URANIUM ISOTOPE SEPARATION IN THE SOLID STATE

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ABSTRACT

Since we were actively able to work on this project, we have been engaged in three separate lines of research. Each of these has been related to laser induced isotope separation of uranium in the solid state. The three areas are: a) improved reaction chemistry for both host materials $\text{Zr}(\text{BH}_4)_4$ and $\text{Hf}(\text{BH}_4)_4$ and $\text{U}(\text{BH}_4)_4$ itself; b) improved spectroscopic techniques in order to obtain sharper spectra; and c) solid state photochemical investigations to study $\text{U}(\text{BH}_4)_4$ photodecomposition mechanism and yield as a function of wave length. These are all integral parts of the solid state isotope separation procedure and are discussed in terms of the overall process proposed.

I. INTRODUCTION

Molecular isotope separation involving photochemical and photon induced processes relies ultimately on spectroscopic resolution of transitions associated with isotopically different species. This invariably means that photochemical reactions and spectroscopic investigations must be carried out on cold molecules (i.e., $T < 77K$). At present, there appear to be two methods for producing cold molecules: supersonic beams and low temperature crystals. We have demonstrated in the original proposal (see references therein) that low temperature mixed crystals such as 2-5% $U(BH_4)_4/Hf(Zr)(BH_4)_4$ can yield a factor of 100 improvement in line width for the $U(BH_4)_4$ vibronic transitions (i.e., $\Delta \sim 200 \text{ cm}^{-1}$ to $\Delta \sim 2 \text{ cm}^{-1}$). Other advantages of low temperature solids are high densities (10^{19} molecules/cm³ in a 1% mixed crystal), the possibility of high through put, and easy scale-up. Additionally, $U(BH_4)_4$ has a very clean and simple photochemistry [$U(BH_4)_4 \xrightarrow{h\nu} U(BH_4)_3$], a number of electronic and vibronic transitions of high energy, and quite reasonable oscillator strengths ($f \sim 10^{-5}$).

The problems, real or imagined, with the above solid state process, are: a) clean materials produced in good yield with a minimum of difficulty; b) sample quality; c) photochemical yield; d) relaxation phenomena; e) solid state properties of the host materials; and f) observation of $U^{235}(BH_4)_4$ - $U^{238}(BH_4)_4$ spectroscopic differences. Of course, the major hurdle for this technique, or any other for that matter, is to identify an isotopic shift. We have postponed this latter task until the coming funding period in order to give us time to improve sample handling, synthetic, and spectroscopic techniques to such a degree that radioactive materials could be manipulated without hazard to new personnel. Moreover, we have felt this phase of the research would not present a real

problem based on the published and unpublished PuF_6 spectroscopic data; PuF_6 , like $\text{U}(\text{BH}_4)_4$, has a $(5f)^2$ electronic configuration and a rich vibronic spectra.

Consequently, in these past six months we have concentrated on: a) improved reaction chemistry for U, Hf, $\text{Zr}(\text{BH}_4)_4$; b) spectroscopic techniques for sharp spectra; and c) solid state photochemical processes and quantum yields. Below we discuss each of these areas separately.

II. EXPERIMENTAL STUDIES ON $\text{U}(\text{BH}_4)_4/\text{Hf}(\text{BH}_4)_4$, $\text{Zr}(\text{BH}_4)_4$

A. Sample preparation - synthetic approach and optical quality.

The reason we have begun exploring reaction chemistry for $\text{U}(\text{BH}_4)_4$ and $\text{Hf}(\text{BH}_4)_4$ is that the present synthetic approaches to these systems are different and the $\text{U}(\text{BH}_4)_4$ reaction takes two steps. These two reactions are:

The processes involved are somewhat inconvenient because the final products of each synthesis must be mixed later to form the material needed for isotope separation. It would clearly be more convenient to use a one-step process. It is not possible, however, to get $\text{U}(\text{BH}_4)_4$ directly from UCl_4 , as occurs with $\text{Hf}(\text{BH}_4)_4$. The reason this reaction will not proceed, we believe, is that the two solids UCl_4 and LiBH_4 do not mix well, and $\text{U}(\text{BH}_4)_4$ on the UCl_4 surface poisons the reaction. We have thus decided to mix 5% $\text{UCl}_4/\text{HfCl}_4$ in the hope that $\text{Hf}(\text{BH}_4)_4$ will dissolve the $\text{U}(\text{BH}_4)_4$ and allow the reaction to proceed. This technique does, in fact, appear to be successful. The final distillate from the reaction mixture looks appropriately pink and behaves like $\text{U}(\text{BH}_4)_4/\text{Hf}(\text{BH}_4)_4$. We feel this is an important step forward for the chemistry of this system; we

are now engaged in determining exactly what the composition of the "one-step" sample is. Until further work is completed this result is of a rather preliminary nature.

The second phase of sample handling is quality of the material used in photochemical processes. We have taken the approach that preliminary work should be performed with materials of high chemical and crystal quality. This is necessary in order to isolate the actual photochemistry and eventual isotopically enriched materials. We have sometimes found decomposition in sample cells directly after mixing the $U(BH_4)_4$ and $Hf(BH_4)_4$; the crystals grown from such samples, however, are quite clear. Thus, with careful crystal growing techniques, it has been possible to maintain excellent sample quality. We have tried to prevent decomposition because eventually we want to work with large polycrystalline masses. Thus the aim is not to have to do the "final purification" step of crystal growth from the vapor. We believe that the chemical techniques used above to get both $U(BH_4)_4$ and $Hf(BH_4)_4$ at the same time will circumvent this problem. We have also been pursuing a program of analyzing these decomposition products to try to improve on chemical and sample handling techniques directly.

B. Spectroscopy.

During this period we have reproduced all our old spectra in order to demonstrate their validity, reproducibility, and to reestablish these techniques in our laboratory. We have found that the lines, especially in the 1.5 to 2.0 μm region, are about 50% sharper than we had previously reported. The reason for this is not completely clear at present, but we feel that sample quality and a higher resolution monochromator have made substantial contributions to this success. The sharpest lines now measured are slightly

less than 1 cm^{-1} full width at half maximum at 4.2K. Presently we are in the processes of varying the temperature to obtain line widths as a function of temperature up to 77K. If sharp lines can be maintained at higher temperatures, isotope separation can be effected at a much more reasonable cost.

C. Photochemistry - Single Photon.

One of the main strong points of this proposed separation technique is the $\text{U}(\text{BH}_4)_4 \longrightarrow \text{U}(\text{BH}_4)_3$ photochemistry. Since $\text{U}(\text{BH}_4)_4$ has a vapor pressure of ca. 1 mm at -30°C , and $\text{U}(\text{BH}_4)_3$ has essentially no vapor pressure at that temperature, physical separation of the photochemical product (say, $^{235}\text{U}(\text{BH}_4)_3$) is a simple matter of vaporizing the "unreacted" portions of the sample. In the last few months we have attempted to measure the efficiency of this photochemistry for single photon events. It is, however, quite difficult to get anything approaching a photochemical reaction cross-section in solids that scatter light and with a set-up whose geometry varies from experiment to experiment. Using a filter that will not transmit light of wavelength shorter than $3200\text{\AA}$, we saw essentially no decomposition; the cutoff is so sharp due to the low temperature solid state sample. At higher energies ($2500\text{-}3000\text{\AA}$) we estimate a 10-50% quantum yield based on 10^{19} $\text{U}(\text{BH}_4)_4$ molecules/cc at a photon flux of roughly 10^{17} photons/sec. in that energy range. What one can conclude from this is that the photochemical step should not be a bottleneck as far as the efficiency of the excited state process is concerned. It is certainly possible to improve this estimate; however, for our present requirements it seems to be an encouraging result. Should the need arise, one could obtain more quantitative results using doubled output of a dye laser.

One could characterize the work discussed above, performed in the last six months in our laboratory, as preparatory for the research to be carried out over the next 15-18 months. We have verified a number of older qualitative

findings, sharpened up some necessary techniques, and have trained personnel in the subtleties of borohydride chemistry. In addition, real progress has been made in sample preparation techniques. The Principal Investigator on this project (E. R. Bernstein) has devoted about 20% of his time in the last six months to contract-related work. During the remainder of this contract, about 25-30% of his time will be devoted to contract-related work.