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6. AUTHOR(S) Paul J. Dagdigian

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Johns Hopkins University Department of Chemistry 3400 N. Charles Street Baltimore, MD 21218-2685 AFRL-SR-BL-TR-98-0394

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13. ABSTRACT (Maximum 200 words) Experimental investigations of the non-bonding interactions of the boron atom, in its ground and resonance-excited electronic states, with the hydrogen molecule and other species have been carried in conjunction with collaborative theoretical work by Millard Alexander, at the University of Maryland. Fluorescence excitation and depletion spectra of weakly bound complexes involving the boron atom have been observed and used to deduce the relevant interaction potentials. The aluminum-neon interaction has also been probed in this way. Chemical reaction within the electronically excited boron-hydrogen complex has been probed through observation of the chemiluminescence of the BH product. A first extension to the study of larger complexes has been made with the observation of the BAr<sub>2</sub> complex.

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**WEAK INTERACTIONS OF BORON, ALUMINUM,  
AND CARBON ATOMS: EXPERIMENT**

**FINAL REPORT**

**Paul J. Dagdigian**

**The Johns Hopkins University**

**Air Force Office of Scientific Research**

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## TABLE OF CONTENTS

	page
I. Summary of Work and Description of Work Accomplished	1
A. Characterization of Boron – Rare Gas Diatomic Interactions	2
B. Boron – Hydrogen Interactions	4
C. Boron in Larger Clusters and Matrices	6
D. Interactions Involving the Aluminum Atom	7
E. Radiative and Nonradiative Decay of $BH(b^3\Sigma^-)$	7
F. Observation and Analysis of Two $Br_2$ Band Systems	8
II. References	9
III. List of Publications Prepared under AFOSR Grant No. F49620-95-1-0046	11
IV. List of Participating Scientific Personnel	13

## I. SUMMARY OF WORK AND DESCRIPTION OF WORK ACCOMPLISHED

A primary goal of this project has been the characterization of non-bonding interactions of the boron atom, in its ground and resonance-excited electronic states, with the hydrogen molecule and rare gases. These interaction potentials are critical ingredients in the theoretical modeling of cryogenic media doped with isolated boron atoms. Since electronic spectroscopy is the primary diagnostic tool in the experimental investigation of such doped cryogenic matrices, knowledge of the interaction between the matrix species and dopant in both its ground and electronically excited states is required to interpret such spectra. Because of the need for a close interaction between experiment and theory in the elucidation of the dopant-matrix bimolecular interactions and the structure of small complexes of these species, we have collaborated very closely with the group of Professor Millard H. Alexander, of the University of Maryland, who has also been funded by AFOSR for this work.

With the support of this grant, we have succeeded in observing the electronic fluorescence excitation spectra of several boron-rare gas diatomic complexes, and these have been used to deduce, in conjunction with electronic structure calculations by Alexander's group, the appropriate diatomic interaction potentials. We have also observed the electronic spectrum of the B-H<sub>2</sub> complex. This spectrum has been modeled successfully with interaction potentials calculated by Alexander's group. In an initial extension to the study of larger complexes, we have observed the BAr<sub>2</sub> complex, whose spectrum was assigned by comparison with theoretical spectra simulated by Alexander and co-workers with our deduced B-Ar interaction energies. These boron interaction potentials are now being used by Alexander and others for simulations of larger boron-doped systems.

In the course of this project, we have serendipitously obtained results relevant to other chemical systems of AFOSR interest. This includes observation of the BH molecule in its lowest, metastable excited electronic state and measurement of its radiative lifetime and observation of several electronic band systems of Br<sub>2</sub>.

The following sections summarize in more detail of these research accomplishments and their relevance to other work.

## A. Characterization of Boron – Rare Gas Diatomic Interactions

**1. The BNe Complex.** There are two resonance transitions in atomic boron with  $\lambda > 200$  nm: a transition to the lowest Rydberg state,  $2s^2 3s \ ^2S \leftarrow 2s^2 2p \ ^2P$  at 249.8 nm, and a transition to an excited valence state,  $2s^2 2p^2 \ ^2D \leftarrow 2s^2 2p \ ^2P$  at 208.9 nm.<sup>1</sup> Extending our initial study of the BAr complex,<sup>2,3</sup> supported by a previous AFOSR grant, we have observed the BNe complex through laser fluorescence excitation (FE) of several electronic transitions. For the  $B^2\Sigma^+ - X^2\Pi$  transition, in which the excited state correlates to the B(3s) Rydberg state, we observed a broad, unstructured feature characteristic of a transition to a dissociative excited state.<sup>4</sup>

In conjunction with these experiments, Alexander's group carried out *ab initio* calculations of the BNe  $X^2\Pi$ ,  $A^2\Sigma^+$ , and  $B^2\Sigma^+$  electronic states using two methods: multireference, internally contracted, configuration interaction (MRCI) and coupled cluster with perturbative inclusion of triple excitations [UCCDS(T)].<sup>4</sup> As a modification of the *ab initio* potentials, the correlation energy was scaled following an earlier suggestion by Brown and Truhlar.<sup>5</sup> With these potential energy curves, we obtained a near quantitative simulation of the experimental free  $\leftarrow$  bound profile, including even a subtle oscillatory structure at high energy. This agreement confirms the accuracy of the calculated potential energy curves.

We also observed the spectrum of BNe in the wavelength region near the atomic transition at 208.9 nm to the excited valence state.<sup>6</sup> From simple molecular orbital arguments, we expect the binding energies of the 3 molecular states arising from the  $B(2s^2 2p^2 \ ^2D) + \text{Ne}$  asymptote to be  $C^2\Delta > D^2\Pi > E^2\Sigma^+$ . We assigned bands in the FE spectrum corresponding to excitation of the *C* and *D* states and also observed the onset to the  $B^* + \text{Ne}$  dissociation continuum, allowing estimation of the binding energies. We find that these are modest for the *X*, *C*, and *D* states. In particular, the ground state dissociation energy [ $D_0'' = 21.3 \pm 0.2 \text{ cm}^{-1}$ ] is well reproduced by the scaled *ab initio* potential energy

curves. The bound nature of the  $C$  and  $D$  valence excited states contrasts sharply with the purely repulsive form of the potential energy curve of the  $B^2\Sigma^+$  Rydberg state.

**2. The BAr Complex.** Extending our initial work on BAr,<sup>2, 3</sup> we succeeded in observing the spin-orbit excited manifold,  $X^2\Pi_{3/2}$ , in the ground electronic state.<sup>7</sup> We found the  $X^2\Pi$  spin-orbit splitting to be slightly larger than a simple estimate of this splitting, *i.e.*  $2/3$  of the B atomic  $^2P_{3/2} - ^2P_{1/2}$  splitting. Our experimental value, in fact, agrees quite well with a theoretical estimate which takes into account the slight transition to Hund's case (c) coupling, through mixing with the low-lying  $A^2\Sigma^+$  state. This good agreement validates the usual assumption that the effect of the spin-orbit splitting on the structure and energetics of weakly-bound clusters involving B atoms can be modeled accurately by assuming that the B atomic spin-orbit constant is unaffected by complexation.

We also used FE and fluorescence depletion (FD) spectroscopy to characterize the BAr electronic states emanating from the  $B(2s2p^2\ ^2D) + \text{Ar}$  asymptote.<sup>8</sup> With FE detection we observed transitions to the modestly bound  $D^2\Pi$  and  $E^2\Sigma^+$  states, as well as the onset to the  $B(^2D) + \text{Ar}$  dissociation continuum. In contrast to BNe, the BAr( $C^2\Delta$ ) state decays nonradiatively. We employed the FD technique to observe this state. This method is a folded variant of optical-optical double resonance, in which the two lasers access the same lower level. Transitions to non-fluorescing states are observed by monitoring the effect of the depletion laser on fluorescence induced by the probe laser. A series of bands for  $^{11}\text{BAr}$  and  $^{10}\text{BAr}$  were separately observed, using the corresponding  $B - X$  (8,0) bands as probe transitions. The derived binding energy for this state is extremely large for a metal – rare gas van der Waals complex [ $D_e = 3705 \pm 10 \text{ cm}^{-1}$ ].<sup>9</sup> We surmised that the  $C^2\Delta$  state decays nonradiatively through spin-orbit induced predissociation through a repulsive  $^4\Pi$  state which correlates with the lower  $B(2s2p^2\ ^4P) + \text{Ar}$  asymptote.

In a collaborative theoretical effort, Sohlberg and Yarkony, also at Johns Hopkins University, calculated the potential energy curve of the BAr( $C^2\Delta$ ) state.<sup>10</sup> The strong binding arises from dative bonding of the Ar  $3p\sigma$  orbital into the empty B  $2p\sigma$  orbital. These authors also found that nonradiative predissociation through the  $^4\Pi$  state correlating with the lower  $B(2s2p^2\ ^4P)$  asymptote is the dominant mode of decay of the  $C^2\Delta$  state.<sup>11</sup>

In summary, the potential energy curves of both the  $B^2\Sigma^+$  and  $C^2\Delta$  states are dramatically different in BNe and BAr. The BAr( $B^2\Sigma^+$ ) state has a substantial binding

energy [ $D_e = 1101 \pm 10 \text{ cm}^{-1}$ ], with a  $108 \text{ cm}^{-1}$  barrier to dissociation and a shallow outer minimum.<sup>2</sup> By contrast, the  $\text{BNe}(B^2\Sigma^+)$  state is purely repulsive, with only a slight inflection hinting at an attractive interaction.<sup>4</sup> Similarly, the  $\text{BAr}(C^2\Delta)$  state is strongly bound,<sup>8</sup> while the binding energy of  $\text{BNe}(C^2\Delta)$  is modest [ $D_0 = 111.3 \pm 0.4 \text{ cm}^{-1}$ ].<sup>4</sup>

**3. The BKr Complex.** In view of the dramatic differences between BNe and BAr, we also carried out a spectroscopic study of the BKr complex.<sup>12</sup> As in BAr, we observe excitation to the  $D^2\Pi$  state in the FE spectrum. However, we could not observe the  $C^2\Delta$  state by either FE or FD detection. In the neighborhood of the B atomic  $3s \leftarrow 2p$  transition, no FE bands assignable to diatomic BKr were found. Instead complicated excitation features were seen, which we believe are associated with higher  $\text{BKr}_n$  clusters. We surmised that the  $\text{BKr}(B^2\Sigma^+)$  state is predissociated by the repulsive  $^4\Pi$  state and thus not seen in the FE spectrum. By contrast, in BAr the corresponding  $^4\Pi$  state also crosses the  $B^2\Sigma^+$  state, but no evidence is seen of predissociation.<sup>2</sup> The one-electron part of the  $B^2\Sigma^+ - ^4\Pi$  spin-orbit matrix element is zero, and, in BAr, the weak two-electron part cannot compete with radiative decay. However, in BKr spin-orbit induced predissociation competes effectively with radiative decay through the heavy atom effect. A review of our work on boron – rare gas diatomic complexes has recently been written.<sup>13</sup>

## B. Boron – Hydrogen Interactions

We have observed laser fluorescence excitation spectra for both the  $\text{B}\cdots\text{H}_2$  and  $\text{B}\cdots\text{D}_2$  complexes near the B atomic  $3s \leftarrow 2p$  transition.<sup>14</sup> Despite the substantial exothermicity of the  $\text{B}(3s) + \text{H}_2 \rightarrow \text{BH} + \text{H}$  reaction, no evidence for chemical reaction was found. For both isotopomeric complexes, we observed a broad, structureless FE feature akin to that observed for BNe to the blue of the 249.8 nm B atomic resonance line. This feature has an asymmetric shape and falls off much more sharply on the blue side of the maximum intensity. Its width is less for  $\text{B}\cdots\text{D}_2$  than for  $\text{B}\cdots\text{H}_2$ .

In order to model these FE spectra of  $\text{B}\cdots\text{H}_2$  and  $\text{B}\cdots\text{D}_2$ , Alexander and co-workers<sup>15, 16</sup> have used MRCI methods to determine the  $\text{B}(2p, 3s)\text{-H}_2$  interaction energies. Following the work of Rebentrost and Lester,<sup>17</sup> the calculated  $\text{B}(2p)\text{-H}_2$  adiabatic energies were transformed to an approximate diabatic basis, characterized by the orthogonal projections of the  $2p$  orbital along the  $\text{B-H}_2$  axis and were fit to a general

angular expansion. These expansions were then used<sup>16</sup> to calculate the energies and vibrational wave functions of the B( $2p$ )-H<sub>2</sub>, D<sub>2</sub> complexes.

With the calculated B( $2p$ )-H<sub>2</sub>, D<sub>2</sub> wave functions and the B( $3s$ )-H<sub>2</sub> interaction energy,<sup>16</sup> it was possible to simulate<sup>14</sup> quite well our observed FE spectra of the  $3s \leftarrow 2p$  transitions in the B $\cdots$ H<sub>2</sub> and B $\cdots$ D<sub>2</sub> complexes. The spectra are consistent with excitation of the complexes of the H<sub>2</sub> or D<sub>2</sub> nuclear spin modifications corresponding to the  $j = 1$  rotational level. Because of their ability of polarize and hence optimize the B-H<sub>2</sub>/D<sub>2</sub> interaction, these are significantly more strongly bound than the corresponding  $j = 0$  complexes. It should be noted that the experimental spectrum could be simulated well only with specific inclusion of the threefold electronic degeneracy of the B( $2p$ ) atom and the threefold rotational degeneracy of the  $o$ -H<sub>2</sub> molecule. The broad, structureless nature of the spectra is found to be due to the purely repulsive nature of the B( $3s$ )-H<sub>2</sub> PES within the Franck-Condon region. The narrower B $\cdots$ D<sub>2</sub> spectral feature is due to a smaller spread of the B-D<sub>2</sub> separation in the ground state vibrational wave function.

In FE scans we were unable to detect electronic transitions of the B $\cdots$ H<sub>2</sub> complex to excited valence states correlating with the B( $2s2p^2\ ^2D$ ) + H<sub>2</sub> asymptote. We were nonetheless successful in observing these electronic transitions by FD spectroscopy.<sup>18</sup> Thus, these excited states must decay nonradiatively. The FD spectrum possesses several broad, unresolved features lying both to the blue and the red of the excitation energy of the B\* + H<sub>2</sub> asymptote. This implies that there are both attractive and repulsive B\*-H<sub>2</sub> PES's in the Franck-Condon region.

We found that these excited states are removed, in part, through chemical reaction, to form electronically excited BH products.<sup>19</sup> In particular, upon formation of electronically excited B( $^2D$ ) $\cdots$ H<sub>2</sub> we observed BH  $A \rightarrow X$  and  $b \rightarrow a$  chemiluminescence due to the formation of BH in its  $A^1\Pi$  and  $b^3\Sigma^-$  electronic states. This chemiluminescence is observed mainly for excitation of the lower-energy B\* $\cdots$ H<sub>2</sub> features and suggests that BH\* is formed preferentially through reaction on attractive B( $^2D$ )-H<sub>2</sub> PES's. From analysis of the BH chemiluminescence spectra, we find that the BH( $A$ ,  $b$ ) products possess considerable internal excitation.<sup>19</sup> All bound BH( $A^1\Pi$ ) and all energetically allowed BH( $b^3\Sigma^-$ ) rovibrational levels have significant populations. This is indicative of the attractive nature of the B( $^2D$ )-H<sub>2</sub> PES's on which the reaction is occurring.

In related work, we succeeded in observing the  $B\cdots N_2$  complex in FE scans near the B atomic  $3s \leftarrow 2p$  transition. We observe several broad peaks in the spectra, all to the blue of the estimated excitation energy to reach the  $B(3s)-N_2$  asymptote. The interpretation of this spectrum is still in progress. We believe that the structured nature of the  $B\cdots N_2$  spectrum is due to the fact that the rotational motion of the  $N_2$  moiety is strongly affected by the anisotropy of the  $B-N_2$  interaction, unlike the nearly free  $H_2$  rotational motion in the  $B\cdots H_2$  complex.

### C. Boron in Larger Clusters and Matrices

As a compliment to the calculations by Alexander's group on  $BAr_n$  ( $n > 1$ ) complexes,<sup>20, 21</sup> we have investigated the FE spectrum of high-pressure supersonic beams of B seeded in Ar. At high Ar source backing pressures, we have observed a new feature in the FE spectrum to the blue of the all the bands assignable to the diatomic  $BAr$  complex.<sup>21</sup> Alexander's group has modeled the  $3s \leftarrow 2p$  excitation spectrum of the  $BAr_2$  complex, and this spectrum agrees quantitatively, both in shape and its spectral shift from the corresponding atomic transition, with our observed feature.<sup>21</sup> This modeling involves semiclassical calculation of the spectrum using the ground  $BAr_2$  vibrational wave function by variational and diffusion Monte Carlo methods. The  $B(2p, 3s)Ar$  potential energy curves employed were modified *ab initio* and RKR potentials adjusted to fit all our experimental observations on the diatomic  $BAr$  complex.

Our results, both theoretical and experimental, on the electronic spectrum of small complexes containing atomic B have implications for the interpretation of the uv absorption spectra of matrix isolated B atoms. Despite the fact that the first B atomic resonance transition occurs at 249.8 nm, spectra of boron-containing matrices, with B atoms prepared either by effusion from a high-temperature oven<sup>22</sup> or by laser ablation,<sup>23, 24</sup> display detectable absorptions only for  $\lambda < 220$  nm. Based on our observations of a strong shift to the blue of the  $3s \leftarrow 2p$  transition as Ar atoms are attached to atomic B, we suspect that this transition is broadened and blue shifted perhaps to the point of undetectability. We also see chemical reaction within  $B(2s2p^2 \ ^2D)\cdots H_2$  complexes. This suggests the possibility of photobleaching upon excitation of this electronic state in a hydrogen matrix.

## D. Interactions Involving the Aluminum Atom

In an initial study of non-bonding interactions of the aluminum atom, we have succeeded in observing the fluorescence excitation spectrum of the AlNe complex, specifically the  $3d \leftarrow 3p$  and  $5s \leftarrow 3p$  transitions.<sup>25</sup> Aluminum atoms were prepared by 193 nm photolysis of trimethyl aluminum at the source orifice. Transitions from both lower-state spin-orbit levels [ $X^2\Pi_{1/2,3/2}$ ] were observed. From observations of the onset to the Al( $3d$ ) + Ne continuum, dissociation energies for the various AlNe electronic states were determined. The experimentally determined dissociation energy for the  $X_2^2\Pi_{3/2}$  level [ $D_0 = 32.3 \pm 0.3 \text{ cm}^{-1}$ ] is larger than that for the ground  $X_1^2\Pi_{1/2}$  level [ $D_0 = 14.1 \pm 0.3 \text{ cm}^{-1}$ ]. These are in good agreement with values calculated using *ab initio* AlNe( $X^2\Pi$ ,  $A^2\Sigma^+$ ) potential energy curves.

This experiment was motivated by our interest in the Al–H<sub>2</sub> interaction. Indeed, the laser fluorescence excitation spectrum of the Al⋯H<sub>2</sub> complex has recently been observed. Data acquisition and analysis are presently in progress.

## E. Radiative and Nonradiative Decay of BH( $b^3\Sigma^-$ )

Supported by a previous AFOSR grant, we detected BH( $X^1\Sigma^+$ ) in supersonic beams containing photolyzed B<sub>2</sub>H<sub>6</sub> and characterized the Ar–BH complex.<sup>26, 27</sup> We have now detected BH in its lowest excited electronic state,  $a^3\Pi$ , through fluorescence excitation in its  $a^3\Pi - b^3\Sigma^-$  band system, which has recently been thoroughly analyzed by C. Brazier,<sup>28</sup> at the Phillips Laboratory (Edwards AFB). This transition has been used by E. Boehmer and D. Benard, at the Rockwell International Science Center, to estimate BH( $a$ ) concentrations in diagnostic experiments on a NF( $a^1\Delta$ )/BH chemical laser.<sup>29</sup>

We have measured decay lifetimes for a number of BH( $b^3\Sigma^-$ ,  $v' = 0 - 4$ ) rotational/fine-structure levels.<sup>30</sup> The lifetimes for  $v' = 3$  and 4 are somewhat smaller than expected for purely radiative decay, confirming that the  $b$  state is predissociated by the repulsive  $1^3\Sigma^+$  state.<sup>31</sup> Our measured decay lifetimes agree well with radiative and nonradiative rates calculated by Yarkony and Pederson.<sup>30</sup> This collaborative work provided an accurate value of the oscillator strength of the BH  $b - a$  band system, so that absorbances in this band system can be reliably converted into BH( $a$ ) concentrations.

## F. Observation and Analysis of Two Br<sub>2</sub> Band Systems

In our initial experiments to generate B atom van der Waals complexes, we employed BBr<sub>3</sub> as the photolytic precursor. Concurrently, we observed an extensive series of molecular bands, which we identified as transitions out of metastable excited electronic states of the Br<sub>2</sub> molecule. In collaboration with Joel Tellinghuisen (Vanderbilt U.) and Michael Heaven (Emory U.), these Br<sub>2</sub> bands, which comprise (v',0) progressions in the  $D'2_g(3P_2) \leftarrow A'2_u(3\Pi)^{32}$  and  $\beta 1_g(3P_2) \leftarrow A 1_u(3\Pi)^{33}$  transitions, have been rotationally and vibrationally analyzed. These transitions have previously only been observed in emission from discharges, and our study has considerably extended the knowledge of the potential energy curves of these states.

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#### IV. LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

Paul J. Dagdigan, Principal Investigator, Professor of Chemistry.

Eunsook S. Hwang, Graduate Student, Ph. D. degree granted in 1995, thesis title: "Spectroscopic Studies of van der Waals Complexes Involving Group 13 Atoms and Their Hydrides," available from Dissertation Abstracts (no. AAI9533267, 170 pages).

Xin Yang, Graduate Student, Ph. D. degree expected in 1998.

Haeryung Lee, Graduate Student, M. S. degree granted in 1997.

Irina Bondarevich, Graduate Student.