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13. ABSTRACT (Maximum 200 words)

A closely coordinated theoretical and experimental investigation of the non-bonded interactions between B, Al, and other atoms with the hydrogen molecule and other partners has 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. Particular emphasis was placed on the study of the complex of an Al atom with molecular hydrogen. Global potential energy surfaces, for this system and others, have been computed through electronic structure calculations. These interaction potentials have been employed to calculate the energetics and structure of the binary complexes, as well as to investigate the properties of Al and B atoms doped in solid hydrogen. Through path integral molecular dynamics calculations employing these interaction potentials, the equilibrium properties of an Al atom trapped in solid *para*-hydrogen has been investigated. A new theory was developed to describe interactions between open-shell atoms mediated by the presence of spherical ligands and was applied to model the recombination of two Al atoms in doped solid hydrogen..

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EXPERIMENTAL AND THEORETICAL INVESTIGATION OF LIGHT-ATOM DOPED CLUSTERS AND SOLIDS

FINAL REPORT

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I. SUMMARY OF WORK AND DESCRIPTION OF WORK ACCOMPLISHED

This project has involved a closely coordinated theoretical and experimental investigation of the non-bonded interaction between boron, aluminum, and other atoms with the hydrogen molecule and other partners. This work has been carried out in support of work in Air Force laboratories on the preparation of atom-doped cryogenic solids, which are potential novel propellant systems. Knowledge of the interaction potentials is necessary to predict the properties of atom-doped cryogenic media, in particular solid hydrogen. Moreover, these interaction potentials must be known for both the ground and excited electronic states, since the primary diagnostic tool to study doped solids in the laboratory is electronic spectroscopy.

With the support of this grant, we have succeeded in observing the electronic fluorescence spectrum of Al–H_2 van der Waals complex involving excitation to several different excited electronic states. This extends previous similar experimental work on the B–H_2 complex. Of special interest is the fact that we are the first, and thus far the only, group to have produced the B–H_2 and Al–H_2 complexes and detected them by any means. We have also observed the fluorescence excitation spectra of a number of other related van der Waals complexes, involving either atoms or other binding partners. These data have been used to infer binding energetics and geometries.

These experimental observations have allowed us to elucidate the nature of the ground and excited potential energy surfaces, in conjunction with the collaborative theoretical effort. In particular, the global potential energy surfaces (PESs) for the interaction of a ground-state boron or aluminum atom with H_2 have been determined by *ab initio* electronic structure calculations. These interaction potentials have been employed to calculate the energetics and structure of the binary complexes, as well as to investigate the properties of Al and B atoms doped in solid hydrogen. The Al–H_2 PESs, as well as calculated Al–Al interactions, have been employed in a new theory, describing interactions between ^2P atoms mediated by the presence of spherical ligands, to model the recombination of two Al atoms in the doped solid. An extension of path-integral methodology has been completed to allow the accurate description of extended systems in which more than one potential energy surface is energetically accessible.

The following sections present in greater detail these research accomplishments and relates our work in the studies of atom-doped solids. More detailed descriptions can be found in publications (listed in Sec. 111) which were prepared with the support of this grant.

A. Electronic Spectroscopy of the Al–H_2 Complex

We have thoroughly investigated the electronic spectrum of the Al–H_2 and Al–D_2 complexes and have spectroscopically characterized the excited states emanating from a number of the Al + H_2 asymptotes.[1-5] In transitions to bound excited states, no resonance fluorescence is observed, as the excited states decay by predissociation to lower potential energy surfaces correlating with lower Al + H_2 asymptotes. In this case, the electronic transitions could be observed by action spectroscopy, in which an emitting, excited Al state, which was a product of the predissociation, was detected. An extensive series of vibronic bands of both the Al–H_2 and Al–D_2 complexes was observed in the energy range of the Al $3d$ and $4p$ atomic states.[2] These bands displayed widely varying Lorenztian widths, in some cases allowing the rotational structure of the bands to be displayed. We were able to organize many of the bands into excited-state van der Waals progressions, which were interpreted with the help of *ab initio* calculations.[2] Predissociation occurs by coupling of the bound Al($3d$, $4p$)H_2 PESs with the repulsive 2^2A_1 Al($4s$)H_2 PES.

The *ab initio* calculations[2] predicted the existence of a strongly bound, partial charge-transfer state, which correlates to Al($3d$) + H_2. This state was not observed in our initial study[2] of the Al($3d$, $4p$)H_2 states since we did not scan far enough to the red. In further work,[5] we identified this state by means of a long excited-state progression in the Al–H_2/D_2 van der Waals stretch mode. We were able to derive an effective one-dimensional potential energy curve as a function of the van der Waals stretch coordinate in the excited state.

In addition, we directly observed[4] the electronic transition to the Al($4s$)H_2 (2^2A_1) state, which manifested itself as a single broad, unstructured feature peaking ~500 cm^{-1} to the blue of the of the Al $4s\ ^2S \leftarrow 3p\ ^2P_{1/2}$ atomic line. This is consistent with the repulsive nature of the 2^2A_1 Al($4s$)H_2 PES. We also investigated the $4s \leftarrow 3p$ transition in the AlNe, Al–N_2, and Al–CH_4 complexes.[4] The excited Al($4s$)Ne state was also found to be repulsive. The $4s$ states of Al–N_2 and Al–CH_4 are bound and show vibrational structure to the red of the Al 4*s* $^2S \leftarrow$ 3p $^2P_{1/2}$ atomic line, and their observation required the use of fluorescence depletion spectroscopy.

Our observations on the binary Al–H_2 complex have implications for the interpretation of the spectrum of Al atom doped solid hydrogen. Krumrine *et al.*[6] investigated the properties of an atomic B impurity in solid *p*-H_2 through path-integral molecular dynamics calculations. They predicted the B atomic 3*s* ← 2*p* transition to be blue shifted by ~6000 cm^{-1}, or 500 cm^{-1} for each of the 12 nearest neighbor H_2 molecules, in reasonable assignment with the longest-wavelength feature in the experimental absorption spectrum for B-doped solid hydrogen.[7]

The first absorption feature for Al-doped solid hydrogen appears at 330 nm.[8, 9] considerably to the blue of the longest-wavelength transition (4*s* ← 3*p*) in the free atom at 394.5 nm. From the observed[4] blue shift of the 4*s* ← 3*p* transition in the binary Al–*o*H_2 complex from that of the free atom, we estimate that this transition should appear in the doped solid at 333 nm, very close to the observed wavelength. The next transition in atomic Al is to the 3*d* state. Our experimental and theoretical work[2] indicates that the PESs emanating from this asymptote are attractive. This suggests that the 3*d* ← 3*p* transition in the doped solid should be red shifted from the wavelength (308.2 nm) of the free atom. Hence, the observed 330 nm feature in the spectrum of Al-doped solid hydrogen can be assigned to the combined 3*d*, 4*s* ← 3*p* transition. This allows us to estimate the oscillator strength of this transition as the sum of the gas-phase oscillator strengths for these two transitions, thus enabling the estimation of Al atomic concentrations from measured absorbances.[9]

B. Potential Energy Surfaces Describing the Al(3*p*)–H_2 Interaction

Because of the orbital degeneracy of the Al(3*p*) atom, three PESs emanate from the Al(3*p*) + H_2 asymptote. Williams and Alexander[10] have computed *ab initio* diabatic PESs which describe the interaction of the Al(3*p*) atom with H_2 at a fixed H–H distance (r_e). In this effort, the computed adiabatic PESs were transformed to an approximate diabatic basis for a more convenient description of the nuclear dynamics. Binding energies of the bend-stretch levels of Al–H_2/D_2 were also computed.

We have investigated in detail the resolved rotational structure displayed in some of the 3*d* ← 3*p* and 4*p* ← 3*p* bands of Al–H_2 and Al–D_2.[3] Using ground-state combination differences and employing optical optical double resonance fluorescence depletion spectroscopy, we determined the rotational constants and parity-doubling parameters for the ground bend-stretch levels of Al(3*p*)–*o*H_2 and Al(3*p*)–*p*D_2.[10] The derived spectroscopic parameters were compared with constants derived from fits to computed energies based on the *ab initio* PESs of Williams and Alexander[10] and a new set of PESs computed with inclusion of the dependence upon *r*, the H_2 vibrational coordinate. The agreement with experiment was excellent for the latter set of PESs, and notably better than for the fixed-*r* PESs. Thus, it is necessary to take into account the dependence of the PESs on the diatom bond distance in weakly bound complexes of atoms with molecular hydrogen. With the T-shaped equilibrium geometry of the ground electronic state of the Al–H_2 complex, taking into account the vibrational motion of the H_2 molecule makes the vibrationally averaged atom-molecule separation smaller, and in closer agreement with experiment. This also makes computed binding energy larger and hence presumably more accurate.

C. Simulations of Al Atom Doped Solid Hydrogen

Simulations of embedded Al impurities in solid hydrogen have been carried out in collaboration with the group of Greg Voth at the University of Utah.[11] In previous theoretical work on embedded B atoms in solid hydrogen,[6] it was found important to incorporate the dependence of the interaction potential on the orientation of the 2*p* electron. The effect of the electronic anisotropy is even more dramatic for Al atom dopants. When a nearest-neighbor vacancy is present, the Al atom becomes dramatically shifted from the original lattice site in order to accommodate better the 3*p* electron.

In this work as well as earlier simulations of B–$(H_2)_n$ and B–Ar_n clusters, the nuclear motion was assumed to take place on the lowest electronically adiabatic PES, obtained by diagonalization of a sum of pairwise Hamiltonian matrices.[12] This may be too drastic an approximation for weakly bound complexes involving open-shell atoms, where excited electronic states may be accessible even at low temperature. We have initiated an extension of imaginary-time, path integral methods[13] to systems in which several electronic states are accessed coherently. In a one-dimensional model system calculation,[14] we have demonstrated that standard path-integral techniques can be easily extended to such systems by exponentiating the full matrix of the potential.

D. Al–Al Interactions in the Presence of Spherical Ligands

From the viewpoint of embedding either B or Al in solid pH_2, it is crucial to consider how recombination of these atoms will be mediated by the solvent molecules. Early work in this direction by Voth and co-workers[15] neglected the electronic anisotropy of both the B–H_2 and B–B interaction. We have recently shown[16] that it is straightforward to go beyond this approximation by extending the ideas inherent in the approach of Balling and Wright[12] to develop an accurate description of the interaction of two ^2P atoms in the presence of multiple spherical ligands.

The model is based on accurate *ab initio* potential energy curves for all the 36 Al_2 (or B_2) electronic states which correlate with dissociation into ground-state (^2P) atoms. With a valence-bond-like model, we transform the 36 molecular orbital states, which have a definite multiplicity and $D_{\infty h}$ spatial symmetry, into a set of 36 Cartesian states which correspond to assigning the two 3*p* electrons to approximate Cartesian orbitals centered on either atom. It is then easy to determine the matrix elements corresponding to the interaction of each ^2P atom with any number of surrounding spherical ligands. The lowest eigenvalue of the resulting matrix defines the adiabatic potential governing the motion of the atoms.

In a demonstration calculation,[16] we showed how the interaction between the two Al atoms is significantly modified by the presence of the intervening pH_2 molecules. At moderate to long range the interaction with the pH_2 molecules impedes the two 3*p* electrons from aligning themselves correctly for the lowest electronic state of Al_2. Consequently, there appears a significant barrier (at long range) to recombination of the two Al atoms. We are now using this extended pairwise Hamiltonian model in a full path integral simulation[13, 17, 18] of the motion of two Al atoms embedded in solid pH_2.

E. Interactions of Al and H atoms

In view of the interest generated by work published in the Russian literature on performance enhancement of propellants by the addition of alane (AlH_3) or other aluminum hydrides,[19-21] we have investigatted bonding interactions between aluminum and hydrogen atoms. This work has thus far involved a study of the metastable excited $a^3\Pi$ state of AlH which emanates from the ground-state Al + H dissociation asymptote. Previous spectroscopic studies[22] have precisely characterized the two singlet states, $X^1\Sigma^+$ and $A^1\Pi$, emanating from the asymptote. We have observed the $b^3\Sigma^- - a^3\Pi$ electronic transition of both AlH and AlD in free-jet supersonic beams. The $a^3\Pi$ state is likely produced by collisional recombination of Al and H atoms in the free-jet supersonic expansion.

We carried out a spectroscopic study of the $b - a$ (0,0) band of both AlH and AlD.[23] Spectroscopic constants describing the states of both isotopomers were determined. We also recorded decay lifetimes for several rotational/fine-structure levels of the excited $b^3\Sigma^-$ state. These are much shorter than in the case of BH.[24] To interpret the experimental observations, *ab initio* multi-reference, configuration-interaction calculations have been carried out for the lower electronic states of AlH.[23] The observed short excited-state decay lifetimes are the result of predissociation of the $b^3\Sigma^-$ state by spin-orbit interaction of this state with the repulsive $1^3\Sigma^+$ state which arises from the Al(3*p*) + H(1*s*) atomic asymptote. The excited state manifold, and the state mixing, is considerably more complex than for the excited states of BH, investigated earlier by Dagdigian, Yarkony, and their co-workers.[24]

F. Complexes Involving B and Ne atoms

In previous work in our research group,[25-28] we investigated the evolution of the $2s^23s\ ^2S \leftarrow 2s^22p\ ^2P$ at 249.8 nm and $2s2p^2\ ^2D \leftarrow 2s^22p\ ^2P$ at 208.9 nm B atomic transitions in the BAr and BAr_2 complexes. In contrast to the corresponding BAr state, the BNe $B^2\Sigma^+$ state is purely repulsive, and the BNe $B^2\Sigma^+ - X^2\Pi$ transition displays a broad, asymmetric feature peaking ~270 cm^{-1} to the blue of the B atomic line, characteristic of a free ← bound transition.[29]

We have recently continued this work, successfully observing the $3s \leftarrow 2p$ transition in the BNe_2 complex.[30] The complex was prepared by a supersonic expansion of B atoms entrained in Ne at high source backing pressures from a cooled beam source. Laser fluorescence excitation revealed a second broad feature further to the blue of the BNe peak.

As in our previous investigation of BAr_2,[27] a variational-Monte-Carlo (VMC) method[31-33] was employed to determine the wavefunction and energy E of the ground vibronic level of BNe_2. A product of Morse functions in the 3 internuclear separations was chosen as a variational approximation to the BNe_2 ground vibronic wavefunction since this function provides very good descriptions for the ground vibronic wavefunctions of BNe and Ne_2. The Monte-Carlo procedure generates sets of internal coordinates which provide a representative sampling of the BNe_2 cluster. We then used these points to simulate, semiclassically[34, 35] the optical excitation spectrum of the complex. We found excellent agreement with experiment, both in terms of the position and the shape, of the free ← bound absorption profile.

G. Complexes Involving Group 14 Atoms

In studies of non-bonding interactions involving other atoms, we have explored non-bonding interactions of the Si atoms through laser spectroscopic studies of the SiAr van der Waals complex. Specific impulse calculations[36] suggest that the embedding of Si atoms in solid hydrogen may also offer advantages over l-H_2/l-O_2 as a propellant.

The electronic spectrum of the SiAr complex in the region of the Si $^3D^o \leftarrow 3s^23p^2\ ^3P$ transition near 220.7 nm was investigated.[37] Previous workers have investigated SiAr electronic states arising from the excited valence Si($3s^23p4s\ ^3P$) + At asymptote.[38] At low resolution, a single excited-state (v',0) progression of bands terminating in a dissociation continuum was observed. The lower state of the transition is the ground $X^3\Sigma^-$ electronic state, and the upper state was assigned in the rotational analysis as $^3\Sigma^-$. The ground-state dissociation energy was determined to be $D_0'' = 178.8 \pm 0.4$ cm^{-1}. *Ab initio* calculations of SiAr $X^3\Sigma^-$ and $A^3\Pi$ electronic states correlating with the ground-state Si($3s^23p^2\ ^3P$) + Ar asymptote were also carried out. Reasonable agreement with the experimental results was obtained. Evidence for mixing of the $X^3\Sigma^-$ and $A^3\Pi$ states was obtained through the determination of the phenomenological spin-spin splitting between the $\Omega = 0^+$ and 1 components of the $X^3\Sigma^-$ state.

We extended the study of interactions involving group 14 atoms to the Ge and Sn atoms,[39, 40] in order to explore the role of the large spin-orbit interaction in moderating van der Waals interactions.[3, 10] Laser fluorescence excitation spectra of the GeAr complex, in the vicinity of the individual fine-structure lines of the Ge $4s^24p5s\ ^3P_{J'}{}^o \leftarrow 4s^24p^2\ ^3P_{J''}$ atomic resonance transition in the region 275 – 260 nm were recorded. Collisional fine-structure relaxation in the free-jet beam was slow, and transitions out of all bound Ge($4p^2\ ^3P$)Ar fine-structure levels were observed. The dissociation energies and vibrationally averaged internuclear separations of these states were found to vary dramatically between the different fine-structure levels, demonstrating again the importance of the spin-orbit interaction in determining the properties of weakly bound complexes.

Similar experiments were carried out on the SnAr complex.[40] Laser fluorescence excitation spectra of the SnAr complex, in the vicinity of the individual fine-structure lines of the Sn $5s^25p6s\ ^3P_{J'}{}^{o} \leftarrow 5s^25p^2\ ^3P_{J''}$ atomic resonance transition in the region 317 – 270 nm were recorded. Transitions out of all bound Sn($5p^2\ ^3P$)Ar fine-structure levels were observed. It was not possible to analyze in detail the rotational structure of the bands since transitions from the different SnAr isotopomers were overlapped. Nevertheless, binding energies could be estimated. For both GeAr and SnAr, the electronic states associated with the ground $np^2\ ^3P$ asymptote are in the case (c) limit, because of the larger spin-orbit interaction. It is found that the large spin-orbit interaction strongly moderates the strength of the non-bonding interactions.

H. Electronic Spectrum of the Ga_2 Dimer

We attempted also to observe the electronic spectrum of the heavier group 13 Ga atom bound to a hydrogen molecule. These experiments were unsuccessful, but we did observe electronic transitions in the gallium dimer,[41] a species for which no high-resolution spectroscopic data exists. All observed excited states are predissociative and were detected by observation of Ga $5s \rightarrow 4p$ atomic emission. Tentative electronic state assignments, based on several *ab initio* studies of Ga_2,[42, 43] were made. More calculations on this molecule are needed. An upper limit for the Ga_2 dissociation energy, $D_e'' < 8891$ cm^{-1}, was derived, which is consistent with previous experimental and computational estimates.

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