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Molecular photodynamics in cryogenic solids are pursued in an effort to characterize the many-body interactions and dynamics that will control the possibilities of preparing, stabilizing, and subsequently using doped solid H_2 as a propellant. While may of the experiments carried out involve inert rare gases, the photophysics sought in these experiments and theoretical developments form the fundamentals that transcend the specific host. In this class of issues are: a) how to describe the interactions of open shell atoms, which by definition will be the nature of dopants in propellants; b) development of a basic understanding for the relation between pair potentials and free energy, which controls diffusion kinetics of dopants in compressible solids; c) to develop time resolved experimental tools to interrogate these in detail; d) finally, we have carried out studies in one of the candidate systems, namely O doped solid D_2. Aspects of this work have already been published. A list of the 1993-1994 publications from our group is included, all of this work has resulted either from the URI or the earlier funded AF contract on HEDM from the Phillips Laboratory.

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Irvine University Research Initiative
on
Advance Cryogenic Propellants

Annual Research Report, FY '93-'94

V. A. Apkarian, R.B. Gerber, K. C. Janda, J. Rutledge, P. Taborek
University of California, Irvine, CA 92717

This progress report covers the first year of operations of the Irvine URI on advanced cryogenic propellants. A rather ambitious program has been initiated and significant progress has been made over the last year. In addition to the five active faculty members in this program, a large number of students and postdoctoral fellows are intimately involved in the project. Below is a list of the personnel who are at least in part involved in the URI projects, some are funded in part, or entirely, by other sources. These are:

S. Clement	Postdoc	Chemistry
R. Zadoyan	Postdoc	Chemistry
A. V. Danilychev	Ph. D. candidate (4th year)	Chemistry
M. Hill	Ph. D. candidate (4th year)	Chemistry
D. Jahn	Ph. D. candidate (4th year)	Chemistry
K. Kizer	Ph. D. candidate (2nd year)	Chemistry
B. Barney	Ph. D. candidate (2nd year)	Chemistry
B. Calicoat	Ph. D. candidate (2nd year)	Chemistry
A. Krylov	Ph. D. candidate (2nd year)	Chemistry
D. Perry	Ph. D. candidate (1st year)	Chemistry
S. Tam	M.S. candidate (1st year)	Chemistry
D. Devecchio	Ph. D. candidate (3rd year)	Physics
T. Zhu	Ph. D. candidate (2nd year)	Physics
J-P Mancinelli	Ph. D. candidate (1st year)	Physics
K. Lamaye	Ph. D. candidate (1st year)	Physics

The URI has kept in close touch with the AF Phillips Lab at Edwards, and in fact S. Tam in the above list is on leave from there. There has also been communication with JPL, and a joint proposal was submitted to the Caltech Presidents Fund for carrying out ESR studies in HEDM. The proposal was not funded. As part of the educational and research activities, the URI has actively engaged in a seminars and tutorials program dedicated to physics, spectroscopy and chemical dynamics in quantum solids. One of the speakers in this series was Prof. E. Gordon of the low temperature physics laboratory in Chernogolovka, Russia, who has been the leading scientist in the USSR on advancement of cryogenic propellants. The URI will also organize and host a symposium on Physics and Chemistry in Quantum Solids and Fluids, in February 1995, in Newport.

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A detailed organizational chart, modes of operation of the URI, progress to date, the collaborations and the rationale behind them have been presented at the annual HEDM meeting in Lake Tahoe, and will therefore not be repeated here. In this annual report the general progress by individual PI's will be summarized.

I. Photodynamics in cryogenic solids (V. A. Apkarian):

Molecular photodynamics in cryogenic solids are pursued in an effort to characterize the many-body interactions and dynamics that will control the possibilities of preparing, stabilizing, and subsequently using doped solid H_2 as a propellant. While many of the experiments carried out involve inert rare gases, the photophysics sought in these experiments and theoretical developments form the fundamentals that transcend the specific host. In this class of issues are: a) how to describe the interactions of open shell atoms, which by definition will be the nature of dopants in propellants; b) development of a basic understanding for the relation between pair potentials and free energy, which controls diffusion kinetics of dopants in compressible solids; c) to develop time resolved experimental tools to interrogate these in detail; d) finally, we have carried out studies in one of the candidate systems, namely O doped solid D_2. Aspects of this work have already been published. A list of the 1993-1994 publications from our group is included, all of this work has resulted either from the URI or the earlier funded AF contract on HEDM from the Phillips Laboratory.

A) Characterization of many-body potentials for open shell atoms, and the implied dynamics of coupled electronic-nuclear degrees of freedom: The cryogenic propellants that are imagined will invariably contain dopants, atoms or radicals, which have open outer electronic shells. This immediately implies an angularly anisotropic interaction potential, one which is dictated by the electronic degrees of freedom of the dopant, which in turn explicitly depend on the nuclear coordinates of the entire lattice. We have approached this problem by starting from anisotropic gas phase pair potentials, and considered the eigenstates that result when the electronic degrees of freedom are much faster than those of the nuclear degrees of freedom. This limit of adiabatic following is the proper one for describing thermal motions. As the simplest test case for this approach, we have scrutinized the one hole system of an I atom isolated in solid Kr and Xe, and the two hole system of O atoms isolated in the same. In the case of I atoms, we were able to successfully treat the spectroscopy of spin orbit transitions which involves a strong Jahn-Teller instability. We were able to identify the many-body modifications to pair potentials, and quantify them. This work has been accepted for publication [7]. In the case of O atoms, in addition to site selective spectroscopy, of atoms trapped in stationary sites· adiabatic potential energy surfaces were generated [8] to address the issues of unusual thermal mobilities which we had measured in free standing crystals [5]. The latter question remains open, and generally the diffusion of open shell atoms in compressible solids remains ill understood. This issue is even more serious in quantum solids, and the thermal mobilities of O and O_2 in solid D_2 which we have recently investigated, indicate that the collective lattice dynamics will play a major role in the stabilization of trapped species (see below).

B) Statistical theories of solid state photodynamics: To rationalize experiments, photodynamics in solids has in the past been mostly treated by simulations. This has been a necessary first approach in establishing insights into dynamics that is complicated due to its many-body nature. There now is a significant body of work, experimental and theoretical, to devise generalizations, in the form of statistical theories. We advanced the first treatment of this type, a statistical theory for cage exit in the sudden limit, and cage induced bimolecular reactivity, and used it to treat our own experimental data on photodissociation of H_2S in solid Ar and Kr[10]. The work will appear in J. Phys. Chem. as a Feature article. The treatment has already been successful in rationalizing the significant body of work on temperature, energy, and mass dependence of photodissociation of hydrides in rare gas solids. An important aspect of this work is that the quantum zero-point motions of the lattice have been incorporated in the model, a feature that cannot be directly incorporated in simulations. We note, that photodissociation is one of the most direct methods for in situ generation of atoms, although the present treatment was limited to H atoms, we are now extending the theory to open shell atoms in general. Due to the fact that the quantum statistics of the lattice is taken into account, the treatment should also be valid to applications in solid H_2. We will test these theories in our experimental work on solid D_2.

C) Femtosecond time resolved studies: Perhaps the most significant accomplishment in the last year was in the area of time resolved femtosecond measurements of reactive dynamics in solids [6, 9, 12, 13]. We reported the first observations of the breaking and remaking of a bond in the solid state. In addition to the experiments, by collaboration with the group of Professor Martens of the Chemistry Department at UCI, we have also carried out simulations and nearly quantitatively reproduced the observables. This non trivial exercise has changed the thinking about exactly what is measured in femtosecond pump-probe experiments. With a detailed understanding of the experiment, we have been able to extract details of dynamics that hitherto would have seemed unattainable. The majority of this work has concentrated on I_2 doped rare gas solids, a choice dictated by the available time resolution to us of 150 fs. In addition to following the I-I coordinate, we have been able to follow the cage motions, and the lattice degrees of freedom that are coupled to the dopant directly. The frequencies and modes of the coupled motions of the lattice and the phase relations between the molecular and lattice degrees of freedom are directly extracted from the experiment, by iteration with theory. These detailed observations enable the detailed characterization of configurations of the system far removed from equilibrium, and far removed from the Franck Condon accessible region. We believe that for the first time we have developed the tools that have the required sensitivity to be useful in scrutinizing many-body reactive dynamics.

D) O doped solid D_2: This is a candidate cryogenic propellant. We have prepared it by photodissociation of O_2 initially doped in the D_2 lattice. The photodissociation could be followed by monitoring laser induced fluorescence from O atoms, and from O_2 molecules. The following very significant conclusions could be made: a) O(^{3}P, ^{1}D, and ^{1}S) do not react with D_2/H_2 at cryogenic temperatures; b) The lattice locally anneals around the O atoms, leading to only one isolation site; c) The doped solid is stable up to 5.1 K, when a structural transition occurs leading to local diffusion of the dopants; d) The O atoms can be kept stable in the solid up to 7.5 K, at which point thermally activated diffusion leads to runaway and recombination; e) The thermally induced recombination can be followed by thermoluminescence, and is accompanied by a pressure burst indicative of simultaneous evaporation of the lattice. These observations are now being summarized for publication and as part of a Ph. D. thesis. For practical applications, one of the most important issues is the absolute atom, and energy content of the solid. To this end, we are now installing the thermometers and bolometers designed and build in the URI, in the groups of Rutledge and Taborek. In a second stage of this development, a micro balance will be added to the bolometer, enabling us to measure mass loss in addition to heat released. These will be the first quantitative measurements of energy content in these potential propellants.

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II. Growth kinetics of solid hydrogen (P. Taborek and J.E. Rutledge)

A special cryostat has been designed and built for hydrogen experiments over the temperature range from 1 to 30 K. As shown in Figure 3, it features a carefully heat sunk copper sample chamber to ensure the highly isothermal conditions these studies require and contains a port for the addition of an atom source. We have been investigating atom sources with particular attention to minimizing the power consumption to allow in situ low temperature growth. The potentially promising technique of forming solid hydrogen with high concentrations of atomic dopants by direct condensation will be conducted in this apparatus.

The first experiments have been studies of the growth of solid molecular hydrogen films under thermal equilibrium conditions using a quartz microbalance technique. A surprising wealth of phenomena are known to accompany the growth of surface films. Among these are surface phase transitions such as wetting and roughening transitions. The location of these transitions in the P-T plane are indicated schematically in Figure 4. The sub-monolayer mass sensitivity of quartz microbalances have made them an important means of exploring these phases. We have modified the microbalance to include thin film heaters and thermometers, as shown in the inset to Figure 3. These modifications will allow calorimetric studies to more thoroughly characterize the growth. The experimental challenges include adding the devices and the leads without sacrificing the mass sensitivity and developing thin film thermometers that can be applied to the quartz surface without substantially increasing the heat capacity of the device. We have developed a technique for sputtering niobium doped silicon films that are well suited for resistance thermometry in the temperature range of interest. A measurement of the resistance versus temperature for one of these thermometers is shown in Figure 5. We have also succeeded in bonding leads onto the films in a way which does not degrade the performance of the microbalance.

To study the growth of solid hydrogen films at temperatures not far below the bulk triple point, we have measured adsorption isotherms. In these experiments, the temperature of the can is held constant and the pressure increased from zero to the bulk sublimation pressure while the mass signal from the microbalance is recorded. The trajectory of such an experiment in the μ-T plane and the resulting isotherm are shown in Figure 4 and 6. The result is typical of most solid films well below the triple point. As the film grows strains develop as the adsorbate accommodates its structure to that of the substrate. After a few layers, the thermodynamic costs of the strains overwhelms the thermodynamic advantage of being in the attractive potential well of the substrate and film growth stops.

At lower temperatures the drastically reduced sublimation pressure is too low to permit direct measurements of isotherms. To study the growth below 4 K we are pursuing thermal desorption experiments. A pulse of heat is applied to the heater sufficient to remove the film from the microbalance. The mass signal is then monitored as a function of time as gas phase molecules collide with and stick to the surface. At 4 K the molecules hit the surface at the rate of one solid monolayer per second, while at 2.4 K the growth rate is a monolayer per year. The result of one such experiment is shown in Figure 7. After the topmost layers of the film are removed and readsorption begins, an instability that affects the resonant frequency of the microbalance develops. Onset time of the instability scales roughly with the monolayer time. Attempts to understand this signal and relate it to properties of the growing film are current under way.

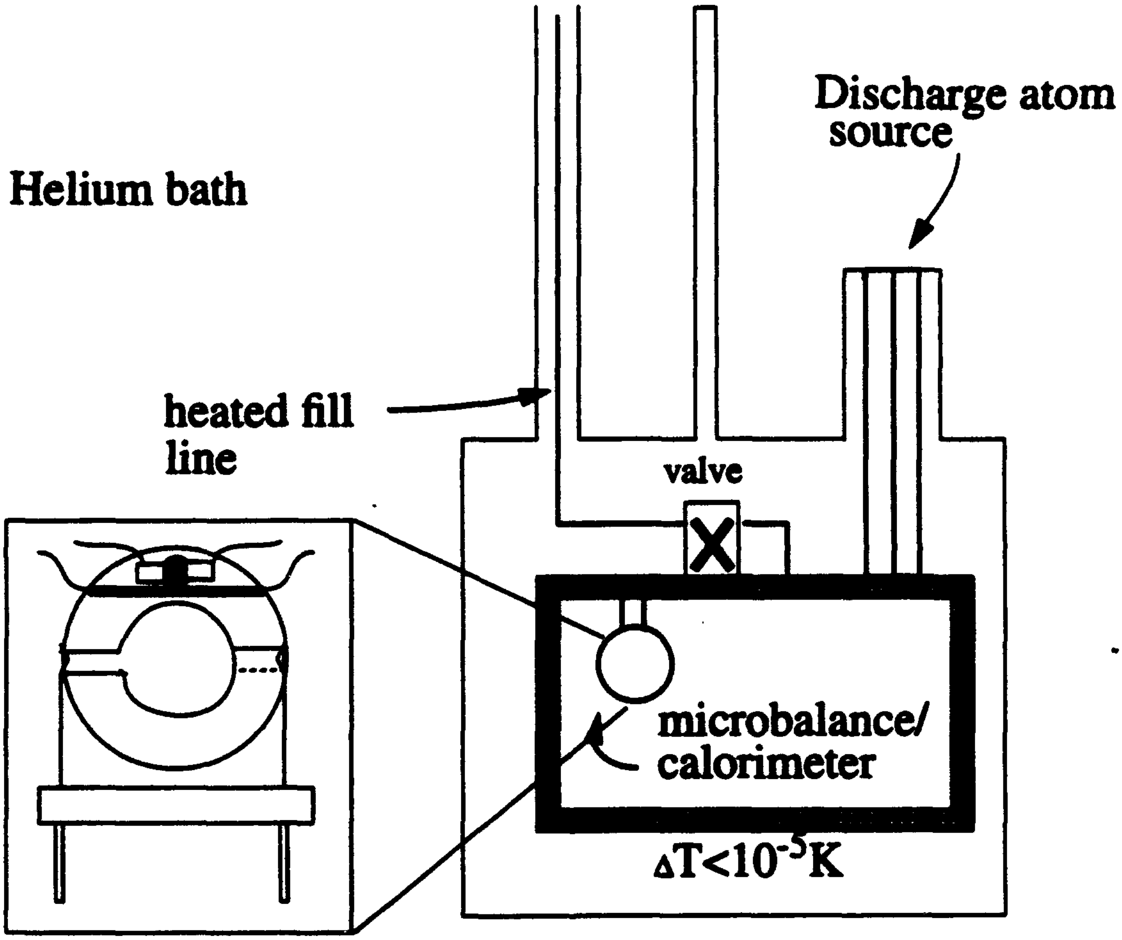

Figure 3. Apparatus for studying growth of hydrogen films. The inset shows details of the thin film heater and thermometer on the microbalance/calorimeter.

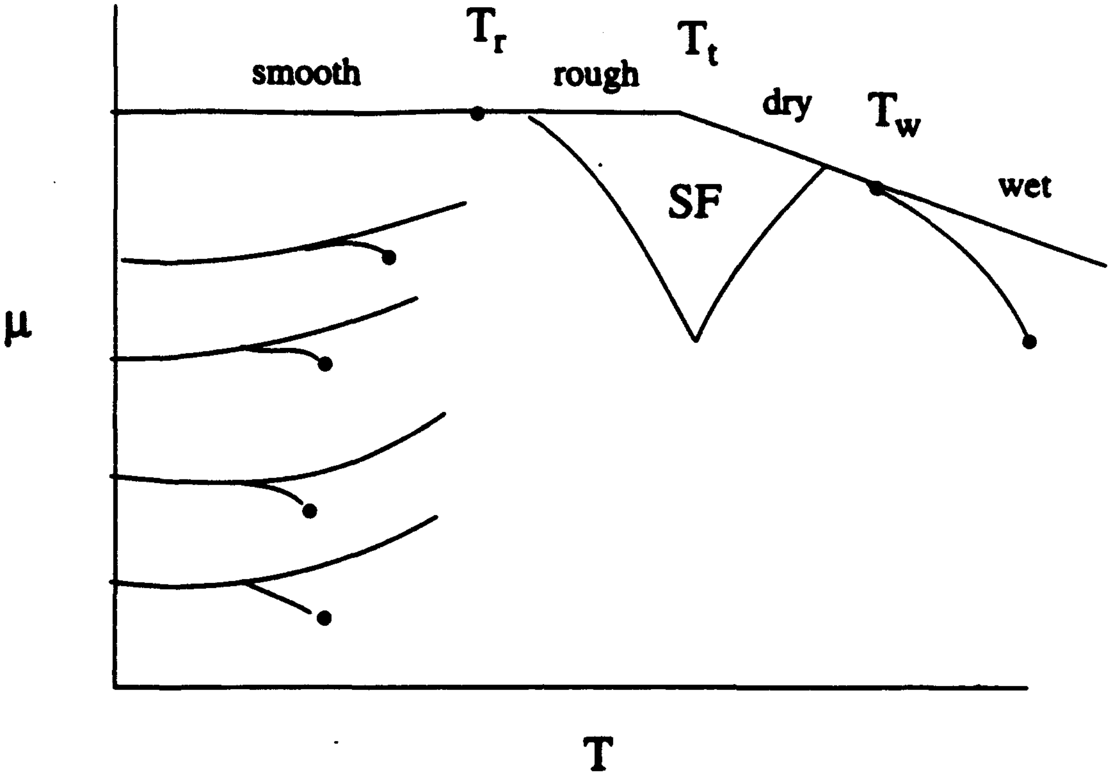

Figure 4. Schematic phase diagram in the μ-T plane of a material growing on a substrate, showing solid, liquid and vapor phases in the adlayers. The 2D liquid-vapor critical points converge to the roughening transition at T_r at bulk coexistence. Other possible phase transitions are wetting at T_w which separates wet and dry regions of the coexistence curve, and prewetting which separates thin and thick film phases. In the vicinity of the triple temperature T_t, it is possible to have stratified films (SF) which consist of layers of solid covered with a fluid layer.

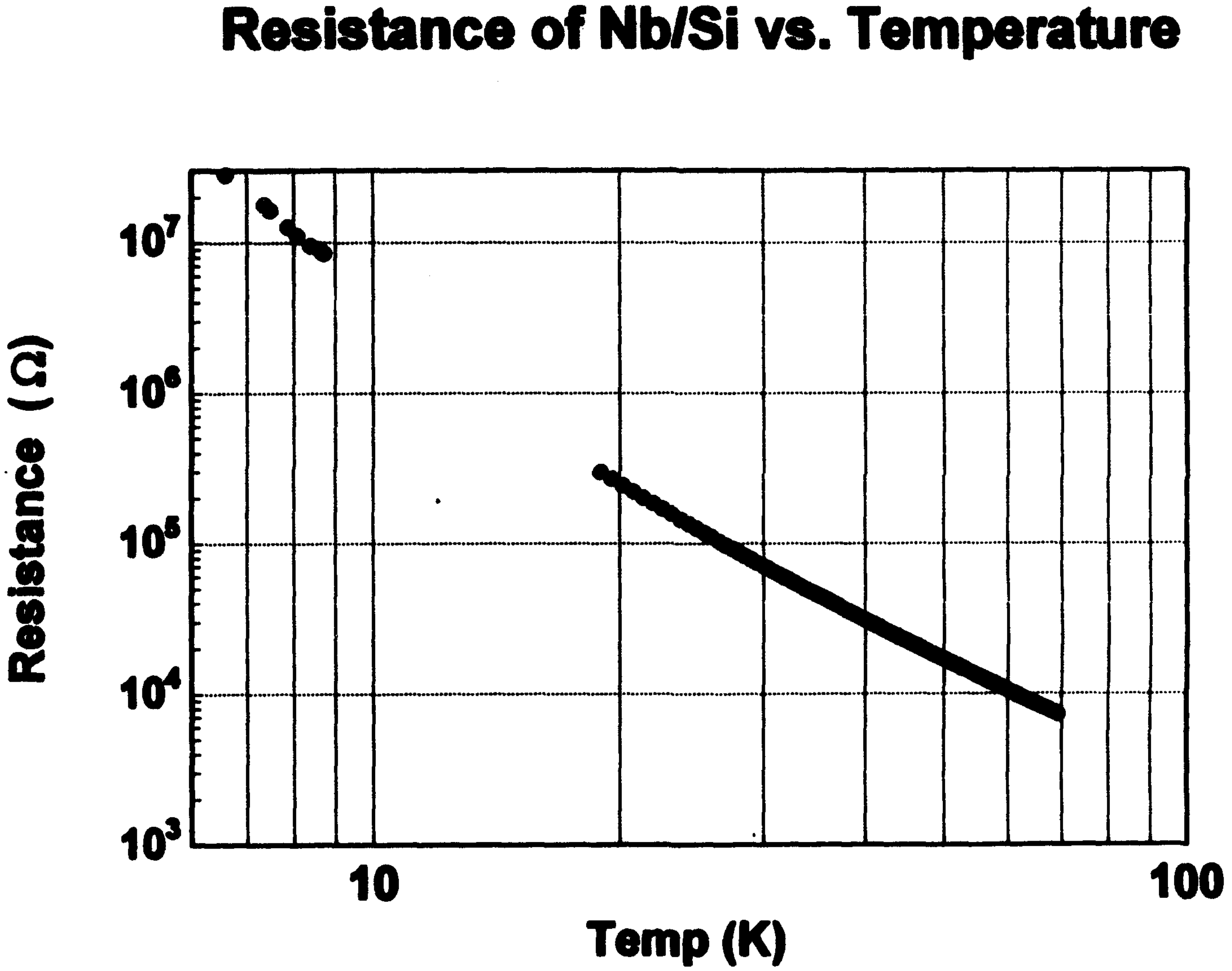
Resistance of Nb/Si vs. Temperature
Resistance (Ω)
10^7
10^6
10^5
10^4
10^3
10
100
Temp (K)

Figure 5.

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Figure 6

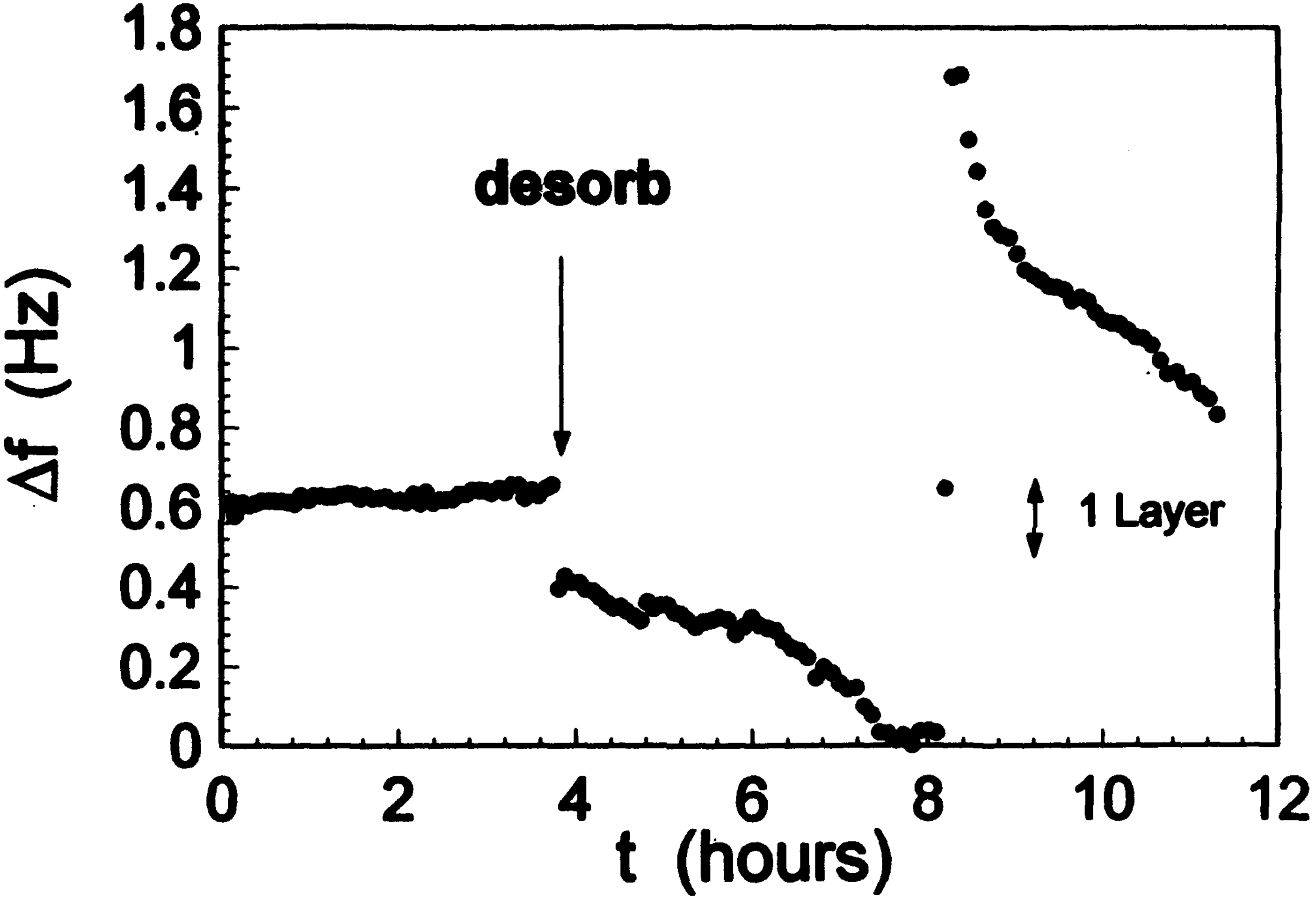

Figure 7. Response of microbalance to flash desorption at t=4 hrs.

II. Theory (R. B. Gerber)

Our theoretical and computational research aims at studying properties of doped solid hydrogen, as well as doped hydrogen clusters, which are of direct relevance to potential advanced cryogenic propellants. This research is closely related to work we pursue in the framework of a contract from the Phillips Laboratory of the U.S. Air Force. However, the specific topics and processes we pursue in the two projects are different, and there has been no duplication of effort. On the whole, our studies on Li in hydrogen, and most of the work on B in hydrogen, is supported by the Phillips Laboratory. Reference to such work in this report is made only for presenting a complete view. Work on systems such as $O(^3P)$ in hydrogen, $Mg(H_2)_n$ clusters, etc. is entirely in the framework of the URI project. Topics such as the survival of doped hydrogen clusters in collisions belong to the present URI project only.

The results presented here on the first year of the project, deal with several topics: (i) Development of potential surfaces for interactions between hydrogen and relevant "guest" atoms or molecules; (ii) Calculations of the energy and the vibrational wavefunction of the ground state of several doped hydrogen clusters, $A(H_2)_n$. These calculations, using the Diffusion Quantum Monte Carlo (DQMC) method were carried out for clusters as large as $n = 100$, give the stability of the cluster, its structure (or rather structural distribution, given the enormous floppiness) and the properties of the vibrations involved; (iii) Development of models for the vibrational wavefunctions. We constructed relatively simply, physically based models that were fitted to the numerical wavefunctions for the ground-states of the $A(H_2)_n$ clusters, small and large. The models provide insight into the geometric and topological properties of the wavefunctions, give the classification of the vibrational modes involved, and have very useful spectroscopic implications. (iv) We calculated, by time-dependent quantum wavepackets, the survival probabilities of quantum clusters such as $B\cdots H_2$, in collisions with molecules, e.g. H_2. This provides data which is useful for potential methods being considered for the preparation of doped solid hydrogen systems. The results are very interesting, in the sense that surprisingly large survival probabilities are predicted. (v) The spectroscopy and dynamics for the UV photoexcitation of Li in the $Li(H_2)_2$ cluster were calculated by wavepacket techniques. This study is part of our project in the framework of the Phillips Laboratory supported contract. However, similar calculations are projected soon for systems in the framework of the URI scheme.

Research Results

A) H_2 *interaction potentials with guest molecules:* This work pertain to our URI project, and was not included in the proposal for Phillips Laboratory contract. In the framework of this research we are developing high-level *ab initio* potential energy surfaces for several pertinent hydrogen-molecule/dopant molecule systems. The calculations carried out so far are for $Cl_2 \cdots H_2$ and $H_2 \cdots HCl$ (Systems for which we can test our potentials against high-resolution spectroscopy). The level of the potentials obtained is at least that of MP-4 calculations, and suffices not only for qualitative conclusions on "solvation" of Cl_2 hydrogen, stability and structure of the cluster, but is also sufficient for spectroscopic calculations. Calculations at this level for $O_2 \cdots H_2$; $O(^3P) \cdots H_2$ $Mg \cdots H_2$ are under way. Consider the results for $Cl_2 \cdots H_2$. The classical minimum corresponds to a well-depth of ~190 cm^{-1}. The classical equilibrium structure has the H_2 center of mass on the Cl-Cl axis, with the H_2 axis perpendicular to that of the Cl_2. The H_2 rotation is very large in amplitude, but the rotation within the cluster is hindered to a significant extent. A second minimum, in which the H_2 c.m. *is normal to the* Cl_2 *axis*, is much higher in energy. The cohesion energy for breaking the cluster into Cl_2 and H_2 is about 60 cm^{-1} (based on the Zero Point Energy calculation). The result suggests good solvation of Cl_2 in solid H_2, Photolysis of Cl_2 in H_2 is expected to result in a fair yield for the Cl + H_2 chemical reaction. The solvation cage is expected to be quite anisotropic.

B) *Vibrational wavefunctions of doped* H_2 *clusters - Quantum Monte Carlo simulations:* We carried out Diffusion Quantum Monte Carlo simulations for several clusters of the type $A(H_2)_n$. Some of the systems studied have up to n = 100 molecules. The method was implemented on massively parallelized SIMD computers (Mas Par computers with 4,000 and 16,000 processors, respectively) and the algorithm and computational technology are, in our view, a significant contribution to simulations of quantum cryogenic materials. The methodology is pertinent both to the Phillips Laboratory and the URI project. The studies of $Li(H_2)_n$, $B(H_2)_n$(1) were carried out in the framework of the Phillips Laboratory project, but the work on $O(^3P)(H_2)_n$ $Cl_2(H_2)_n$ is for the purpose of the URI. $Hg(H_2)n$ was studied in detail as a useful model system (e.g. for $Mg(H_2)_n$), since much is known on

Hg···H_2 interactions, theoretically and experimentally.(2),(3) Table I lists most of the systems studied, and the cohesion energies obtained for clusters. (Several more systems are being analyzed and the results are not listed). We draw attention also to the study we carried out in cooperation with Pr. M. Alexander on $B(H_2)_n$ clusters, which will appear soon in J. Chem. Phys. (1) (This study was supported by the Phillips Laboratory). On the whole, systems with stable small clusters are expected to have advantages for HEDM, since usually this correlates with lower diffusity.

C) $A(H_2)_n$ *Cluster-models for the wavefunctions:* To understand the vibrational properties of the quantum clusters, we developed simple models for the wavefunctions, fitted to the numerical wavefunctions. The high dimensionality of the wavefunctions makes direct interpretation of the numerical data very hard. As an example, consider our results for $Mg(H_2)n$, in particular for n =13. The wavefunction was approximated by:

$$\psi(r_i,\dots,r_n) = \prod_{i>j} J(r_{ij}) \prod_{k} f(r_k) \qquad (1)$$

Here r_{ij} is the distance between the i and j hydrogen, r_i is the distance vector of the *i hydrogen* form the Hg, and rk = $|r_k|$. The functions and $J(r)$ were *obtained by fitting* the Monte Carlo results. Figs. 1,2, show how remarkable is the fit by Eq. (1). The results show that $Hg(H_2)n$, $n \leq 12$ is a spherical cluster, with radial-localized vibrations of the H_2 against the Hg. On each sphere away from the Hg, the H_2 motion can be visualized a free, except for mutual H_2-H_2 avoidance at short distances. These results have important spectroscopic implications.

D) $A(H_2)_2$ *as hyperspherical oscillators:* We found that small clusters of the type of $A(H_2)_2$ have vibrational states that are almost perfectly factorizable in hypershperical coordinates. The results have strong implications for the vibrational and electronic spectroscopy of these systems - these should be viewed as "hyperspherical oscillators" in the same sense that harmonic molecules are "normal mode" oscillators. This work is part of the URI project.

E) *Survival of quantum clusters in collisions:* Using quantum wavepacket methods, we calculated the outcomes for collisions of quantum clusters such as A···H_2 with H_2 molecules. The focus was on the probability of cluster survival. The most interesting findings were fairly high probabilities for survival (≥10%), also for collision energies that greatly exceed the (extremely weak) binding energy. Figure 3 shows a representative result for the simple case of collinear collisions of H_2 with B-H_2 - the survival probability is high whether the H_2 strikes the B end or the H_2 of the cluster. The results are encouraging for certain methods proposed for the preparation of doped hydrogen systems.

F) *Spectroscopy and dynamics in electronic excitation of Li in* $Li(H_2)_2$: This result will be mentioned only briefly, since it was obtained as part of our contract from the Phillips Laboratory. The UV photoexcitation of Li in $Li(H_2)_2$ was computed using wavepacket methods. The excitation spectrum, and the lifetimes of the excited state were computed, and the dissociation of the excited cluster was analyzed. A component of fairly long lifetimes (> 1 ps) was found. Interesting spectroscopy for ultrafast spectroscop experiments was predicted.

Cluster	**Potential**	**$E_{cohesion}$ [in cm^{-1}]**
$(H_2)_2$	**ab-intio**	**1.842**
$(H_2)_3$	**"**	**6.832**
$(H_2)_4$	**"**	**14.058**
$(H_2)_5$	**"**	**25.006**
$(H_2)_6$	**"**	**34.648**
$(H_2)_{10}$	**"**	**85.925**
$(H_2)_{13}$	**"**	**133.233**
$(H_2)_{45}$	**"**	**515.543**
$(H_2)_{100}$	**"**	**901.268**
$(Ar)_2$	**experimental**	**113.974**
$(Ar)_{13}$	**"**	**4634.878**
O-H_2	**empirical (crude)**	**15.001**
O-D_2	**"**	**19.789**
F-H_2	**"**	**14.064**

Cluster	Potential	$E_{cohesion}$ [in cm^{-1}]
$Hg\text{-}H_2$	empirical (crude)	14.166
$Hg(H_2)_2$	"	31.8
$Hg(H_2)_3$	"	50.82
$Hg(H_2)_4$	"	70.647
$Hg(H_2)_6$	"	114.428
$Hg(H_2)_{10}$	"	212.297
$Hg(H_2)_{12}$	"	272.65
$Hg(H_2)_{24}$	"	485.01
$Hg(H_2)_{40}$	"	687.685
$Hg(H_2)_{54}$	"	850.949
$Hg(H_2)_{100}$	"	1123.929
$Li\text{-}H_2$	ab-initio	0.758
$Li(H_2)_2$	"	3.86

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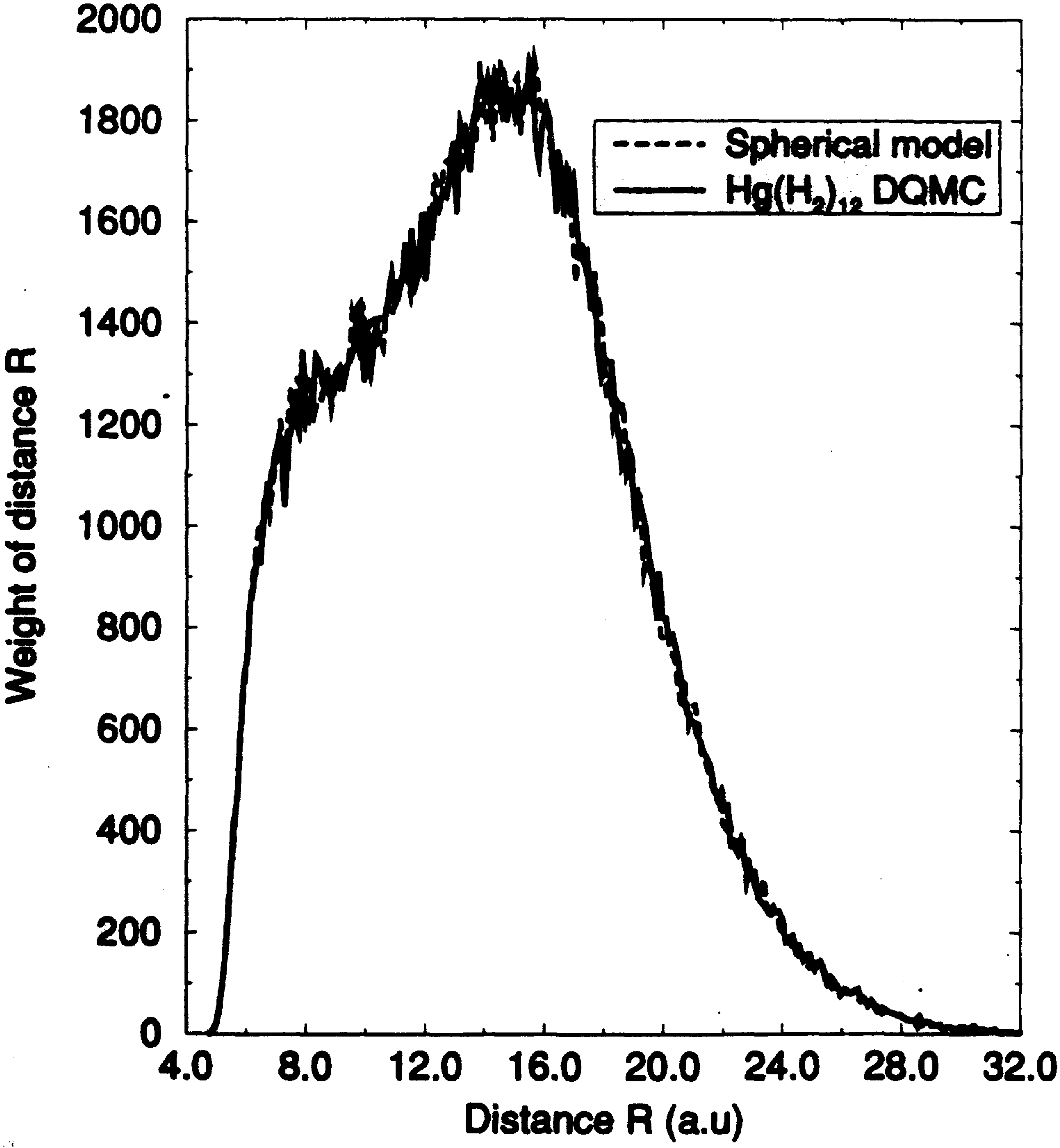
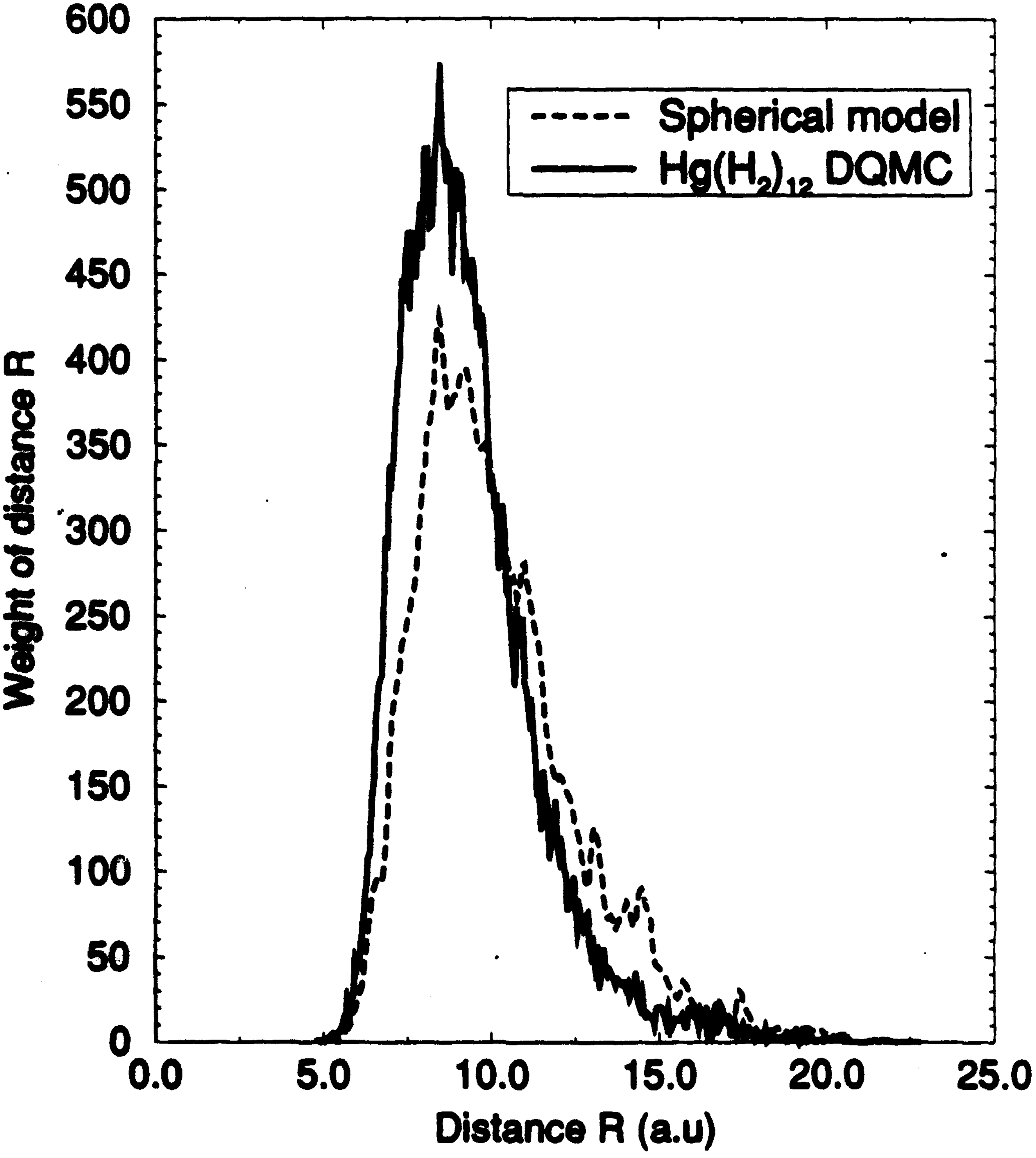
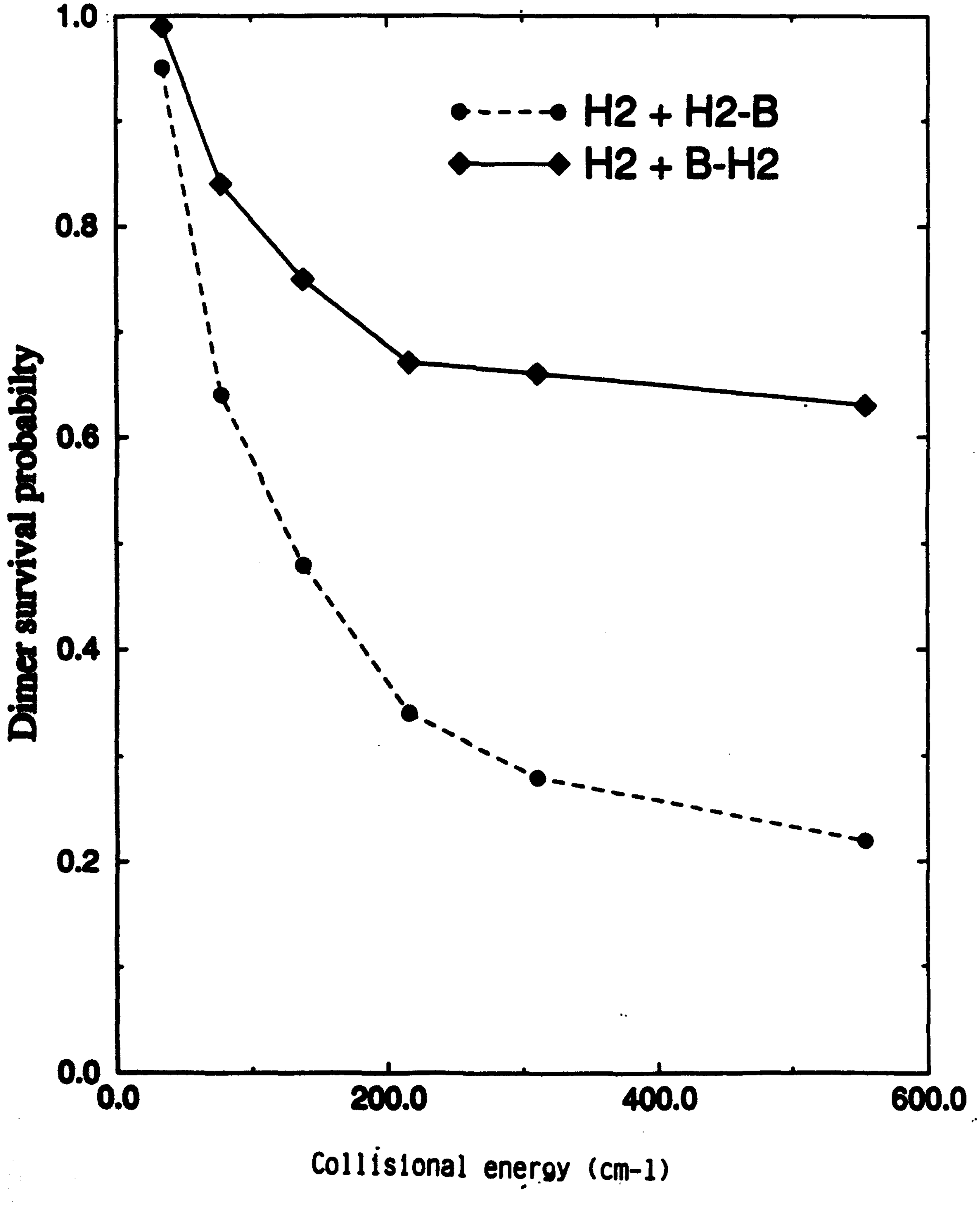
(3) W.H. Breckenridge, *Accts. Chem. Res.* 22, 21 (1989).

H_2-H_2 Distance Distribution



Hg-H_2 Distance Distribution




H2 + H2-B
H2 + B-H2
Dimer survival probability
0.0
0.2
0.4
0.6
0.8
1.0
0.0
200.0
400.0
600.0
Collisional energy (cm-1)

Beam and Cluster Development Effort

Overview: For this portion of the project, we are concentrating our efforts on preparations for depositing reactive atoms in hydrogen via the cluster deposition method. Our working hypothesis is that the pick-up source will be the best way to combine the H_2 with reactive species without inducing immediate reaction. Also, if we are to beat statistical deposition techniques, the pick up technique will give us the means to try to control the stoichiometry of the doped solid. The sequence of events would be to first make a cluster that contains n H_2 molecules and m He atoms. We expect that the structure of such a cluster would consist of a solid H_2 "core" surrounded by He atoms. The H_2/He cluster would then be collided with the reactive atom, for instance, a carbon atom. At this point we expect that the in the initial collision, the C atom would first encounter the He "coating" and be cooled off. The C atom would then diffuse in to the H_2 core with a kinetic energy of 1-2 K. If the reaction barrier for $H_2 + C$ is greater than 50 K, then we expect the C atom to survive the collision. Multi-photon ionization spectroscopy will be used to interrogate the composition of the cluster after the "pick-up". If the C atom survived, then the will observe the spectrum of C atoms surrounded by H_2 molecules, and this will be useful later in the analytical spectroscopy of the deposited C/H_2 matrix. If the C atom reacted, then we expect to see either CH or CH_2 reaction products. Although C atoms were used in this example, the analogous experiments will be tried with H, B, C, N, and O atoms.

After the H_2/He/C clusters are prepared and characterized, then the goal is to use them to build up a solid matrix. Again, the expectation is that the He atoms would coat the outside of the cluster so that when the cluster collides with the surface the He atoms would bear the brunt of the impact and provide a "soft landing" for the H_2/C "core". At that point MPI spectroscopy will be used to determine what whether the C atom was deposited without inducing a reaction.

We are pursuing these goals on three fronts. 1. We are developing pulsed discharge sources for the reactive atoms. 2. We are developing a cryogenic beam source for the He/H_2 clusters. 3. We are constructing the scattering/deposition chamber for combining the reactive species with the cluster, for spectroscopically probing the cluster and for eventual deposition to form matrices.

1. Atomic Discharge sources:

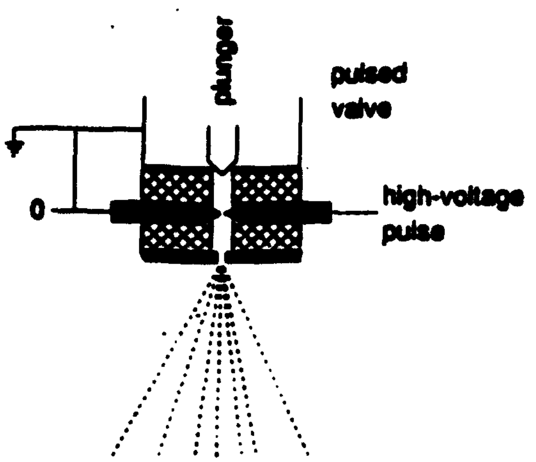
We have constructed and tested a pulsed discharge source as illustrated in Fig. 1. The discharge was run with diborane in Ar, and good laser excited fluorescence spectra for boron atoms were observed as shown in Fig. 2. From the intensity of the two spin orbit components of the transition, we estimate that the relative translational kinetic energy of the B atoms was 20 K. We are currently trying to find a geometry for the discharge nozzle that will give more cooling of the atomic beam. We are also constructing a multi-photon-ionization time-of-flight mass spectrometer (MPI-TOF) that will allow us to run the discharge with C_3O_2 and detect carbon atoms.

2. Cryogenic Beam Source for Clusters:

We have built and are in the early stages of testing a cryogenic He/H_2 beam source. The design is illustrated in Fig. 3. A closed cycle helium cryostat is employed to pre-cool the gas mixture to temperatures as low as 12 K.

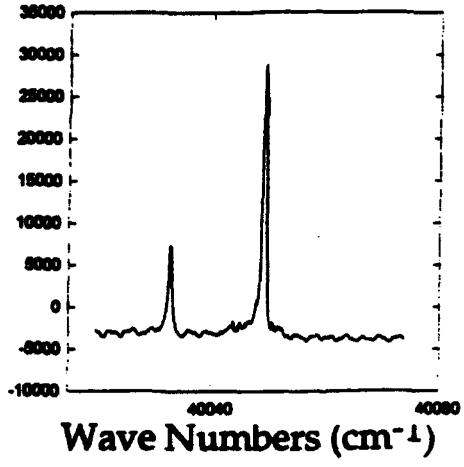
As part of our source development effort, we have been testing conical nozzles for cluster production. In principle, conical nozzles have several advantages over the more common thin nozzles. First, since the expansion is constrained to occur over a longer distance the pressure drops more slowly and more clusters are formed. Second, the resulting molecular beam is more highly collimated leading to higher beam intensity and on the main beam axis. We tested this concept on a study of the laser excited fluorescence spectrum of the $HeBr_2$ cluster. The output of a 300 psi supersonic expansion that consisted of a few Torr of Br in He carrier gas was probed by laser excited fluorescence. The probing laser was a pulse amplified ring laser with about 100 MHz (0.003 cm^{-1}) line width. The resulting excitation spectra are shown in Figs 4-6. The low resolution spectrum shown in Fig. 4 illustrates the excellent signal to noise ratios that can be obtained with the conical nozzles. The portion of the spectrum labeled $HeBr_2^*$ is an excitation to an excited bending mode of the $He\text{-}Br_2$ bond. Previous spectra for $HeBr_2$ were too weak to resolve this spectrum from the noise. Figure 5 shows the main $HeBr_2$ band at high resolution. This is the highest resolution spectrum ever recorded for the molecule and allows us to refine the structural constants. Figure 6 shows a high resolution recording of the transition to the excited bending mode. Analysis of this spectrum is still in progress. We hope that this conical nozzle technology will can be applied to discharge sources for HEDM dopant atoms in He/H_2 clusters. In order to do so, we have to find a way to form conical nozzles out of insulator materials.

3. Main scattering and deposition chamber: Construction of the main scattering and deposition chamber is proceeding on schedule. The vacuum system is essentially complete, both for the beam source chambers and for the main scattering chamber. During the coming year, we will start to design and install the spectroscopy detection components and the cryogenic surface mounts.



Schematic Diagram of Pulsed Atom Source

Figure 1. This is a schematic diagram of the atomic beam source that we are using to produce the atoms that will be embedded in clusters. We have machined an extended nozzle out of Teflon that is mounted on the front of a standard pulsed molecular beam valve. Two electrodes are mounted in the Teflon, and these are used to discharge the gas when the pulsed valve is open. We have successfully tested the design using B_2H_6 as the precursor for making B atoms. We will soon be trying C_3O_2 as a source of C atoms.



LIF Spectrum of Boron Atoms

Figure 2. This is a boron atom laser-induced fluorescence spectrum recorded using the source described in Figure 1. The spectrum shows resolved hyperfine structure on the $^2S \leftarrow {}^2P$ transition. The temperature of the expansion can be estimated from the intensity of the two hyperfine components. So far, the lowest temperature that we have achieved is 20 K.

Schematic Diagram of He/H2 Cluster Beam Source

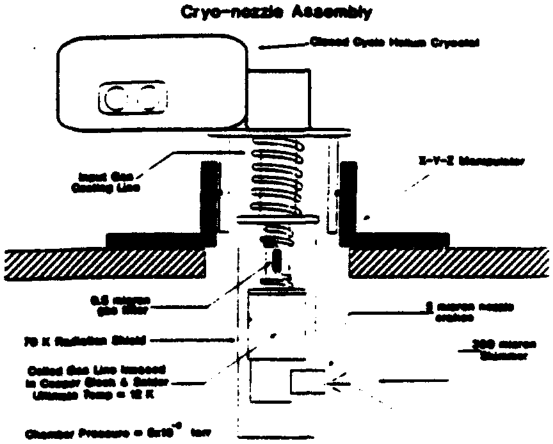


Figure 3. This is a schematic diagram of the He/H2 cluster source that we have constructed. A closed cycle He cryostat is used to cool the incoming gas before expansion. The gas is then expanded out of a 5μm nozzle. We are currently debugging and testing this source.

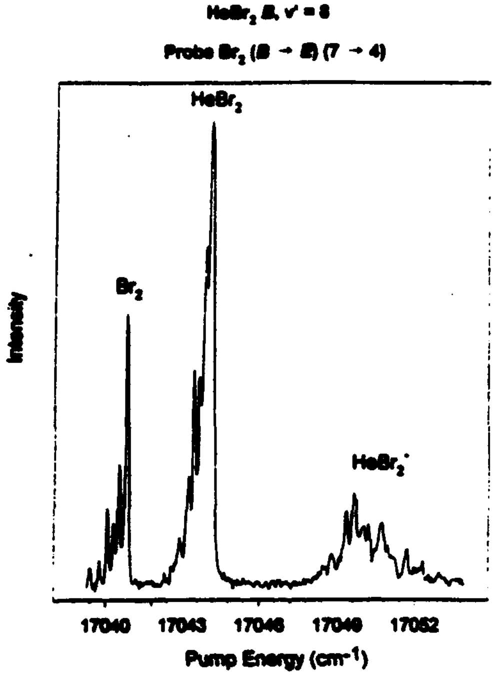


Figure 4. This is a low resolution pump-probe laser excited fluorescence spectrum of $HeBr_2$ clusters produced by expanding from a conical nozzle. The set of peaks on the left hand side of the spectrum are due to excitation of Br_2 from the expansion. The middle set of peaks is due to the main excitation band of $HeBr_2$. The right set of peaks is due to excitation of $HeBr_2$ with one quantum of bending vibrational excitation. This band has not been previously observed, and we attribute the improved signal-to-noise ratio that allows the observation of this band to the use of the conical nozzle.

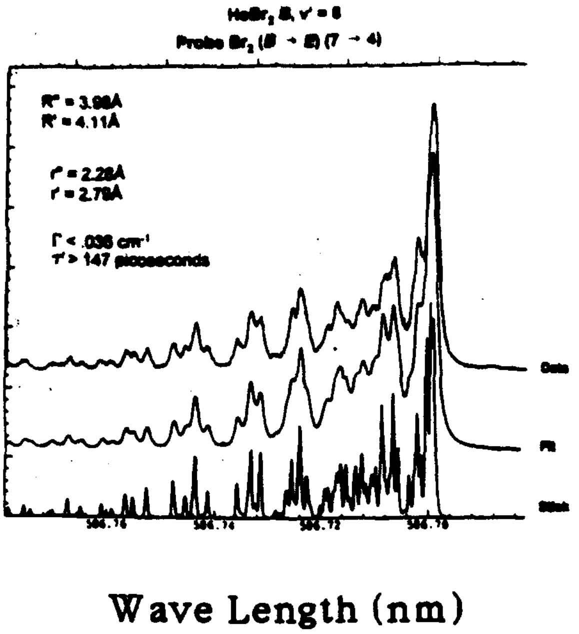


Figure 5. The pump-probe, laser induced fluorescence spectrum of $HeBr_2$. The top trace is the spectrum as recorded using a conical super-sonic nozzle source. The signal to noise of this spectrum is much higher than previously obtained using conventional nozzles. The fit to the spectrum uses a rigid rotor Hamiltonian in which the molecules is assumed to have a "T" shaped structure. R" and R' are the He-Br_2 distances in the ground and electronic excited states, respectively. r" and r' are the Br_2 distances. The lifetime broadened line width for the transition is 0.036 cm^{-1}.

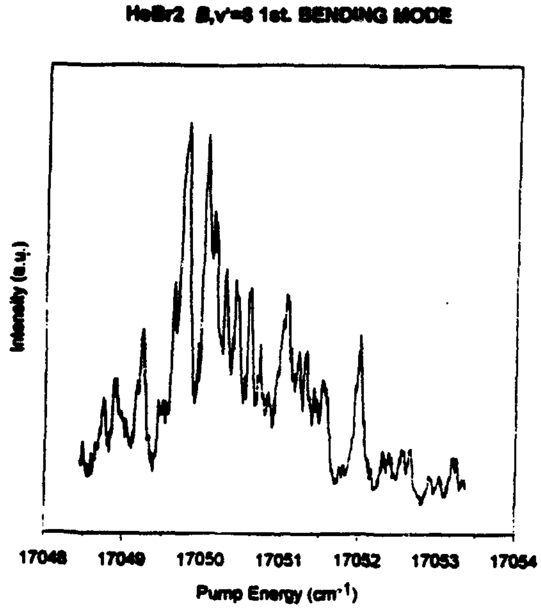


Figure 6. This is a high resolution recording of the $HeBr_2$ excited bending mode that is shown on the left had side of Fig. 4. We are still trying to assign and interpret this spectrum.