting of iodine 5p_z and 5d_{z^2} and hydrogen 2s and 2p_z orbitals, is predicted theoretically but is not resolved in the experimental data. It is attributed to an antibonding σ* molecular orbital.

A chemical shift is observed between the theoretical spectra for I⁺ and IH⁺ [Fig. 5(c)]. Peaks A–D observed in IH⁺ originate from similar atomic orbitals and are shifted to lower energies as compared to I⁺. The calculated value of this shift is larger for peaks C and D (0.7 eV) than for A and B (0.4 eV). Qualitatively this can be understood in terms of the different size of molecular orbitals responsible for the transitions A, B and C, D. The core charge of the iodine in IH⁺ is partially screened by means of the σ orbital, shown in Fig. 4. Due to its smaller size, the molecular orbital A and its spin-orbit counterpart B experience a larger energy shift than the delocalized C and D orbitals. Thus, the resulting difference between the energy of the core 3d^5/2 orbital (which is also subjected to chemical shift) and the corresponding unoccupied molecular orbitals will be smaller for A, B than for C and D. The excitations shown in the theoretical spectrum include transitions to the hybridized iodine p and d and hydrogen s and p states. Higher excitations would require iodine f orbitals to be considered. Such calculations are beyond the scope of the present article and DFT should be used with special care there. The first issue here is the limited quality of the time-dependent functionals presently available for the excited-state calculations, in contrast to the rapid development of a large variety of reliable ground-state functionals. The second issue is related to the many-body effects on d–f transitions, including the 4f wave-function collapse (e.g., [45]) where multiconfigurational approaches should be used.

IV. SUMMARY

Ion yields after photoexcitation and photoionization of the singly charged atomic I⁺ and molecular IH⁺ ions have been measured by recording the IV⁺ (q ≥ 2) product-ion yields and adding them together. In the energy region below the iodine 3d ionization threshold, resonances have been observed which can be attributed to 3d → np (n = 5, 6, 7) transitions for the atomic
parent ion. The iodine I$^+$ 3$d^{-1}n$,$p$ levels show a spin-orbit splitting of the order of 10.8 ± 0.3 eV. For the molecular cation IH$^+$, in addition to the resonances observed with atomic iodine ions, one more resonance is found which is caused by the hybridization of the iodine and hydrogen orbitals. Using DFT calculations we assigned this resonance to a transition of a 3$d_{5/2}$ inner-shell electron to an antibonding $\sigma^*$ orbital. The ($n$,$p$) resonances observed in the IH$^+$ spectrum show a chemical shift compared to corresponding resonances in the atomic ion I$^+$, caused by the hydrogen atom bonded to the iodine, of the order of 0.3 eV (averaged) for the almost atomlike (5$p$,$p$) levels, whereas for the (6$p$/7$p$,$p$) molecular Rydberg levels a 3–4 times larger shift is observed. Simulations using DFT can predict the relative chemical shift to lower binding energies from the I$^+$ to the IH$^+$ ion as observed in the experiment. The increased energy shift for the 6$p$/7$p$ excitations compared to 5$p$ can be understood in terms of the larger size of the molecular orbitals responsible for these transitions. Both 3$d$ core levels and unoccupied orbitals experience a chemical shift when the hydrogen atom bonds to the I$. Due to its smaller size, the molecular orbital A and its spin-orbit counterpart B experience a larger energy shift than the delocalized C and D orbitals. Thus, the resulting difference between the energy of the 3$d_{5/2}$ core orbital and the corresponding unoccupied molecular orbitals will be smaller for A, B than for C and D.

To conclude, we were able to show that the resonances in the iodine 3$d$ pre-edge regime are sensitive to the molecular electronic state, as can be seen from the different values for the chemical shift of the lines observed. Due to this sensitivity these lines might be exploited in various iodine-containing molecules to examine the dynamics of electron excitation using inner-shell x-ray spectroscopy. Furthermore, we have demonstrated that the photon-ion merged-beams method as implemented at the PIPE setup can be employed for the inner-shell absorption spectroscopy of mass-selected molecular ions. The accuracy of the present measurements on I$^+$ ions was mainly limited by the counting statistics. We are confident that further improvements of our experimental apparatus and, in particular, of our ion-source technology will, in the future, facilitate even more precise spectroscopic studies of molecular ions at the PIPE setup.

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