1. INTRODUCTION AND BACKGROUND

The research we are pursuing on electronic structure of weakly bound helium and hydrogen species is supported by Contract Number DE-AC02-79ER10470, with Dr. Walter J. Haubach as Technical Monitor. This work grew from interest in a remarkable experimental observation at Los Alamos, and our studies are complementary to further experiments being conducted there by R. D. Taylor and his colleagues of Group P-10. The Los Alamos work shows that the helium generated from radioactive decay of liquid tritium remains in solution at concentrations which exceed the known solubility by much more than a factor of 100. The understanding of this "supersolubility" phenomenon is a challenging problem with significant implications for other condensed phase systems, as outlined in our original proposal and discussed further in last year's report.

In the hope of discovering the mechanism of the "supersolubility", we have carried out extensive electronic structure calculations employing several methods to evaluate the binding energies of complexes of the form \( \text{He}(H^+)(H_2)_n \), with \( n = 2, 3, 4 \). For comparison we have made similar calculations for the complexes \( H_2(H^+)(H_2)_n \). We have likewise calculated the binding of the negative counter-ion species of the form \( (H^-)(H_2)_n \). The methodology and some of the preliminary results were presented in some detail in last year's report. These calculations have now been completed and a full description is provided in a manuscript which will soon be submitted for publication. However, although the calculations show that such complexes have sufficient binding energy to account for the enhanced solubility at the low temperature (20 K) of interest, major questions remain to be clarified. These include the mechanism for formation of the complexes, which may well involve excited, Rydberg-like states in solution. Another quite
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
crucial question is how such weak complexes could persist in solution for months without displacement of the He by solvent molecules. Indeed, our calculations comparing the He and H₂ cationic complexes show that in the gas phase such a displacement process would be energetically favored; thus it is essential to develop methods of estimating the effect of the condensed phase environment.

In our current work, and that we propose for next year, our theoretical calculations focus on three topics: (1) Rydberg states; (2) condensed phase interactions; and (3) estimates of ionic conductivity in tritium solutions, as an aid to the interpretation of experiments now underway at Los Alamos.

This year we also undertook a molecular beam experiment in our laboratory to obtain some information about hydride complexes by means of techniques we have developed in recent work on electron attachment to weakly bound molecular clusters. Again, this complements the Los Alamos experiments, which do not offer any means to characterize the negative counter-ion.

II. CURRENT WORK

A. Electronic Structure of Complexes

A manuscript, "Electronic Structure of Helium and Hydride Complexes," is nearly finished. It compares results obtained by several computational methods for a variety of geometrical structures of complexes of the form X(H₂)ₙ with X=HeH⁺, H₂, or H⁻ and n=2, 3, 4.

B. Vibrational Spectra

Another manuscript "Vibrational Spectra of Tritium-doped Solid Hydro-
gen Isotopes," is also nearing completion. This reports the calculations started last year for comparison with the theoretical results obtained by P. C. Sowers and his coworkers at Lawrence Livermore Laboratories. They found the IR spectra of solid T₂, D₂, tritium-doped D₂ and HT at low temperatures shows three new lines which appear between 20 and 127 cm⁻¹ below the Qₐ peaks for the diatomic molecules. We use the results from part A above to evaluate frequency shifts for T₂ vibrations in various conformations of T₅⁺ and T₃⁻. We also carried out a normal mode vibrational analysis and obtained estimates of the relative intensities of the peaks, as well as the frequency shifts. The results are in quite good agreement with experiment.

C. Rydberg States

According to the analysis presented in our original proposal and in last year's report, we expect the radioactive decay of liquid tritium to produce a cation-anion pair, (³He-Tₙ⁺)...(T⁻-Tₘ⁻). However, as a precursor species, it seems likely that the emitted β-ray, before localization of the electron, exists in what amounts to a "solvated Rydberg state." This viewpoint has led us to undertake calculations on Rydberg states of the H₃ molecule. This species consists of H₃⁺ ion-core with the electron in a quasi-hydrogenic orbit. Herzberg has recently obtained beautiful spectra for several excited Rydberg states of H₃. It is highly likely that the corresponding T₃ species is formed as at least an intermediate in the β-decay of liquid tritium.

Our study of H₃ has led to recognition of a previously unnoticed relationship between the energy levels of the H₃ excited Rydberg states and those of the corresponding united atom, in this case lithium. A "symmetry reversal" seems to occur as indicated by the following correspondence:
\[ \begin{align*}
\text{Li} & \quad \text{H}_3(D_{3h}) \\
\text{np} & \leftrightarrow \text{ns}A_{1}^1 \\
\text{ns} & \leftrightarrow \text{np}E^1 \\
\text{for } n = 2, 3, 4
\end{align*} \]

We find the same reversals occurs when comparing excited Rydberg states of H\(_2\) and He, for both the singlet and triplet spin configurations.

D. Pressure-Induced Changes in Electronic Structure

In order to develop a tractable method for estimating the condensed phase interactions, we have naturally turned attention to previous treatments of the solvated electron. Such treatments primarily use a model in which the electron is located in a spherical "bubble" (often referred to as a "box") imbedded in a continuous dielectric medium. In studying the published treatments of this kind, we were struck by the fact that they do not seem to consider explicitly the role of "internal pressure" in the liquid. Long ago, Hildebrand showed that internal pressure is the key parameter in understanding solubility. Furthermore, it is a well defined thermodynamic quantity, given by the negative derivative of the energy with respect to volume. These considerations have led us to undertake electronic structure calculations for molecular species confined in "bubbles" or "boxes."

For the first such study, we carried out a rather rigorous calculation for a hydrogen molecule in a rigid spheroidal box. A paper describing these results has been submitted for publication. This system was chosen because it involved only two electrons and recent experimental results on the pressure dependents of the vibrational frequency are available. An abstract of the paper is attached.
E. Molecular Beam Experiments

We have proceeded as outlined in the proposal submitted last year. The hydrogen cluster source has been designed, constructed, and put into operation. Preliminary attempts to produce an \((\text{H}^-)(\text{H}_2)_n\) complex have not yet succeeded. As anticipated, the experiment faces two chief difficulties: (1) the need to achieve a sufficiently high collision energy and (2) the "time-scale" inhibition of electron-transfer. The latter effect, which we have characterized in other work in our laboratory, arises when a complex containing a sizable number of monomer units is required for the initial trapping of the electron. In that case, the short time scale (in effect subpicosecond) of the fast collision inhibits the electron transfer because the target complex does not have time to allow monomer units to rearrange and solvate the electron in the optimal way. As described below, we have now devised a strategy which should deal with both these difficulties.