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13. ABSTRACT (Maximum 200 words) Collaborative experimental and theoretical investigations of non-bonding interactions of the light atoms boron, carbon, oxygen, and aluminum with the hydrogen molecule and other species (rare gases and small molecules) have been carried out. Fluorescence excitation and depletion spectra of weakly bound atom – molecule complexes, prepared in supersonic molecular beams, have been recorded and analyzed to derive information on the relevant interaction potentials involving the ground and excited electronic states of the atoms. In a theoretical approach toward understanding these interactions, sophisticated quantum chemical methods have been employed to compute accurate interaction potentials. The derived potential energy surfaces have been employed to estimate the binding energies and spectroscopic parameters of binary complexes. Comparison with experimental data provides important information to calibrate the accuracy of the computed interactions. Monte-Carlo methods have been employed to determine the binding energies of larger complexes. Using path integral molecular dynamics and interaction potentials derived from our work, the equilibrium properties of a boron impurity trapped in solid <i>para</i> -hydrogen have been investigated. A semiclassical Franck-Condon technique was employed to simulate the $3s \leftarrow 2p$ absorption spectrum of the B chromophore.					
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**THE INTERACTION OF LIGHT ATOMS
WITH SMALL MOLECULAR CLUSTERS**

FINAL REPORT

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I. SUMMARY OF WORK AND DESCRIPTION OF WORK ACCOMPLISHED

The goal of this project has been the characterization of non-bonding interactions involving primarily the aluminum atom, and secondarily the boron, oxygen, and carbon atoms, in their ground and lower excited electronic states, with the hydrogen molecule, and also rare gases and other molecular species. These interaction potentials are critical in the theoretical modeling of cryogenic media, in particular solid hydrogen, doped with isolated atoms and in the interpretation of their electronic spectra, which are the primary diagnostic tool in the experimental investigation of such systems. An understanding of these interactions and how they affect the structure and stability of the doped solid and the electronic spectrum of the dopant chromophore is greatly facilitated by a collaborative theoretical and experimental approach. The long-standing and successful collaboration of Dagdigian's and Alexander's groups illustrates the utility of a joint experimental-theoretical research program.

With the support of this grant, we have succeeded in observing the electronic fluorescence excitation spectra of a number of important target complexes, including Al-H₂, Al-N₂, Al-CH₄, AlNe, CAr, and Al⁺-Ar. In addition, we have observed higher excited electronic states of the previously observed B-H₂ and BAr₂ complexes. These observations have allowed us to make incisive inferences into the nature of the ground and excited state potential energy surfaces, in conjunction with the collaborative theoretical effort. In particular, we have determined the binary interaction potentials governing the ground electronic states of the Al-H₂, AlNe, and O-H₂ system and have computed improved potential energy surfaces for B-H₂. The potential energy surfaces of these and other systems have been used to predict the structure and electronic spectrum of larger complexes. In particular, the spectrum of the BAr₂ complex for both the $3s\ 2S \leftarrow 2p\ 2P$ and $2s2p^2\ 2D \leftarrow 2p\ 2P$ transitions has been computed and found to agree well with our experimental observations.

The equilibrium properties of a boron impurity trapped in solid *para*-hydrogen have been investigated with path-integral molecular dynamics, using our derived B-H₂ potential energy surfaces. In groundbreaking work, the effect of the singly-filled nature

of the boron $2p$ orbital was assessed by comparison with similar simulations in which an orientation-averaged B–H₂ potential energy surface was used. To help in the interpretation of electronic absorption spectra taken by M. Fajardo and co-workers at the Air Force Research Laboratory (Edwards AFB, CA), $3s \leftarrow 2p$ absorption spectra of B-doped solid *para*-hydrogen were computed by a semiclassical Franck-Condon technique. These calculations provided a reasonable rationale for a spectral assignment and estimated band intensity.

The following sections summarize in more detail these research accomplishments and present some conclusions relevant to experiments probing B and Al atoms in cryogenic solids.

A. Spectroscopic Characterization of Non-bonding Interactions of Group IIIA Atoms

1. The AlNe Complex. Prior to our work, only the heavier Al–rare gas complexes, and not AlNe, had been observed. In order to motivate study of the Al–H₂ complex, we first sought to generate the weakly bound AlNe complex. In this work,¹ transitions out of both spin-orbit manifolds of AlNe($X^2\Pi$) to the $C^2\Delta$ and $D^2\Pi$ states, which correlate with the Al($3d$) + Ne asymptote, and the $H^2\Sigma^+$ state, which correlates with Al($5s$) + Ne, were observed by laser fluorescence excitation. Spectroscopic parameters and dissociation energies of the ground and excited electronic states were determined. As an example of the importance of considering the importance of electron spin in determining the strength of non-bonding interactions, we found that the dissociation energies D_0 for the $X^2\Pi$ spin-orbit manifolds were significantly different [14.4 ± 0.3 and 32.3 ± 0.3 cm⁻¹ for $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, respectively].

The potential energy curves of the AlNe($X^2\Pi$, $A^2\Sigma^+$) states, which correlate with the ground Al($3p$) + Ne asymptote, were also calculated by *ab initio* methods.¹ When consideration of the electrostatic + spin-orbit interactions were taken into account, the calculated D_0 values for the $X^2\Pi_{1/2}$ and $X^2\Pi_{3/2}$ manifolds were in excellent agreement with the experimental values.

2. The Al-H₂ Complex. We have employed laser fluorescence excitation to characterize the electronic spectra of Al-H₂ and other weakly-bound Al-molecule complexes. In other laboratories, attempts to observe the Al-H₂ complex by resonance-enhanced multiphoton ionization (REMPI) detection schemes failed because of the rapid pre-dissociation of the electronically excited state. In recent work, several laboratories have applied zero-kinetic energy electron spectroscopy to obtain vibrational information on the ground electronic states of the several neutral and ionic Al-molecule complexes.^{2,3} However, this technique has not been applied to the very weakly bound Al-H₂ complex; in any case, this approach does not provide structural information on the excited neutral electronic states.

In our laboratory, we have employed a unique detection scheme suitable for laser fluorescence detection. In an electronically excited atom-molecule complex and in contrast to atom-rare gas binary complexes, we can anticipate that there will be a high probability that the excited state will decay by predissociation through coupling with lower PES's. We have succeeded in detecting Al atom-molecule complexes by excitation to excited electronic states higher than the lowest [Al(4s)-M here]. In this case, the transition can be detected even if predissociation occurs so long as the final state is an emitting excited state.

With this excitation and detection scheme, we have observed transitions from the ground vibronic level of the Al-H₂ complex to bound vibrational levels of Al(5s)-H₂.⁴ These transitions were observed both by detection of emission from lower Al atomic states (4s, 3d) and chemiluminescence of AlH(A¹Π) product by reaction within the complex. Resonance fluorescence from excited Al(5s)-H₂ levels was very weak. From the relative intensities for formation of the various emitting products and the estimated decay rate of the 5s → 3p transition, the excited-state lifetime was estimated to be ≤ 35 ps.

Accompanying this experimental study of the Al-H₂ complex, we have carried out extensive theoretical studies, which will be described in Sec. IIIB below. As discussed there, the Al-H₂ complex can exist in two nuclear spin modifications. Because of its larger binding energy, we believe that we are observing the Al-*o*H₂ isotopomer.

For some bands, partial rotational resolution was achieved, despite the observable Lorentzian broadening. Analysis of this structure would confirm the assignment of the isotopomer and also provide an estimate of the Al-H₂ separation and equilibrium geometry. As discussed in detail in Sec. IIIB, the equilibrium geometry for the lowest Al(3*p*)-H₂ PES is *T*-shaped. Unfortunately, we have not yet worked out a definitive rotational analysis, and this will be a subject for future work.

The AlH $A \rightarrow X$ chemiluminescence from reactive decay of Al(5*s*)-H₂ was spectrally resolved.⁴ The $A^1\Pi$ state is orbitally degenerate; each rotational level splits into a closely spaced pair of Λ -doublets of A' and A'' reflection symmetry in the plane of rotation. The Λ -doublets can be spectrally distinguished since they separately emit in the *P/R* and *Q* branches, respectively. We find that the excited AlH(*A*) product is formed predominantly in A' and not A'' Λ -doublet levels. This Λ -doublet propensity implies that the reflection symmetry is conserved in the nonadiabatic Al(5*s*)-H₂ \rightarrow AlH($A^1\Pi$) + H reaction.

In more recent work, we have extended our study of the electronic spectrum of Al-H₂ to the transitions to the 3*d*, 4*p*, and 4*d* levels.⁵ As for the 5*s* \leftarrow 3*p* transition, these transitions were detected by monitored emission from lower Al atomic states formed by predissociation of the excited Al-H₂ complex. The transition to the 4*p* state is forbidden in the isolated Al atom and is allowed by the distortion of the Al atomic wave function in the complex. The Lorentzian widths of the bands vary widely, in some cases allowing resolution of the rotational lines. The mechanism of predissociation is investigated theoretically through *ab initio* calculation of C_{2v} cuts of the excited PES's. We conclude that predissociation occurs through coupling with the repulsive Al(4*s*)-H₂ PES.

3. The Al-N₂ Complex. We have also detected the Al-N₂ complex with vibrational and partial rotational resolution by excitation to electronic states correlating with the Al(5*s*, 4*d*) levels and detection of emission from lower Al atomic levels.⁶ In previous work on this complex, Brock and Duncan⁷ investigated this complex by photoionization spectroscopy. Quantum chemical calculations by Chaban and Gordon⁸ predict that the equilibrium geometry of the Al(3*p*)-N₂ complex to be linear and provide an estimate of the ground-state dissociation energy. The different geometries of the

Al-H₂ and Al-N₂ complex are consistent with the opposite signs of the electric quadrupole moments of the molecules.⁹

Partial rotational resolution was achieved in vibrational bands of the $5s \leftarrow 3p$ transition. Consistent with the linear equilibrium geometry, the profiles were well reproduced by simulations of $^2\Sigma^+ - ^2\Pi$ transition and a Voigt profile consisting of a Lorentzian component due to nonradiative decay and a Gaussian laser line shape profile. The fitted Lorentzian widths corresponded to a decay rate of $7 \times 10^{10} \text{ s}^{-1}$. From the derived excited-state rotational constant, the $5s \leftarrow 3p$ transition is estimated to involve a contraction of the Al-N bond length by 0.6 Å.

4. The Al-CH₄ Complex. We have also recorded fluorescence excitation action spectrum for the $5s \leftarrow 3p$ and $4d \leftarrow 3p$ transitions in the Al-CH₄/CD₄ complex.¹⁰ As in the other Al atom-molecule complexes studied, a progression in the van der Waals stretch mode was observed. The widths of the bands are much greater than for Al-H₂ and Al-N₂ and are indicative of an increased nonradiative decay rate and/or more complicated rotational structure. The widths of the corresponding Al-CD₄ bands are significantly less, suggesting that H-atom motion is involved in the nonradiative decay. It was not possible to obtain a definitive vibrational assignment for spectra of these complexes and only lower bounds to the excited-state binding energies were derived.

As in the case of the Al-H₂ complex, AlH chemiluminescence, as well as emission from lower excited Al atomic levels, was observed from excited Al-CH₄. In sharp contrast to the preferential Λ -doublet formation seen for reaction within the Al($5s$)-H₂ complex, the AlH($A^1\Pi$) product from reaction within Al($4d$)-CH₄ was found to have approximately equal populations of the A' and A'' Λ -doublet levels. This is likely the result of the fact that the plane of rotation of the AlH product is not well defined with respect to planes of symmetry in the complex.

The excited-state dissociation energies determined from our studies of Al atom-molecule complexes are presented in Table I and compared the corresponding Al⁺ ion-molecule binding energies. These values were taken from work from our and other laboratories.^{1,4,6,10-13}

Table I. Binding energies (cm^{-1}) of the excited Al-M and ionic Al^+ -M complexes.

M	$D_0(\text{Al}(5s)\text{-M})$	$D_0(\text{Al}(4d)\text{-M})$	$D_0(\text{Al}^+\text{-M})$
Ne	81 ^a		
Ar	692	787	982 ± 5
Kr	1216	1429	1529 ± 2
H_2	300 (+160,-10)		472 ± 52
N_2	1218 ± 10	2705 ± 165	1924 ± 175
CH_4	≥ 1489	≥ 1824	2120 ± 105

5. Chemical Reaction within the Excited $B(^2D)\text{-H}_2$ Complex. Following an earlier study of the $3s \leftarrow 2p$ transition in the B- H_2 complex,¹⁴ we investigated the transition to the excited $2s2p^2\ ^2D$ valence state. No fluorescence was observed from the excited $B(^2D)\text{-H}_2$ complex, but with fluorescence depletion spectroscopy we were able to observe the transition.¹⁵ Formation of BH in its $A^1\Pi$ and $b^3\Sigma^-$ states through chemical reaction within the complex was detected through observation of BH $A-X$ and $b-a$ chemiluminescence.¹⁶ All bound $A^1\Pi$ and all energetically allowed $b^3\Sigma^-$ levels were found to be significantly populated.

Comparing the fluorescence depletion and chemiluminescence action spectra, we find that the excited state chemical reaction occurs most efficiently in the lower-energy portion of the electronic transition. There are 5 PES's which emanate from the $B(^2D) + \text{H}_2$ asymptote. The above observations were used to draw inferences on the nature of these surfaces. It is to be noted that the reactive nature of the $B(^2D)\text{-H}_2$ PES's contrast sharply with the apparent nonreactive nature of the $B(3s)\text{-H}_2$ PES. These results may have implications for the lower excited Al- H_2 PES, which correlates with $\text{Al}(4s) + \text{H}_2$; this PES may also be repulsive like the $B(3s) + \text{H}_2$ PES.

B. Theoretical Characterization of Interactions of Hydrogen with Aluminum, Boron, and Oxygen

In earlier work supported by an earlier AFOSR grant, we used multi-reference, configuration-interaction (MRCI) methods to determine the 3 adiabatic potential energy surfaces (PES's) describing the $B(^2P)\text{-H}_2$ system.¹⁷ Then, following Rebentrost and Lester,¹⁸ we used the matrix elements of the electronic angular momentum l to define the

transformation into an approximate diabatic basis, characterized by the 3 orthogonal projections of the $2p$ orbital along the B–H₂ axis. Our work provided the benchmark for later *ab initio* investigations by Chaban and Gordon¹⁹ [on the energetics of M–H₂ complexes in high symmetry] and Bauschlicher²⁰ [on the fragmentation energies of B(H₂)_{*n*} complexes], both of which confirmed the accuracy of our earlier work. More recently, our B–H₂ PES's have been used by Niday and Weeks, in a time-dependent study of inelastic scattering,²¹ and, as will be described below, by Voth and co-workers²² in a path-integral simulation of the properties of solid *p*H₂ embedded with a number of B atoms.

We fitted the calculated B(2P)–H₂ diabatic PES's to the general angular expansion of Dubernet and Hutson²³ in terms of reduced rotation matrix elements. These expansions were then used²⁴ in variational calculations of the bend-stretch wave functions of the complex. The adiabatic bender approximation²⁵ was used to gain additional insight into the characterization of the levels of the complex. Our research program is unique in that we have the capability and expertise both to determine accurate *ab initio* PES's and, subsequently, to treat the nuclear dynamics correctly to determine the rovibronic levels of the weakly-bound complex.

During the past three years, we carried out similar studies of the O(3P)+H₂ and Al(2P)+H₂ systems.^{26,27} The reaction of O(3P) with H₂ has a barrier > 13.5 kcal/mol in height. Because of this high barrier to reaction it may be possible to stabilize ground-state oxygen atoms in liquid or solid H₂. For this reason, doping of atomic O into solid H₂ has been suggested as a possible pathway to enhancing the specific impulse of cryogenic propellants.²⁸ Motivated by this suggestion, Li, Apkarian, and Harding (LAH) carried out²⁹ an *ab initio* investigation of the O(3P)H₂ PES's in the region of the van der Waals minimum.

In independent work we carried out²⁶ similar MRCI calculations with a large (augmented quadruple zeta) basis set. The transformation of the two electronic states of A'' symmetry into a diabatic basis was performed equivalently to our earlier work on BH₂. To correct for the incomplete recovery of the electron correlation energy, we scaled the external correlation energy, as originally proposed by Truhlar, Werner and

their co-workers,^{30,31} fixing the scaling factor to match the results of coupled-cluster calculations in linear and perpendicular geometry. Our resulting well depth was substantially smaller than that reported by LAH (79 cm⁻¹ vs. 108 cm⁻¹). In addition, LAH predict the deepest well to occur in linear geometry, whereas we predict the deepest well to occur in perpendicular geometry. We used several tests to confirm to accuracy of our calculations; the origin of the discrepancy with the earlier work of LAH is not yet clear.

Using our *ab initio* PES's in the subsequent simulation of the bound states of the O(³P)-H₂ complex, we predict zero-point binding energy of 15 cm⁻¹ and 23 cm⁻¹ for the complexes with *p*H₂ and *o*H₂, respectively. This is considerably smaller than the comparable binding energies for the B(²P)-H₂ complexes (40 cm⁻¹ and 60 cm⁻¹ for *p*H₂ and *o*H₂).²⁷ The weak dispersion energy, along with a favorable quadrupole-quadrupole interaction, provides the binding in these complexes. The single *p* electron of the B can be easily oriented to maximize the quadrupole-quadrupole interaction as well as reducing the Pauli repulsion with the filled H₂ 1σ_g orbital. However, the O atom has four *p* electrons. In its ³P ground state, two of these are triplet coupled, so that no matter from which direction the H₂ moiety approaches, at least one *p* electron will experience Pauli repulsion with the filled H₂ 1σ_g orbital. It is for this reason that the binding is weaker.

We have also carried out similar MRCI calculations for the Al-H₂ complex. *Ab initio* calculations for this system had already been reported by Gordon, Bauschlicher and their colleagues,^{19,32,33} but only for high symmetry geometries (collinear and *T*-shaped). Our MRCI calculations determined the PES's over the complete range of geometry necessary to characterize the binary complex. Calculations were carried out with double-, triple-, and quadruple-zeta basis sets and then extrapolated to the complete basis set limit.³⁴ Similar calculations were carried out for B-H₂, to improve the accuracy of our earlier¹⁷ PES's. For the Al-H₂ calculations, in order to obtain a smoothly varying potential energy surface over the full range of the configuration space, we find it necessary to carry out, at each geometry, multi-configuration self-consistent field (MCSCF) calculations with a small specified subset of reference configurations. The orbitals and wavefunctions were then used as initial input for both the complete-active-

space, self-consistent-field (CASSCF) and subsequent MRCI calculations. The calculated well-depths in the minimum energy geometry (*T*-shaped) were 137 cm⁻¹ and 220 cm⁻¹ for B-H₂ and Al-H₂, respectively. The latter number compares well with the best estimate of 227 ± 8 cm⁻¹ of Bauschlicher and co-workers.³³

Determination of the energies of the rovibronic levels of the complex was done as in our earlier work on B-H₂.²⁴ These calculations are currently implemented in our Hibridon 4 code,³⁵ (development of which was partially supported by previous AFOSR grants) for the investigation of bound-states and scattering. Table II shows the calculated zero-point corrected dissociation energies (*D*₀) for the B-H₂ and Al-H₂ complexes. Although the Al-H₂ well depth is nearly twice as large as that of B-H₂, the zero-point corrected dissociation energies are only ~ 25% larger. This is because the spin-orbit splitting of Al atom is so much larger (112 cm⁻¹ vs. 15.3 cm⁻¹).³⁶

Table II. Zero-point corrected dissociation energies (cm⁻¹) of the lowest bend-stretch levels of the B(²*P*)-H₂ and Al(²*P*)-H₂ complexes.^a

B + <i>p</i> H ₂	B + <i>o</i> H ₂	Al + <i>p</i> H ₂	Al + <i>o</i> H ₂
39.7	59.8	50.4	74.3
33.8 ^d	56.9 ^d	36 ± 18 ^b	69.7 ^d
		39.1 ^d	

a. The zero of energy is defined by M(²*P*_{1/2})+H₂(*j* = 0) for the complexes with *p*H₂ and by M(²*P*_{1/2})+H₂(*j* = 1) for the complexes with *o*H₂.

b. Bauschlicher *et al.* (Ref. 33)

d. Binding energies for H₂ restricted to its lowest rotational state (*j* = 0 for *p*H₂ and *j* = 1 for *o*H₂); free rotation limit.

This past year we have begun the study of the dependence of the potential energy surface on the H₂ bond distance *r*, which was held fixed in our previous investigations. The inclusion of the dependence on *r* will be of importance in the interpretation of the infrared spectroscopy, in a project in which we are collaborating with R. J. Hinde at the University of Tennessee.

C. Boron in Larger Clusters and Matrices

In past AFOSR-supported work, we have used our binary B-M interaction potentials (where *M* is either a noble gas atom or the *p*H₂ molecule) to simulate the energetics and nuclear dynamics of larger clusters, with multiple noble-gas or *p*H₂

ligands.³⁷⁻³⁹ For the ground electronic state of these complexes, we follow Balling and Wright⁴⁰ and assume that the interaction potential is given by the lowest state of a 3×3 electronic Hamiltonian.⁴¹ To model the structure and electronic absorption of these complexes, we have used^{37, 39} quantum Monte-Carlo techniques^{42, 43} to determine the zero-point energy and an approximation to the vibrational wavefunction of the complex.

Our first application to the simulation of an optical excitation spectrum was to the $3s \leftarrow 2p$ transition in the BAr_2 cluster.⁴¹ Here the excited state is non-degenerate. More recently, Yang and Dagdigian⁴⁴ observed transitions in the BAr_2 cluster which can be attributed to the $2s2p^2 \ ^2D \leftarrow 2s^22p \ ^2P$ valence transition of the B-atom chromophore. Size-selected fluorescence depletion spectra show that these features in the excitation spectrum are primarily due to the ternary complex.

To model the electronically excited state of the complex, we use the Balling and Wright⁴⁰ approach, modified here to incorporate the five-fold degeneracy of the 2D state. The resulting Hamiltonian matrix is 10×10 . Each root of these matrix corresponds to a separate excited state of the complex, all of which can be accessed in the transition. Within this modification, we invoke the same Franck-Condon approximation⁴⁵ which we used earlier to model the $3s \leftarrow 2p$ transition. The underlying diatomic $\text{B}(^2D)\text{Ar}$ potential energy curves are those which reproduce our previous experimental observations⁴⁶ on the electronic states emanating from the $\text{B}(^2D) + \text{Ar}$ asymptote. The intensity of the transition to each excited electronic state was completed by projecting the eigenvector of each excited state onto the ground electronic state, and using standard atomic line-strength factors. The simulated spectrum provides a reasonable reproduction of the experimental fluorescence depletion spectrum and facilitates the understanding of the major features.

In earlier work, we have used variational and diffusion Monte-Carlo methods to simulate the energetics of small clusters of B with Ar and $p\text{H}_2$.^{37, 41} During the past several years, we have continued this work, concentrating on single B atoms site-substituted in a hexagonal close-packed lattice of $p\text{-H}_2$ molecules. The total interaction Hamiltonian is taken to be the pairwise sum of 3×3 $\text{B-}p\text{H}_2$ ^{17, 24} interaction matrices and pairwise $p\text{H}_2\text{-}p\text{H}_2$ scalar potentials.⁴⁷ Standard periodic box boundary conditions are

used.⁴⁸ We have written a fast subroutine for the calculation of the potential and its gradient for the interaction of any number of B atoms with any number of p -H₂ molecules, in which we use⁴⁹ a table lookup and interpolation in the inverse square of the interparticle distances.⁵⁰

Our initial investigation involved variational, followed by diffusion Monte-Carlo, calculations. The variational functions were based on a combination of Jastrow and pinning functions, similar to those used by Cheng and Whaley in their study of Li atoms embedded in solid H₂.⁴⁵ More recently, we have collaborated with Jang and Voth, in path-integral simulations^{22, 51, 52} of B atoms in solid H₂. This past year Jang and Voth completed an important study²² based on just the spherically symmetric component of our B-H₂ interaction potential.¹⁷ During several visits to the University of Utah, a graduate student in our group, Jennifer Krumrine, helped Jang to incorporate our new 3×3 pairwise B-H₂ Hamiltonian, based on our most recent *ab initio* calculations,²⁷ into the Jang-Voth path integral code.

Subsequent simulations of the optical excitation spectra of B in p H₂ have been carried out,⁴⁹ which involve also our *ab initio* potential for the electronically excited B($3s^2S$)H₂ system. The electronic degeneracy was treated by means of the sum of pairwise 6×6 Hamiltonian matrices, discussed above. Simulations were performed with a periodic box containing 1 B atom and 179 p H₂ molecules. The presence of a defect was simulated by removal of one p H₂ in the nearest-neighbor (NN) shell. The $3s \leftarrow 2p$ absorption spectra of the B chromophore was predicted by a semiclassical Franck-Condon technique using path integrals to sample the quantum lattice configurations. Most importantly, these simulations indicate that the $3s \leftarrow 2p$ transition in the solid is substantially blue shifted from its position in the free B atom, because the excited state is purely repulsive. These calculations provide a reasonable explanation of the electronic spectra of B in solid *para*-H₂ recently reported by Fajardo and co-workers,⁵³ building upon earlier work on B-doped solid *n*-H₂.^{28, 54} We also argued that the second peak seen in the experimental spectrum corresponds to the $2s2p^2 (^2D) \leftarrow 2s^22p (^2P)$ transition in the solid, which we did not include in our simulation.

D. VUV Spectroscopic Characterization of the Al⁺-Ar Interaction

In order to extend the wavelength range and hence the types of weakly bonded systems which can be studied, we have constructed an apparatus for the study of electronic spectra of complexes in a free-jet expansion by VUV LIF detection. Tunable VUV radiation was generated by resonant 4-wave mixing in Mg vapor.⁵⁵

The first complex studied with this apparatus was the Al⁺-Ar complex.⁵⁶ The laser fluorescence excitation spectrum of this complex was recorded in the spectral region around the Al⁺ ion $3s3p\ ^1P \leftarrow 3s^2\ ^1S$ transition at 167.1 nm. A $^1\Sigma^+ - X^1\Sigma^+$ band system of the Al⁺-Ar complex was observed. Based on the previously reported¹¹ ground state dissociation energy $D_0'' = 982 \pm 5\text{ cm}^{-1}$, D_0' for the excited state was determined to equal $1036 \pm 5\text{ cm}^{-1}$. The rotational constant of the $X^1\Sigma^+$ state is close to those of neutral AlAr Rydberg states. The ground and excited states of this transition has electron occupancy $3s\sigma^2$ and $3s\sigma 3p\sigma$. The excited state is more strongly bound than the ground state despite the fact that the repulsion of the more directional $3p\sigma$ orbital would be expected to be greater than for the $3s\sigma$ orbital.

E. VUV Spectroscopic Characterization of the C-Ar Interaction

We have carried out the first spectroscopic study of non-bonding interactions of the carbon atom.⁵⁷ The lowest resonance transitions of the C atom are in the VUV, the $2s^2 2p 3s\ ^3P \leftarrow 2s^2 2p^2\ ^3P$ Rydberg transition at 165.7 nm and the $2s 2p^3\ ^3D \leftarrow 2s^2 2p^2\ ^3P$ valence transition at 156.1 nm. Naumkin and McCourt⁵⁸ have calculated *ab initio* potential energy curves for the CAr electronic states which arise from the ground state $C(2s^2 2p^2\ ^3P) + \text{Ar}$ asymptote. The ground electronic state of CAr is $X^3\Sigma^-$, which has electron occupancy $2s\sigma^2 2p\pi^2$, for which the repulsion is less than in the low-lying $A^3\Pi$ state [$2s\sigma^2 2p\pi p\sigma$ electron occupancy].

Sohlberg and Yarkony⁵⁹ have carried out a computational study of the binding and nonradiative decay of the CAr($B^3\Pi$) state, which arises from the first excited triplet asymptote, $C(2s^2 2p 3s\ ^3P) + \text{Ar}$. This state is predicted to be strongly bound [$D_e = 5100\text{ cm}^{-1}$] and could be convenient in the laser fluorescence detection of the CAr complex, but it might be predissociated by spin-orbit coupling with a repulsive quintet state. Their

calculations suggest that the high vibrational levels which are Franck-Condon accessible from the CAr ground electronic state should not be strongly affected by this predissociation.

In our experiments, carbon atoms were generated in a supersonic expansion by 193 nm photolysis of several different precursors [CCl₄, (CH₃)₃CO, CH₃Br]. A single weak band, assigned to the CAr $B - X$ transition, was observed near the 165.1 nm atomic resonance transition. In the region of the 156.1 nm transition an excited-state ($v', 0$) progression was observed. The vibrational assignment was confirmed by ¹³C isotopic substitution of a CCl₄ photolytic precursor, and the band system was assigned as a ${}^3\Pi - X^3\Sigma^-$ transition, with excited state electron occupancy $2s\sigma 2p\pi 2\sigma^2$. Comparison of the partially resolved rotational contours yielded an excited-state rotational constant $B_e' = 0.111 \text{ cm}^{-1}$. The dissociation energies of the upper and lower states of this band system were determined: $D_0' = 54.8 \pm 0.5 \text{ cm}^{-1}$ and $D_0'' = 120.4 \pm 0.5 \text{ cm}^{-1}$. The latter is somewhat larger than the dissociation energy 97.4 cm^{-1} obtained from the potential energy curves computed by Naumkin and McCourt.

From the fact that only a single weak band was observed in the region of the ${}^3P \leftarrow {}^3P$ atomic transition, we conclude that the CAr($B^3\Pi$) state is significantly affected by predissociation. We were also unable to detect a dipole-allowed transition to an expected strongly bound state correlating with $C(2s2p^3 {}^3D) + \text{Ar}$, in addition to the weakly bound state. This suggests that all strongly bound states of CAr may be predissociated by repulsive states correlating with lower atomic states.

F. Observation and Spectroscopic Characterization of AlNC and AlCN Isomers

In the course of our study of the Al-N₂ complex,⁶ we observed a set of bands in the wavenumber range $35\,800 - 37\,700 \text{ cm}^{-1}$ not assignable to any previously reported electronic transitions. These bands have been ascribed⁶⁰ to the AlNC molecule from the observed change in the rotational constant upon ¹⁵N isotopic substitution and the agreement with the rotational constant measured by pure rotational spectroscopy.⁶¹ This transition has been assigned as a ${}^1\Pi \leftarrow X^1\Sigma^+$ electronic excitation and is analogous to the $A^1\Pi \leftarrow X^1\Sigma^+$ transition of the aluminum monohalides. The excited state is orbitally

degenerate and is subject to a large Renner-Teller splitting, as in the isoelectronic C_3 $A^1\Pi_u$ electronic state.

We also observed one band at $28\,755\text{ cm}^{-1}$ which we assign to the AlCN isomer. It is interesting that both the AlNC and the less stable AlCN isomer are observed in our supersonic beam of photolyzed trimethylaluminum (TMA) seeded in N_2 and a rare gas. The observation of these triatomic species is surprising since 193 nm photodissociation of N_2 is a multiphoton process and likely not very efficient. It is possible that N_2 bond cleavage occurs through reaction with electronically excited Al atoms formed by multiphoton absorption of TMA. It is likely that supersonic beams containing photolyzed precursors will be productive sources of other novel transient species.

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