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Attachment of molecular hydrogen to an isolated boron cation: an infrared and ab initio study

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Keywords
infrared, ab, attachment, molecular, initio, hydrogen, study, isolated, boron, cation, GeoQUEST

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Attachment of Molecular Hydrogen to an Isolated Boron Cation: An Infrared and ab initio Study

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Abstract: Structural properties of the B⁺−H₂ electrostatic complex are investigated through its rotationally resolved infrared spectrum in the H−H stretch region (3905−3975 cm⁻¹). The spectrum, which was obtained by monitoring B⁺ photofragments while the IR wavelength was scanned, is consistent with the complex having a T-shaped structure and a vibrationally averaged intermolecular separation of 2.26 Å, which decreases by 0.04 Å when the H₂ subunit is vibrationally excited. The H−H stretch transition of B⁺−H₂ is red-shifted by 220.6 ± 1.5 cm⁻¹ from that of the free H₂ molecule, much more than for other dihydrogen complexes with comparable binding energies. Properties of B⁺−H₂ and the related Li⁺−H₂, Na⁺−H₂, and Al⁺−H₂ complexes are explored through ab initio calculations at the MP2/aug-cc-pVTZ level. The unusually large red-shift for B⁺−H₂ is explained as due to electron donation from the H₂ σ bonding orbital to the unoccupied 2pₓ orbital on the B⁺ ion.

1. Introduction

One obstacle to the use of hydrogen as a clean fuel is the lack of suitable storage materials. Viable storage media must possess high capacity, favorable uptake and release kinetics, and, to achieve a large weight percentage of hydrogen, contain primarily lighter elements. Additionally, to maximize storage capacity, the material’s microstructure should be optimized for high porosity and surface area. Among a variety of promising materials, which include metal hydrides, complex hydrides, high porosity and surface area. Among a variety of promising materials, which include metal hydrides, complex hydrides, metalorganic frameworks, and zeolites, are several boron-containing substances including boron nitride nanotubes and boron-doped fullerenes and nanostructures. Recent density functional and quantum Monte Carlo calculations on boron-doped carbon nanostructures suggest that H₂ attaches nondissociatively at the boron sites, with typical binding energies having a T-shaped structure and a vibrationally averaged intermolecular separation of 2.26 Å, which decreases by 0.04 Å when the H₂ subunit is vibrationally excited. The H−H stretch transition of B⁺−H₂ is red-shifted by 220.6 ± 1.5 cm⁻¹ from that of the free H₂ molecule, much more than for other dihydrogen complexes with comparable binding energies. Properties of B⁺−H₂ and the related Li⁺−H₂, Na⁺−H₂, and Al⁺−H₂ complexes are explored through ab initio calculations at the MP2/aug-cc-pVTZ level. The unusually large red-shift for B⁺−H₂ is explained as due to electron donation from the H₂ σ bonding orbital to the unoccupied 2pₓ orbital on the B⁺ ion.

Attachment of $H_2$ to an Isolated $B^+$

ARTICLES

Figure 1. Stable forms of the [BH$_2$]$^+$ system: (a) the minimum energy BH$_2^+$ covalent structure and (b) the weakly bound B$^-$H$_2$ complex. Energies are with respect to the $B^+$ + $H_2$ limit. Structural and energetic parameters are taken from ref 21.

The lower energy BH$_3^+$ form (Figure 1a) features covalent B–H bonds, sp hybridization on the B$^+$ atom, and a linear, $D_{∞h}$ structure. In comparison, the electrostatic B$^-$H$_2$ complex (Figure 1b), which is predicted to lie 53 kcal/mol higher in energy, has a $C_2v$ structure, a relatively long, weak intermolecular bond, and an almost undistorted $H_2$ subunit. This T-shaped configuration for the B$^-$H$_2$ complex is favored by the electrostatic interaction between the B$^+$ cation and the $H_2$ quadrupole moment. The binding energy of the electrostatic complex with respect to the B$^+$ + H$_2$ fragments was measured by Bowers and co-workers as 3.8 kcal/mol through clustering equilibrium measurements, in good agreement with the calculations of Sharp and Gellene (3.4 kcal/mol). Conversion from the B$^-$H$_2$ complex to the covalent BH$_2^+$ form is predicted to entail surmounting a considerable 57 kcal/mol barrier. Intriguingly, transformation from the electrostatic form to the covalent form is expedited in larger B$^-$H$_2$ clusters with a drastic lowering of the barrier to 3.4 kcal/mol for the $n = 3$ cluster.

Here we present and analyze the first rotationally resolved infrared spectrum of the B$^-$H$_2$ complex in order to characterize the bond between a hydrogen molecule and an isolated B$^+$ cation and as a step toward understanding the interaction between H$_2$ and bulk boron-containing materials. Prior to this study, neither the electrostatic B$^-$H$_2$ complex nor the covalent BH$_3^+$ molecule had been observed spectroscopically.

The current investigation complements earlier spectroscopic studies of similar complexes, including Li$^+$-$H_2$, Li$^+$-D$_2$, and Al$^+$-H$_2$, using photodissociation spectroscopy in the H–H or D–D stretch region. The cohesive forces in these metal ion–dihydrogen clusters originate predominantly from electrostatic charge–quadrupole interactions and charge-induced-dipole induction interactions. The spectra, which are obtained by monitoring charged photofragments, generally feature rotationally resolved substructure and provide fundamental structural and vibrational data, including the intermolecular bond length, the frequency of the H$_2$ stretch vibration, and an estimate for the intermolecular stretch frequency.

One significant issue we wish to explore is the correlation between a cluster’s binding energy ($D_0$) and the red-shift in the H$_2$ stretch frequency ($\Delta\nu_{HH}$). This is an important point given that in solid media the dihydrogen binding energy is often estimated from the magnitude of $\Delta\nu_{HH}$; generally, large dissociation energies are associated with large $\Delta\nu_{HH}$ values. Vitillo, Damin, Zecchina, and Ricciardi compiled experimental and theoretical data for dihydrogen interacting with a range of cations, finding a roughly linear correlation between $D_0$ and $\Delta\nu_{HH}$ data for 25 different weakly to moderately bound complexes ($D_0 \leq 8$ kcal/mol). Whereas the Li$^+$-$H_2$ and Na$^+$-$H_2$ data fit the general linear trend, the B$^+$-$H_2$ point lies clear from the other data. Here we confirm experimentally the rather large vibrational red-shift predicted computationally for B$^+$-$H_2$ and investigate its origin through ab initio calculations for B$^+$-$H_2$ and similar dihydrogen complexes that have recently been characterized spectroscopically (Li$^+$-$H_2$, Na$^+$-$H_2$, and Al$^+$-$H_2$). Ultimately, we find that the large vibrational red-shift for B$^+$-$H_2$ is associated with significant electron donation from the H$_2$ orbit bonding orbital to the cation’s empty 2p orbital, which, in the case of B$^+$, lies energetically close by.

2. Experimental and Computational Approaches

The infrared (IR) spectrum of $^{11}$B$^+$-$H_2$ in the H–H stretch region was obtained using infrared photodissociation (IRPD) spectroscopy, whereby $^{11}$B$^+$ photofragments were monitored while the IR wavelength was scanned. The IRPD process entails absorption of an IR photon (having an appropriate frequency to excite the H–H stretch vibrational mode), followed by migration of the vibrational energy into the weak intermolecular bond causing its rupture and liberation of a detectable B$^+$ fragment. The IRPD scheme’s efficacy for obtaining a rotationally resolved infrared spectrum of B$^+$-$H_2$ relies on two factors. First, photoexcitation of the H–H stretch vibrational mode must provide sufficient energy to sever the B$^+$•••H$_2$ bond. This condition is likely satisfied as the B$^+$-$H_2$ dissociation energy has been measured as $\sim$1330 cm$^{-1}$, considerably less than the H–H stretch frequency, which is predicted to be only $\sim$5% lower than that of the free H$_2$ molecule (4161 cm$^{-1}$). Second, the dissociation process must be relatively slow so that individual rovibrational lines are not drastically affected by lifetime broadening, thereby obscuring rotational structure in the spectrum. This implies that the coupling between the H–H stretch vibrational mode and the dissociation coordinate (i.e., the intermolecular bond) should be relatively weak. This has proven to be the case for Li$^+$-$H_2$ and Al$^+$-$H_2$ dihydrogen complexes which exhibit rotationally resolved IRPD spectra in the H–H stretch region.

The IRPD strategy was implemented using a tandem mass spectrometer coupled to a pulsed, tunable IR source (Continuum Mirage 3000 optical parametric oscillator, bandwidth $\sim$0.017 cm$^{-1}$). The B$^+$-$H_2$ complexes were generated in a supersonic expansion of H$_2$ (8 bar) passed over a laser-ablated BN rod. The translating/rotating rod was irradiated with the fundamental (1064 nm, 7 mJ/pulse), doubled (532 nm, 3 mJ/pulse), and quadrupled (266 nm, 1 mJ/pulse) output of a pulsed Nd:YAG laser running at 20 Hz. The B$^+$–H$_2$ ions were mass-selected by a quadrupole mass filter and deflected through 90° by a quadrupole bender into an octopole ion guide where they were overlapped by the counter-propagating IR pulse. Resulting B$^+$ photofragments were mass-selected by a second quadrupole mass filter and detected using a microchannel plate coupled to a scintillator and a photomultiplier tube. We estimate that each IR pulse irradiated $\sim$100 B$^+$–H$_2$ ions. Calibration of the infrared wavelength was achieved using the methods described in refs 24 and 25.

Ab initio calculations at the MP2/aug-cc-pVTZ level were performed to determine optimum geometries, vibrational frequencies, and dissociation energies for the $\text{B}^+$–$\text{H}_2$, Li$^+$–$\text{H}_2$, Na$^+$–$\text{H}_2$, and Al$^+$–$\text{H}_2$ complexes. The calculations were performed using the Gaussian 03 suite of programs. For comparison with experimental values, the calculated $\text{H}–\text{H}$ stretch vibrational frequencies were scaled by the factor required to reconcile the calculated and experimental frequencies for the free $\text{H}_2$ molecule (0.921). Harmonic zero-point energies were accounted for in the determination of cluster dissociation energies. The effect of basis set superposition error (BSSE) on the calculated binding energies was ignored.

3. Results

The infrared spectrum of $\text{B}^+$–$\text{H}_2$ over the 3905–3975 cm$^{-1}$ range is shown in Figure 2. The observed band is associated with excitation of the $\text{H}–\text{H}$ stretch vibrational mode and has the unmistakable form expected for an A-type transition of a T-shaped $\text{B}^+$–$\text{H}_2$ complex (Figure 1b); the observed $K_a = 1–1$ transitions follow $\Delta K_a = 0$ and $\Delta J = 0$, ±1 selection rules, where $J$ is the quantum number associated with the total angular momentum exclusive of nuclear spin, and $K_a$ is the quantum number associated with the projection of the total angular momentum onto the molecule’s A-axis (corresponding to the $\text{B}^+$–$\cdot\cdot\cdot\text{H}_2$ bond). Altogether, 28 transitions were assigned to the $K_a = 1–1$ sub-band (P-branch 12 lines, Q-branch 3 lines, and R-branch 13 lines), with asymmetry doublets resolved in the P and R branches. Transition wavenumbers and assignments are provided as Supporting Information.

The $K_a = 1–1$ transitions were fitted using an A-reduced Watson asymmetric top Hamiltonian, yielding the ground and excited state $B$ and $C$ rotational constants (related to the length of the $\text{B}^+$–$\cdot\cdot\cdot\text{H}_2$ bond), and the $\Delta c$ centrifugal distortion constant (related to the stretching force constant of the $\text{B}^+$–$\cdot\cdot\cdot\text{H}_2$ bond). It is not possible to determine ground and excited state A rotational constants through analysis of the parallel A-type transition. Therefore, for the fit, $A^\prime$ and $A^\prime\prime$ were constrained to 59.33 and 56.37 cm$^{-1}$, the rotational constant of free $\text{H}_2$ in the $n_{\text{HH}} = 0$ and $n_{\text{HH}} = 1$ states, respectively. Note that the fits are quite insensitive to the values of $A^\prime$ and $A^\prime\prime$; virtually identical results are obtained when $A^\prime$ and $A^\prime\prime$ are varied in the range of 58.33 to 56.37 cm$^{-1}$.

![Figure 2](image-url) Infrared spectrum of $\text{B}^+$–$\text{H}_2$ in the $\text{H}–\text{H}$ stretch region obtained by monitoring $\text{B}^+$ photofragments while the infrared wavelength was scanned. The $K_a = 1–1$ transitions are labeled.

### Table 1. Spectroscopic Constants for $\text{B}^+$–$\text{H}_2$ Obtained by Fitting the $\nu_{\text{HH}} K_a = 1–1$ Transitions to a Watson A-Reduced Hamiltonian

<table>
<thead>
<tr>
<th>$\omega_h$</th>
<th>$\Delta\sigma_{\text{HH}}$</th>
<th>$\Delta\nu_{\text{HH}}$</th>
<th>$\nu_{\text{HH}}$</th>
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<tbody>
<tr>
<td>1886</td>
<td>1953</td>
<td>1983</td>
<td>1993</td>
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Unless otherwise indicated, the units are inverse centimeters. For each value, the error in the last significant figure(s) is given in brackets. Calculated values are from CCSD(T)/aug-cc-pVTZ and MP2/aug-cc-pVTZ calculations. Sub-band origin for $K_a = 1–1$ transitions.

### References

(26) Frisch, M. J.; et. al. Gaussian 03, revision D.01, 2005.
leading to a relative stabilization of $B^+\text{-H}_2$ (ortho) relative to $B^+\text{-H}_2$ (para). Therefore, in the ion source, $B^+\text{-H}_2$ (para) complexes are rapidly converted to $B^+\text{-H}_2$ (ortho) complexes through exothermic ligand switching reactions.

Because $K_a = 0-0$ transitions are not observed in the spectrum, at this stage it is not possible to ascertain precisely the band center for the $\nu_{\text{HH}}$ transition. However, one can anticipate that the band center will lie between $\Delta b$ and $2\Delta b$ higher in energy than the $K_a = 1-1$ sub-band center ($\Delta b \sim 3$ cm$^{-1}$ is the difference in the $B_2$ rotational constant in the $n_{\text{HH}} = 0$ and $n_{\text{HH}} = 1$ states). The lower limit (3939 cm$^{-1}$) is based on the $B^+\text{-H}_2$ complex being a rigid prolate rotor, whereas the upper limit (3942 cm$^{-1}$) corresponds to a complex with free internal rotation of the hydrogen subunit—the actual situation will lie some way between these two extremes. The average of the limiting values (3940.6 cm$^{-1}$) corresponds to a red-shift of $-220.6$ cm$^{-1}$ with respect to the $Q_{\text{II}}(0)$ transition of the free H$_2$ molecule.

4. Discussion

The spectroscopic data for $B^+\text{-H}_2$ can be interpreted to yield quantitative structural and vibrational information, which together with the dissociation energy measurement of Kemper et al. would serve as solid benchmarks for ab initio calculations. Tables 1 and 2 summarize the calculated and spectroscopic data. Generally, the spectroscopic data confirm that $B^+\text{-H}_2$ is a weakly bound electrostatic complex as predicted by previous ab initio calculations and bond dissociation energy measurements.

Due primarily to the charge–quadrupole electrostatic interaction, the complex prefers a T-shaped configuration with the linear configuration lying 998 cm$^{-1}$ higher in energy (according to the MP2/aug-cc-pVTZ calculations). Despite the considerable energetic barrier for internal rotation, the complex should exhibit a relatively large zero-point bending excitation because of the H$_2$ molecule’s large rotational constant. As previously pointed out, the main consequence of this, insofar as the spectroscopic constants are concerned, is that $B - C$ is larger than it would be for a rigid T-shaped molecule (that is, there is large asymmetry splitting). Note that even under these circumstances the vibrationally averaged intermolecular separation ($R_o$) can be estimated from $B = (B + C)/2$.

The vibrationally averaged $B^+\cdots\cdot\text{H}_2$ intermolecular separation estimated from $B$ ($R_o = 2.26$ Å) is close to the equilibrium separation determined from the CCSD(T)/aug-cc-pVTZ and MP2/aug-cc-pVTZ calculations of Sharp and Gellene ($R_e = 2.25$ and 2.27 Å, respectively). Because of zero-point vibrational motion in the intermolecular stretching coordinate, one might expect $R_o$ to be slightly larger than $R_e$. The similarity of the experimental $R_e$ and computed $R_o$ values may indicate that the existing calculations slightly overestimate the equilibrium intermolecular bond length. Ultimately, the best way of estab-

<table>
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<th>Table 2. Experimental and Calculated Dissociation Energies ($D_0$), H-$\text{H}$ Stretch Vibrational Frequency Shifts ($\Delta \nu_{\text{HH}}$), Intermolecular Separations ($R_e$ and $R_o$) and H-$\text{H}$ Bond Length Changes ($\Delta R_{\text{HH}}$) for Selected M$^+\text{-H}_2$ Clusters$^a$</th>
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<tr>
<td>Species</td>
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<td>Li$^+$-H$_2$</td>
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<td>B$^+$-H$_2$</td>
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<td>Na$^+$-H$_2$</td>
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<td>Al$^+$-H$_2$</td>
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$^a$ Calculated values were obtained at the MP2/aug-cc-pVTZ level. Also listed the metal cation charges and electronic configurations determined from NBO calculations. From rovibrational calculations described in ref 34. Reference 20. Reference 35. Reference 26. Reference 23. Reference 25.

Figure 3. H-$\text{H}$ stretch vibrational frequency shift ($-\Delta \nu_{\text{HH}}$) plotted against dissociation energy ($D_0$) for Li$^+$-H$_2$, B$^+$-H$_2$, Na$^+$-H$_2$, and Al$^+$-H$_2$. Both experimental and calculated values are shown. The line shows the predicted relationship between vibrational red-shift and dissociation energy for a point positive charge interacting with an H$_2$ molecule.32,33

lishing contact between theory and experiment is through rovibrational calculations using a full three-dimensional potential energy surface, as has been accomplished for the Al$^+$-H$_2$ complex.25

Excitation of the H-$\text{H}$ stretch mode leads to a slight shortening of the intermolecular bond (by 0.04 Å), which may be a consequence of the enhanced charge–quadrupole electrostatic interaction resulting from a ∼10% increase in the vibrationally averaged quadrupole moment of the H$_2$ molecule.32 It is not possible to deduce the H-$\text{H}$ bond length from the $B$ and $C$ rotational constants. However, on the basis of the MP2/aug-cc-pVTZ calculations, the H-$\text{H}$ bond is predicted to be 0.014 Å longer than for the free H$_2$ molecule (the CCSD(T)/aug-cc-pVTZ calculations predict a 0.013 Å increase).31 There is also excellent agreement between the experimental estimate for the intermolecular stretch mode determined from $\Delta J$ and $B$ and the calculated value (346 cm$^{-1}$, Table 1).

An exceptional attribute of the $B^+\text{-H}_2$ complex is the relatively large frequency shift for the H-$\text{H}$ stretch mode ($-\Delta \nu_{\text{HH}} = -220.6$ cm$^{-1}$) given its modest dissociation energy ($D_0 = 1330$ cm$^{-1}$). Generally, for dihydrogen complexes, the dissociation energy and the magnitude of the vibrational red-shift are strongly correlated.3,33 The unusual nature of $B^+\text{-H}_2$ is apparent from Figure 3 where the $-\Delta \nu_{\text{HH}}$ is plotted against binding energy for Li$^+$-H$_2$, B$^+$-H$_2$, Na$^+$-H$_2$, and Al$^+$-H$_2$. Most noticeably, the $B^+\text{-H}_2$ complex has a smaller dissociation energy than Li$^+$-H$_2$ (1330 vs 1675 cm$^{-1}$) and a longer intermolecular bond (2.26 vs 2.06 Å), yet the frequency shift of the H-$\text{H}$ stretch mode for B$^+$-H$_2$ ($-221$ cm$^{-1}$) is more than twice that of Li$^+$-H$_2$ ($-108$ cm$^{-1}$). For Li$^+$-H$_2$ and Na$^+$-H$_2$, the relationship between the vibrational red-shift...
and binding energy is compatible with predictions based on consideration of the electrostatic and induction interactions between H₂ and a point charge (solid line in Figure 3). This is obviously not the case for B⁺–H₂ (and to some extent Al⁺–H₂) where the red-shift is clearly larger than expected from purely electrostatic and induction influences.

To rationalize the larger than expected vibrational red-shift for B⁺–H₂ it is instructive to consider the valence molecular orbitals (MOs). As shown in Figure 4, the two occupied valence MOs can be considered as superpositions of the H₂ σ_g bonding orbital and the B⁺ 2s orbital. The lower of the two, a bonding combination with respect to the intermolecular bond, has more 2s character, whereas the highest occupied molecular orbital (HOMO), which is an antibonding combination with respect to the intermolecular bond, has more σ_g character. Importantly, the HOMO also has a significant admixture of the B⁺ 2p orbital such that the amplitude of the MO is diminished in the intermolecular region and enhanced on the opposite side of the B⁺ atom. The net effect of this 2s/2p hybridization on the B⁺ ion is that electron density is transferred from the H₂ σ_g orbital to the opposite side of the B⁺ ion resulting in a weakening of the H–H bond (and consequently a large vibrational red shift). A similar although less pronounced effect occurs for Al⁺–H₂, which has a comparable vibrational red-shift to Na⁺–H₂, but a somewhat lower binding energy (see Figure 3). The Al⁺ 3s hybrid forms bonding and antibonding combinations with the H₂ σ_g orbital with the HOMO having some 3p character. The effect is weaker for Al⁺–H₂ than for B⁺–H₂ because of the Al⁺ ion’s larger valence radius (which also decreases the intermolecular bond strength). In contrast, for the Li⁺–H₂ and Na⁺–H₂ complexes, the unoccupied valence s and p orbitals lie well above the H₂ σ_g orbital and play little role in the intermolecular bonding.

The MO considerations outlined above are supported by a natural population analysis. Results for B⁺–H₂, Li⁺–H₂, Na⁺–H₂, and Al⁺–H₂ are summarized in Table 2. For B⁺–H₂, the B⁺ atom was found to have a charge of +0.98 and an effective [He]2s²2p⁹ configuration. Electron donation to the B⁺ atom’s 2p orbital occurs predominately from the H₂ σ_g bonding orbital, consistent with the large ν_HH red shift. In contrast, significantly less electron donation is found for Li⁺–H₂, Na⁺–H₂, and Al⁺–H₂ (see Table 2). The appreciable electron donation from the H₂ σ_g bonding orbital to the B⁺ atom’s 2p orbital in B⁺–H₂ is also consistent with the significant 0.014 Å lengthening of the H–H bond (compared to the free H₂ molecule), which is substantially greater than for Li⁺–H₂ (0.009 Å), Na⁺–H₂ (0.005 Å), and Al⁺–H₂ (0.005 Å).

The current study implicates hybridization of the B⁺ ion’s 2s and 2p orbitals in the unusually large vibrational red-shift for the B⁺–H₂ complex. Hybridization of a metal atom cation’s half-filled or filled valence s orbital induced through polarization by an attached ligand was originally proposed to explain the properties of M⁺–H₂ and M⁺–CH₄ complexes. The molecular ligand essentially pushes electron density to the opposite side of the atomic cation thereby mitigating the Pauli repulsion between the ligand and the s orbital. A further consequence is that complexes such as B⁺–(H₂)₂, Al⁺–(H₂)₂, Mg⁺–(H₂)₂, Mn⁺–(H₂)₂, and Zn⁺–(H₂)₂ are predicted to have a bent structure because in this configuration the two ligands can concertedly polarize the metal cation core. In contrast, complexes such as Li⁺–(H₂)₂ and Na⁺–(H₂)₂, which possess M⁺ cores that are not easily polarized, are predicted to have structures in which the hydrogen molecules are on opposite sides of the metal cation core so that ligand–ligand repulsion is minimized.

Finally, it is worth commenting on the vibrationally induced breakup of the B⁺–H₂ complex. The experimental strategy relies on the excitation of metastable B⁺–H₂ (ν_HH = 1) resonances that result in B⁺ + H₂ fragments. An estimate for the metastable state lifetime can be obtained through the uncertainty principle from the transition linewidths, which are on the order of 0.1 cm⁻¹. Taking the 0.017 cm⁻¹ bandwidth of the infrared light source into account, the lifetime broadening contribution is estimated as ~0.05 cm⁻¹. This corresponds to a lifetime of 100 ps or 1.3 × 10⁴ oscillations of the H₂ subunit. This lifetime should be taken as a provisional lower limit due to possible power broadening of the transitions.

5. Concluding Remarks

In conclusion we have obtained the first infrared spectrum of the B⁺–H₂ complex, providing fundamental structural and vibrational data that can be used to test and refine computational approaches for describing the attachment of dihydrogen to boron ions and boron-containing materials.

The main outcomes of this work can be summarized as follows:

1. The B⁺–H₂ complex possesses a rotationally resolved H–H stretch band red-shifted by 220.6 ± 1.5 cm⁻¹ from the stretch fundamental of the free H₂ diatomic molecule.
2. The complex has a T-shaped equilibrium structure with an average intermolecular B⁺···H₂ separation of 2.26 Å, decreasing by 0.04 Å when the H₂ subunit is vibrationally excited.
3. A 100 ps lower limit for the predissociation lifetime for B⁺–H₂ (ν_HH = 1) is estimated from the line broadening.

(37) Glendenning, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO, version 3.1.
4. The unusually large vibrational red-shift for the H–H stretch mode of B⁺–H₂ (220.6 ± 1.5 cm⁻¹) is explained as due to electron donation from the H₂ σ_g bonding orbital to the empty B⁺ 2p_z orbital. This orbital effect augments the familiar electrostatic and induction causes for the H–H red shift which operate for complexes such as Li⁺–H₂ and Na⁺–H₂.

Ideally, the studies of the electrostatic B⁺–H₂ complex described in this paper will be complemented by spectroscopic investigations of the yet uncharacterized BH₂⁺ molecular cation. Due to the large binding energy of BH₂⁺, infrared photodissociation studies in which the fragment B⁺ cation is detected are not feasible. Instead, it may be possible to probe the BH₂⁺–Ar species by monitoring the argon atom loss channel; unfortunately this strategy involves sacrificing the prospect of obtaining a rotationally resolved spectrum of the bare BH₂⁺ ion. Alternatively, it may be feasible to probe the species directly using conventional infrared absorption in a plasma discharge.

Ultimately, a comprehensive understanding of the BH₂⁺/B⁺–H₂ system will be derived from more extensive theoretical studies. Existing ab initio investigations have focused on stationary points of the potential energy surface. The future challenge is to develop potential energy surfaces describing the BH₂⁺/B⁺–H₂ system and to use these for computations of the rovibrational energy levels. Such studies will yield theoretical data directly comparable with the spectroscopic data reported in this work, deliver more reliable values for vibrational frequencies, give more accurate values for the dissociation energy by accounting properly for zero-point vibrational energy, and provide insights into rearrangement processes connecting the BH₂⁺ and B⁺–H₂ configurations.

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