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13. ABSTRACT (Maximum 200 words)

Four new workstations were acquired, and five existing workstations were upgraded, to use in continuing investigations of weak interactions between atomic boron and various atomic and molecular partners (Ar, H_2, N_2). The theoretical techniques used involved *(i)* the *ab initio* determination of potential energy surfaces, *(ii)* the quantum determination of bend-stretch levels of weakly bound complexes, and *(iii)* the simulation, using genetic algorithm and diffusion Monte-Carlo techniques, of the structure of larger clusters. The acquisition of the new workstations has made possible new calculations, at a level of complexity and sophistication not hitherto possible. These calculations have allowed the interpretation of ongoing, related experimental work at the The Johns Hopkins University.

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THEORETICAL STUDIES OF WEAK INTERACTIONS OF LIGHT ATOMS

FINAL REPORT

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ITEMIZATION OF EQUIPMENT PURCHASED

The funds awarded under grant no. F49620-95-1-0046 were used to (*i*) acquire four workstations (two UNIX and two Macintosh) and associated peripherals and (*ii*) upgrade five existing workstations (two IBM RS/6000 and three Macintosh). The following specific items were purchased:

A. Two IBM RS/6000 39H Workstations, configured as follows:

> 2 GB L2 Cache Memory
>
> SCSI F/W adapter and two 4.5 GB F/W SCSI internal drives
>
> Power GXT150 8 bit color display adapter and 17" Color monitor
>
> 128 MB RAM (one workstations has 256 MB RAM)

B. Upgrade of an existing IBM RS/6000 370 Workstation

> Seagate 4.5 GB F/W Disk Drive and SCSI 2 F/W Controller
>
> 2.3 GB 8mm DAT Drive in external enclosure
>
> Panasonic Double Speed CD-ROM Drive in external enclosure

C. Upgrade of two existing IBM RS/6000 32H Workstations

> GT3i 8 bit color display adapter and reconditioned 16" Color Monitor

D. Two PowerPC Macintosh Workstations

> Power Macintosh 7500/100 including:
>
> > 500 MB internal disk, 20" Apple Multiscan monitor
> >
> > 4 MB VRAM, 256 K L2 cache, and 32 MB RAM
>
> Power Macintosh 7200/75 including:
>
> > 500 MB internal disk, 17" Apple 1705 Multiscan Monitor
> >
> > 2 MB VRAM, 256 K L2 cache, and 16 MB RAM
>
> LaserWriter 4/600

E. Upgrades to two existing Macintosh Workstations

> 66 MHz Turbo 601 w/ 256 K cache for Mac IIci
>
> Powerpro 601 card for Centris 650
>
> 17" Apple Multiscan monitor for Mac 7100/80

The equipment purchased differs slightly from the list itemized in the proposal. At the time the proposal was written, the IBM RS/6000 39H had not been released. This machine is a factor of two faster than the 390 (which had been included in the proposal) by reason of a larger memory $\rightarrow$ cpu bandwidth and a large L2 cache. Some of the remaining funds were used to upgrade three of our existing RS/6000 workstations to extend their useful life as well as to acquire two new Macintosh workstations based on the new PowerPC 601 processor and incorporating fast PCI busses. Finally, PowerPC accelerator cards were acquired to replace the aging 68040 cpu's of two existing Macintosh workstations.

SUMMARY OF RESEARCH ACCOMPLISHED

The equipment acquired under grant no. F49620-95-1-0046 is being used in the following projects:

1. *Ab Initio* Studies of complexes involving atomic boron

Extending earlier work on the BAr complex,[1] we carried out *ab initio* calculations of the BNe $X^2\Pi$, $A^2\Sigma^+$, and $B^2\Sigma^+$ electronic states.[2] Two highly correlated *ab initio* methods were used: multireference, internally contracted, configuration interaction (MRCI) and coupled cluster [UCCSD(T)]. To carry out these calculations, we have installed the latest version of the MOLPRO program suite[3] on the new RS6000/39H workstations.

For the previously studied B–Ar system, two minima with an intervening barrier were found for the B state. For the Ne complex, no well is seen at shorter distances. Only a slight inflection in this repulsive wall hints at a vestige of an attractive interaction.

As a modification of the *ab initio* potential, following an earlier suggestion by Brown and Truhlar,[4] we scaled the correlation energy by multiplication by a geometry-independent constant. This scaling will compensate, in an *ad hoc* manner, for missing external correlation energy due to both the finite size of the orbital basis and the exclusion of higher order (triple, quadruple, ...) excitations out of the reference space. Ours is the first application of a scaled correlation energy correction to a weakly bound complex.

The predicted dissociation energy, rotational constant, and Λ-doublet splitting constant of the lowest vibrational level of the BNe $X^2\Pi$ state were all in excellent agreement with experimental estimates from Dagdigian's group.[2]

In earlier work supported by AFOSR we used MRCI methods to determine the three adiabatic potential energy surfaces for the $B(^2P)H_2$ system. Using our new workstations, we extended these calculations in two directions. The earlier calculations use an approximate method,[5] to define the transformation from the *adiabatic* electronic states (which result from the *ab initio* calculation) into the *diabatic* electronic states (needed[6,7] in the determination of the bend-stretch levels of the BH_2 complex). Our new calculations, based on a more exact treatment, confirmed the accuracy of this earlier work.

Secondly, to investigate the interaction of electronically excited boron [B(... $2s^23s$)] with H_2, we carried out additional MRCI calculations.[8] Over the range of configuration

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space explored, for collinear approach of the H_2 molecule the interaction is purely repulsive. For perpendicular approach, however, the behavior of the interaction potential is reminiscent of what we found earlier for the interaction of $B(^2S)$ with Ne: a broad, gradually repulsive shoulder, and then, at smaller R, a steep repulsive wall.

Using our calculated electronic-vibrational wavefunctions for the ground-state complex, and calculated wavefunctions for the simpler, electronically non-degenerate excited state, we simulated the laser fluorescence excitation spectra of the $B\cdots H_2$ and $B\cdots D_2$ complexes observed by Dagdigian and co-workers.[9] One must include fully the rotational orientation of the o-H_2 (p-D_2) moiety, as a function of the B–H_2 separation.

In more recent work, we have initiated the study of the complexes of ground and electronically excited boron with molecular nitrogen. The determination of the energies, adiabatic states, and bend-stretch levels of the ground state complex follows our earlier work on the $B\cdots H_2$ complex.[6] However, the investigation of the excited state complex is considerably more difficult, because the approach of the N_2 molecule induces a mixing between the ... $2s^23s$ and ... $2s2p^2$) electronic states of of B. Thus, the accurate determination of the potential energy surfaces involves MRCI calculations of higher excited electronic states. The two RS/6000 39H workstations acquired by the present grant represent an increase in our computational capacity of ~ 4.5. Without this, the new calculations on $B\cdots N_2$ would have been impossible.

2. Simulation studies of $B(Ar)_n$ clusters

In work involving larger clusters we have developed a modified genetic algorithm (GA) method for the determination of the global minimum of atomic clusters described by pairwise analytic interaction potentials.[10] Our modification involves a coarse local minimization of each member of the population at every generation, as well as inclusion of the gradient into the fitness function. For Lennard-Jones $(Ar)_n$ clusters with $n < 20$, the new method converges far more quickly (up to two orders of magnitude) to the local minimum than either conventional GA methods or random search procedures.

An application of this modified GA was made[10] to heterogeneous clusters of $B(^2P)$ with multiple Ar atoms. Following Balling and Wright,[11] we assume that the interaction potential is given by the lowest state of a 3×3 electronic Hamiltonian. The Ar–Ar

potential[12] and the lower energy (Π state) B–Ar potential, taken from our own earlier work,[1] are very similar. In contrast, the higher energy (Σ state) B–Ar interaction is essentially repulsive. Consequently, the B atom was always found to substitute for one of the peripheral atoms in the corresponding $(Ar)_{n+1}$ cluster.

In this published work, we ignored the spin-orbit splitting of the B atom. In more recent work, currently in progress, we are including the spin-orbit splitting. At each point the interaction potential is now given by the lowest root of a 6×6 Hamiltonian, which increases considerably the computational effort.

With improvements in their experimental apparatus, Dagdigian's group has been able to take spectra of boron-argon complexes at higher backing pressures. Features due to higher BAr_n ($n > 1$) have been seen. We are currently involved in simulating the excitation spectra of BAr_2 clusters, using the diffusion Monte-Carlo method[13-15] we used in earlier, AFOSR supported work on complexes of B with multiple p-H_2 molecules.[16]

3. Development of version 4.0 of the Hibridon scattering code

Over the past decade, in collaboration with David Manolopoulos of Oxford University (UK) and Hans-Joachim Werner of the University of Stuttgart (Germany) we have built up a new hybrid computer code – the Hibridon code – for solution of the close-coupled equations which arise in the quantum description of inelastic scattering.[17] This package combines two sophisticated propagation algorithms,[18, 19] both of which combine great speed and numerical stability. The Hibridon code has been written in a modular fashion and designed to take advantage of fast library routines for matrix inversion, multiplication, and diagonalization which are available on most computer systems, in particular the Engineering and Scientific Subroutine Library (ESSL) which is available on IBM RS/6000 workstations. Scattering problems involving up to ~1000 coupled channels can be solved routinely. In performance and speed, the HIBRIDON code is considerably superior to most, if not all, available inelastic scattering packages.

Recently we have extended the Hibridon code to calculate photo-dissociation cross sections,[20] determine bound states of van der Waals molecules,[21] and determine the collision[22] or photodissociative[23, 24] current density as an aid to the understanding of the

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mechanism of collisions and photofragmentation. During the past year, using the new workstations purchased with the present grant, we have completed version 4.0 of the Hibridon code. Among the particular features are a new user manual, written entirely as an HTML document, to be read using any of the current generation web browsers. Version 4.0 is now available for installation on IBM RS/6000, HP-9000, SGI, and DEC Alpha workstations. More information is available at the web site

http://www-mha.umd.edu/~mha/hibridon/

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