Spectroscopic experiments on autoionization and neutral fragmentation in the high-Rydberg states of BH

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Abstract. We report optical-optical-optical triple-resonant spectroscopic structure for BH that corresponds with scattering resonances formed by high-lying Rydberg states that couple strongly to decay channels for electron loss and boron-hydrogen bond cleavage to neutral atoms. Lineshapes and intensities provide information on state-to-state relaxation dynamics and interference between bound-bound and bound-continuum transition moments.

1. Introduction
When a molecular cation and an electron combine, the potential energy present initially in Coulomb attraction dissipates in the relaxation of the energized system along a complex path of transient electronic configurations. Inelastic electron scattering competes with dissociative charge neutralization as non-adiabatic coupling dynamics act to decide final products. Work in storage rings, where cooled ions collide with mono-energetic electrons, can reveal structured cross sections that reflect the underlying physics [1]. Laser spectroscopy offers similar information, in some cases with superior precision and state specificity [2].

The present work reports multiphoton spectroscopic results for BH that characterize scattering resonances formed by high-lying Rydberg transients strongly coupled to decay channels for electron loss and bond cleavage to neutral atoms. Analysis of these resonances provides information on state-to-state coupling dynamics and interference between bound-bound and bound-continuum transition moments.

Our approach uses optical-optical-optical triple resonance to select scattering states labeled by electron orbital, vibrational and total angular momentum quantum numbers. Here, we report spectroscopic details concerning electron-cation resonances built on the vibrational ground state and first excited state of BH⁺ with approximately good core rotational quantum numbers \( N = 0, 1 \) and 2. Below the lowest ionization threshold, we observe efficient loss in resonant channels to form higher excited states of the boron atom. Above the total-energy threshold to form vibrational ground-state BH⁺, neutral dissociation competes with electron loss. We characterize these dynamics in terms of competitive yields and resonant lineshapes. Our results show that, when energetically accessible, electron loss dominates detectable neutral fragmentation.

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2. Experimental

Figure 1 shows an energy-level diagram. Final excited states are produced by stepwise absorption of photons from three lasers. A first step promoted by a Nd:YAG pumped β-barium borate (BBO) optical parametric oscillator (OPO) tuned to $\omega_1 = 480.1$ nm, transfers population from the $X^2\Sigma^+ (v = 1, N = 0)$ state of $^{11}$BH to the $v' = 0, N' = 1$ level of the first excited singlet state, $A^1\Pi$. A second pulse from a XeCl excimer-pumped dye laser tuned to $\omega_2 = 341.9$ nm specifically promotes this population to the $N' = 0$ rotational level of $v' = 0$ in the $B^1\Sigma^+$ state.

This optically selected gateway state serves as an originating point for transitions driven by a third pulse ($\omega_3$) from a second XeCl excimer-pumped dye laser tuned to $\omega_3 = 341.9$ nm specifically promotes this population to the $N' = 0$ rotational level of $v' = 0$ in the $B^1\Sigma^+$ state.

BH is produced for spectroscopic study at the exit of a pulsed nozzle by the 193 nm ArF excimer laser photolysis of B$_2$H$_6$, seeded at 5 percent in H$_2$. The resulting pulsed molecular beam travels 10 cm from the source chamber to enter the collection region of a Wiley-McLaren time-of-flight mass spectrometer. The laser interaction region between the repeller and extractor grids of the mass spectrometer is held to a potential of 0.0 V cm$^{-1}$ during the laser pulse excitation sequence. Following a delay of 50 ns after the third laser pulse, we switch the potential difference between the repeller and extractor to 400 V cm$^{-1}$, accelerating ions toward the TOF drift tube.

Mass separated ions are detected by a multichannel plate and recorded with a mass resolution of 1:100 by a 125 Mhz digital oscilloscope under control of a laboratory computer running a LabVIEW data acquisition program. The dye laser and OPO wavelengths are calibrated optogalvanically using a Fischer Scientific Fe/Ne hollow cathode lamp.

3. Results
Figure 2 shows a portion of an extended spectrum of the ionization-detected absorption signal observed in the 11 amu (\textsuperscript{11}B\textsuperscript{+}) and 12 amu (\textsuperscript{12}BH\textsuperscript{+}) mass channels recorded in scans originating from the photoselected \textsuperscript{11}BH state, B \Sigma(v' = 0, N' = 0), over a region beginning 1300 cm\textsuperscript{-1} below the threshold for producing BH\textsuperscript{+} in v' = 0 to 1500 cm\textsuperscript{-1} above.

The lower spectrum, recorded at the \textsuperscript{11}B\textsuperscript{+} mass, shows strong sharp features forming Rydberg series that converge to apparent limits consisting of the rotational levels N' = 0, 1 and 2 of the ground vibrational state of BH\textsuperscript{+}. Above this limit, the spectrum recorded for the channel forming \textsuperscript{11}B\textsuperscript{+} appears as a weak continuum, characterized by broad undulations and sharp window resonances, the latter of which form series that can be assigned to rotational limits associated with the v' =1 vibrational state of BH\textsuperscript{+}.

Figure 2. Scans showing ionization-detected absorption structure recorded at 11 amu (\textsuperscript{11}B\textsuperscript{+}) and 12 amu (\textsuperscript{12}BH\textsuperscript{+}) for transitions originating from the B \Sigma(v' = 0, N' = 0) state of \textsuperscript{11}BH. The mass 11 scan is expanded to show features in the above-threshold boron atom signal that mirror structure observed in the vertical continuum for photoionization to produce \textsuperscript{11}BH(v' = 0).
The upper spectrum, recorded at the \(^{11}\text{BH}\) mass, shows no signal below the \(v' = 0\) ionization threshold of BH except for a short interval of lines between \(v_0 = 26178 \text{ cm}^{-1}\) and \(26535 \text{ cm}^{-1}\) that match with structure appearing with reduced intensity in the \(^{11}\text{B}^+\) spectrum. Above the adiabatic ionization threshold, the \(^{11}\text{BH}\) spectrum appears as a strong continuum with broad undulations and window resonances. In all cases, the window resonances in the BH continuum match with those assigned in the B\(^+\) spectrum to Rydberg series built on BH\((v' = 1)\). However, certain of these features exhibit markedly different lineshapes, and the broad intensity of the BH continuum signal intensity oscillates with a phase opposite to that found in the B\(^+\) spectrum.

4. Discussion

4.1 Source of the 11 amu signal

Ordinarily, in analyzing a diborane fragment ion mass spectrum, one ought to consider two boron-containing ions as candidates for signal observed at a mass-to-charge ratio of 11 amu, \(^{11}\text{B}^+\) and \(^{10}\text{BH}\). However, in the present case, the hydride of the rarer isotope (20 percent abundance) can be excluded, because optical selection by \(\omega\) promotes the \(\Lambda \, \Pi(v = 0, N = 1) \leftrightarrow \chi \, \Sigma(v' = 1, N = 0)\) transition exclusively for \(^{11}\text{BH}\). Thus, the signal at mass 11 must be carried by \(^{11}\text{B}^+\) alone.

This \(^{11}\text{B}^+\) signal could conceivably come from two sources, non-resonant laser fragmentation of \(^{11}\text{BH}\) ions, resonantly produced by autoionization of BH, or non-resonant ionization of neutral boron atoms, resonantly produced by the predissociation of BH. Either way, the variation in intensity with wavelength can be assigned to high-lying excited states of BH, and represents an action spectrum for production of the parent species, either \(^{11}\text{BH}\) or boron atom.

For third-photon frequencies that fall short of the \(v' = 0\) adiabatic ionization threshold of BH, photofragmentation of boron hydride cations is not an option. BH Rydberg signal at these frequencies must therefore reflect photoproduct boron photoionization. Above threshold, this is not the sole mechanism accessible, but over local energy regions where spectra can be compared, the \(^{11}\text{BH}\) and \(^{11}\text{B}^+\) spectra show broad features that anti-correlate in intensity. This suggests that the \(^{11}\text{B}^+\) signal does not simply reflect the fragmentation of \(^{11}\text{BH}\). Instead, here as well it appears that the \(^{11}\text{B}^+\) signal arises from the non-resonant ionization of boron atoms, produced in this case by the competitive dissociation of \(^{11}\text{BH}\) molecules excited to the \(v' = 0\) continuum.

Signals in the \(^{11}\text{B}^+\) channel are strong below the \(v' = 0\) ionization threshold. Separate studies using focused radiation at 411.4 nm in two-photon resonance with the BI atomic boron \((2s^2 \, 3p)^3\Pi \rightarrow \chi \, \Sigma\) transition tell us that a substantial population of ground state boron atoms exists as a background produced by the photolysis of diborane in our pulsed-nozzle source [3]. However, at wavelengths corresponding to the baseline between features detected in the \(^{11}\text{B}^+\) mass channel, none of this background, ground-state boron atom population ionizes under our measurement conditions. The lack of such signal here is consistent with the low-intensity laser fields used in the present experiment.

The absence of signal from this background of ground state boron atoms suggests that the resonant \(^{11}\text{B}^+\) signal we see must arise from the laser ionization of electronically excited boron atoms, which, it follows from arguments above, must be formed in the predissociation of BH Rydberg states populated as we tune \(\omega\). Atoms produced under such conditions are formed in the still-present laser fields of \(\omega\), and \(\omega_0\). With a frequency of 29248.9 cm\(^{-1}\), \(\omega_0\) provides sufficient energy to photoionize all electronic configurations of B except those of the ground state, \(2s^22p \, \chi \) and the quartet state, \(2s2p^{3} \) [4,5]. The radiative lifetimes of many of the excited states in the 2s-ns and 2s-nd sequences have been measured [6]. These lifetimes fall in the range from 4 to 20 ns, which compares with the duration of our dye laser pulse. Thus, it is reasonable to expect boron atom excited states formed by predissociation to retain population on the timescale of our measurement.

4.2 Assignment of Rydberg series

The discrete structure evident in figure 2 resembles \(l = 0\) and 1 (s and p) Rydberg series that we have assigned earlier in the spectrum of vibrational autoionization resonances observed in transitions from the photoselected intermediate state, B \(\Sigma(v' = 1, N = 0)\) [7]. That work found an \(l = 0\) (ns) series converging to \(N' = 1\) with an average quantum defect of 0.908 and a pair of \(l = 1\) (np) series...
converging to \( N' = 0 \) and 2 with quantum defects averaging about 0.53. The \( np \) series mix by means of an \( l \)-uncoupling interaction that systematically perturbs measured quantum defects near series crossings.

The same series appear as discrete features in the \(^1\text{B}^+\) channel spectrum, converging to rotational levels of the \( \nu' = 0 \) threshold. Such transitions, originating from \( \nu' = 0 \) in the B \(^3\Sigma^-\) state, can be expected to have substantial cross sections for absorption on the basis of the Franck-Condon principle for Rydberg-Rydberg transitions. That these features appear below the adiabatic ionization potential as ions in the \(^1\text{B}^+\) mass channel, says that these high Rydberg states must dissociate to form boron atoms, which for reasons argued above, must be electronically excited and ionize by single photon absorption in the still-present laser field.

The \( ns \) series exhibits a relatively constant quantum defect, averaging 0.93. The interaction between series converging to \( N' = 0 \) and 2 conforms with the behavior established for the same series converging to the \( \nu' = 1 \) limit. In most cases, isolated features appear as Lorentzians with linewidths limited by the resolution of the dye laser used to produce \( \omega_0 \). A few bands are broader with asymmetric Fano profiles reflecting stronger coupling to a continuum to which there exists an interfering transition moment for direct absorption.

Above the \( \nu' = 0 \) threshold, the line positions of features that appear principally as Fano \( q = 0 \) window resonances in spectra recorded for both \(^1\text{BH}^-\) and \(^1\text{B}^-\) match exactly with the positions of discrete autoionizing series converging to \( \nu' = 1 \) observed in Franck-Condon vertical transitions from B \(^3\Sigma^-(\nu' = 1, N' = 0)\). Their window-resonance structure of in the \(^1\text{BH}^-\) spectrum signifies a large Franck-Condon factor for vertical excitation to the \( \nu' = 0 \) ionization continuum, combined with a very small Franck-Condon factor for \( \Delta \nu' = 1 \) transitions to the \( \nu' = 1 \) discrete states. This pattern of interfering discrete-continuum transition moments for primary absorption extends to channels for production both of \(^1\text{BH}^-\) and \(^1\text{B}^-\). However, the \(^1\text{BH}^-\) and \(^1\text{B}^-\) spectra also exhibit broader features that vary in opposition as \( \omega_0 \) is scanned. These intensity differences show that the boron ion signal above the BH ionization threshold cannot come from the photodissociation of \(^1\text{BH}^-\), but rather from the competitive coupling of excited BH to dissociation as well as ionization continua. Variations in the branching ratio for this competition give rise to anti-correlated features in the continuum structure.

4.3 The appearance of structure in the \(^1\text{BH}^-\) mass channel below the three-photon ionization threshold

Structure that appears in the \(^1\text{BH}^-\) mass channel coincides with features in the \(^1\text{B}^-\) spectrum, which can readily be assigned to fragmentary Rydberg series with \( n = 14–23 \) converging to \(^1\text{BH}^-\) \( X \Sigma^+ \) (\( \nu' = 0, N' = 0 \)) and \( n = 13–19 \) converging to \(^1\text{BH}^-\) \( X \Sigma^+ \) (\( \nu' = 0, N' = 2 \)). Several other exceedingly weak features match with structure that converges to \(^1\text{BH}^-\) \( X \Sigma^+ \) (\( \nu' = 0, N' = 1 \)) with principal quantum numbers \( n = 14–21 \). These states of neutral BH exist at a total energy that is too low to ionize spontaneously. As in the production of \(^1\text{B}^-\), electron loss requires the absorption of another photon by the excited neutral, in this case a photoselected s or p Rydberg state built on a vibrationless \( \text{BH}^-\) core. The photon fields available to drive these transitions include \( \omega_v \) at 341.9 nm and \( \omega_0 \), which is scanned from 382 to 376 nm.

These high-Rydberg states are unlikely to absorb light at 341.9 nm, because transitions at this energy reach far into the continuum where ejected electron velocities are high and corresponding absorption cross sections are low. A similar conclusion might be reached for absorption of an additional photon at the frequency of \( \omega_0 \). However, it so happens that the 26376 cm\(^{-1}\) energy separation between the \( X \Sigma^+ \) and A \(^3\Pi\) states of the BH ion core \(^8\) falls close to the range over which \( \omega_0 \) is scanned. Thus, for certain principal quantum numbers, Rydberg states populated by a first step of \( \omega_0 \) excitation lie within an energy interval where accidental double resonance is possible with a Rydberg state converging to the A \(^3\Pi\) state of the cation. To a first approximation then, the initially prepared high-Rydberg electron can act as a spectator to a strongly allowed A \(^3\Pi \leftarrow X \Sigma^+\) valence electronic transition in the ion core. Finite linewidths of features \(<n_\lambda \mid \lambda \) converging to the A \(^3\Pi\) state determine the interval of \( n_\lambda \) for which the transition A \(^3\Pi \leftarrow n_\lambda \mid \lambda \leftarrow X \Sigma^+ \leftarrow n_\lambda \mid \lambda \) satisfies a
resonance condition for vertical transitions ($n_A = n_X$). Core excited states prepared in this manner yield $^{11}\text{BH}^+$ by $X \,^2\Sigma \leftarrow A \,^2\Pi$ electronic autoionization.

The position of the $A \,^2\Pi$ state is precisely known [8]. In preliminary model calculations, we have found linewidths for series converging to the $A \,^2\Pi(v' = 0)$ threshold that account well for the distribution of $^{11}\text{BH}^+$ features centered around $n_X = 17–8$ as core $A \,^2\Pi \leftarrow X \,^2\Sigma^+$ transitions that are vertical in principal quantum number. Details of this molecular isolated core excitation model will be presented in a future publication [9]. For present purposes, the competitive balance between feature intensities for dissociative ($^{11}\text{B}^+$) and photoionization ($^{11}\text{BH}^+$) pathways suggests that the fragmentation of Rydberg states to neutral atoms occurs on a time scale that is not substantially faster than the laser pulse width. Above the $X \,^2\Sigma^+(v' = 0)$ ionization threshold, a weak contribution to the spectrum at the $^{11}\text{B}$ mass shows that channels for B-H neutral fragmentation extend to couple with the direct ionization continuum.

5. Conclusions

The mass-resolved ionization-detected absorption spectrum of BH pictured in figure 2 offers a direct view of resonances that characterize channels for electron-cation scattering leading to ionization and neutral dissociation continua. One can read dynamical information straight from lineshapes and intensities. Strong $^{11}\text{B}$ signal in the spectral region below the lowest ionization threshold of BH reflects the decay of extravalent states to neutral products. Resonances here are sharp, suggesting relatively long lifetimes. This is confirmed by the appearance of $^{11}\text{BH}$ structure in this region owing to competitive isolated core excitation, which occurs on a timescale of nanosecond laser excitation. Fano lineshapes for certain features indicate some direct absorption to the dissociative continuum.

Above the $v' = 0$ threshold, vertical photoionization from $B \,^1\Sigma^+(v' = 0)$ produces a strong $^{11}\text{BH}$ continuum signal. The spectrum of this signal is structured by window resonances associated with transitions to interloping series converging to $v' = 1$ for which Franck-Condon factors are nearly zero. This sharp structure is mirrored in the absorption spectrum detected by monitoring the formation of neutral boron atoms above the $v' = 0$ ionization threshold. However, broader continuum features vary in opposition, suggesting that dissociation competes with ionization, and the branching ratio varies with excitation energy. The meaning of these spectroscopic results for dissociative recombination is clear: non-resonant as well as resonant electron-cation scattering processes yield both neutral and ionic products.

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References

[1] Phaneuf R A, Dunn G H, Havener C C and Müller A 1999 Rep. Prog. Phys. 62 1143
[2] See for example: Mayer E E, Hedderich H and Grant E R 1997 Phil. Trans. Roy. Soc. A 355 1569
[3] Clark J, Gilkison A T, Viteri C R and Grant E R, unpublished results
[4] Zou Y, Brage T and Martinson I 1998 Adv. Quantum Chem. 70 301
[5] Roig R A and Tondello G 1976 J. Phys. B: Atom. Molec. Phys. 9 2373
[6] Lundberg H, Li Z S and Jönsson 2001 Phys. Rev. A 63, 032505
[7] Gilkison A T, Viteri C R and Grant E R 2004 Phys. Rev. Lett. 92, 173005
[8] Almy G M and Horsfall Jr R B 1937 Phys. Rev. 51 491
[9] Viteri C R, Gilkison A T and Grant E R, to be published