

A low-temperature source for the generation of uranium vapor

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Uranium is a highly refractory metal, boiling at 4135 °K and having a vapor pressure of 1 torr at 2729 °K.¹ At these elevated temperatures, the corrosiveness of uranium poses severe materials problems in its gasification. An alternative approach for the production of uranium atoms is to make a volatile chemical derivative of uranium and then to find a simple means of reducing this compound to elemental uranium in the gas phase. We report here the generation of uranium vapor from the dissociation of uranocene² [bis(cyclooctatetraenyl)uranium, U(COT)₂] by collisions with metastable argon atoms.

The most popular methods³ for chemical vapor deposition of refractory metals involve thermal decomposition of metal alkyls, metal halides, and metal sandwich compounds,⁴ or the reduction of metal halides by H₂. In all these methods, wall collisions and surface chemistry seem to play a primary role in the metal reduction. Indeed, the liberation of free atoms of the refractory metals in the gas phase appears not to have been demonstrated previously.

Recently, flow-discharge studies have shown that small molecules can be dissociated efficiently in the gas phase by collisions with metastable argon atoms. It is reported that the quenching rates of Ar(³P_{0,2}) are first order in the foreign gas added and that the quenching cross sections are often greater than gas kinetic.⁵⁻⁷ For example, the total quenching cross section of Ar(³P_{0,2}) by CS₂ is 115 Å², although the branching ratio for product formation appears not to have been reliably measured.^{8,9}

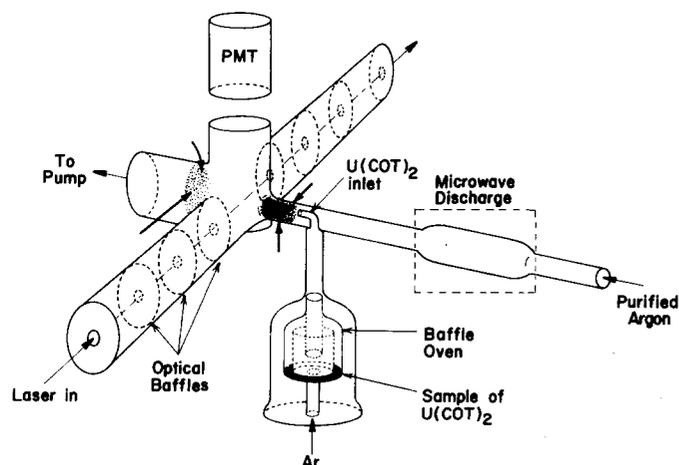


FIG. 1. Schematic diagram of low-temperature uranium vapor source. The four boldface arrows point to where a mirror-like film is deposited when microwave-discharged argon decomposes U(COT)₂ vapor. The baffle oven is designed so as to reduce particulates in the reaction zone.

Figure 1 shows a schematic diagram of the experimental setup. Uranocene (~1 g), synthesized² with a yield of 50%, is placed inside a baffle oven, designed to reduce the emission of particulates upon evaporation. This oven is operated at 460 °K at which temperature uranocene has a vapor pressure of about 10⁻³ torr.¹⁰ The uranocene vapor is entrained in a stream of argon and carried into a small reaction zone where it mixes with metastable argon atoms and ions generated about 8 cm upstream in a 40 W microwave discharge.¹¹ After 30 min of operation, a film having a metallic luster appears on the walls at positions indicated in Fig. 1. It is interesting to note that when U(COT)₂ is passed directly into a microwave discharge, the film is black in appearance, caused by the deposition of carbon.

A laser-induced fluorescence technique is used to prove that uranium atoms are being produced in the gas phase by collisions of U(COT)₂ with Ar(³P_{0,2}). The output from a nitrogen-laser-pumped, pulsed dye laser enters the flow system 3.5 cm downstream from the U(COT)₂ inlet. The wavelength is set at 5915.4 Å, causing a transition from the ⁵L₈⁰ ground state level to a J=7 even parity level at 16 900.4 cm⁻¹.¹² The atomic fluorescence is detected by an RCA 7265 photomultiplier (S-20) used in conjunction with a Keithley model 881 and 882 boxcar integrator.

Figure 2(a) shows a typical laser excitation spectrum when the baffle oven is used to produce vapors of urano-

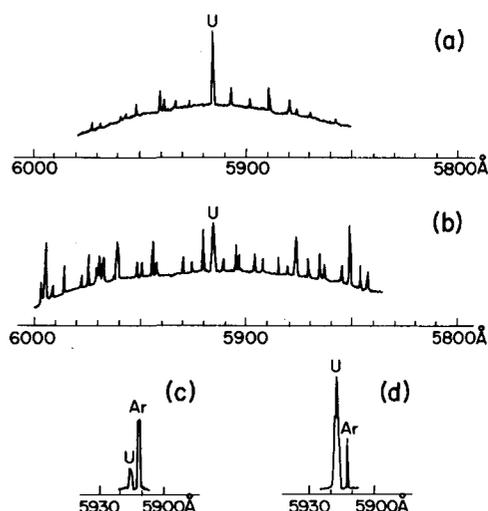


FIG. 2. Excitation and emission spectra: (a) laser-induced fluorescence of U(COT)₂+Ar (³P_{0,2}) using a baffle oven to generate the uranocene vapor; (b) same as (a) but with a glass oven to generate the uranocene vapor; (c) microwave-excited emission of UCl₄ in 1 torr Ar using a closed capillary tube; and (d) microwave-excited emission of U(COT)₂ in 1 torr Ar using a flow system.

cene. A strong line is observed at 5915 Å with a lifetime between 100–250 ns, depending upon the pressure inside the reaction zone. The 5915.4 Å transition of uranium is reported to have a lifetime of about 300 nsec.¹⁰ We conclude that free *U* atoms are being released. Figure 2(b) shows how the laser excitation spectrum changes its appearance when the baffle oven is replaced by a Nichrome-wire-heated glass oven. In addition to the 5915 Å *U* line, hundreds of other “lines” are detected having a “lifetime” of 10–15 nsec, the same as that of the dye laser pulse. The origin of these “lines” is laser scattering from particulates. In Fig. 2(c) we show two prominent emission lines between 5910 and 5920 Å, obtained from the microwave discharge of UCl_4 in ~1 torr argon. The 5915 Å *U* line is again apparent along with a 5912 Å line due to argon. Finally, Fig. 2(d) shows a similar tracing, but with different relative line intensities. This emission spectrum is obtained from the microwave discharge of $\text{U}(\text{COT})_2$ in ~1 torr argon.

No attempt has been made to optimize the yield of uranium vapor. With the present argon pressure of 5 torr and low flow rate provided by the Welch model 1397B mechanical pump (500 l/min) almost all metal vapor released is deposited on the walls prior to the laser fluorescence observation zone. Nevertheless, these first studies demonstrate that it is possible to develop low-temperature sources for uranium atom generation based on the decomposition of volatile uranium compounds.

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Spline bases for atomic calculations*

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The use of spline bases has been proposed for *ab initio* electronic structure calculations.¹ They offer the apparent advantage that no nonlinear parameters occur, so that exponent optimization is unnecessary, and the number of two-electron integrals in SCF calculations increases only as n^2 rather than n^4 , where n is the number of basis functions. Preliminary test calculations on the hydrogen atom using a cubic cardinal spline basis indicated that the accuracy was comparable to that for a Gaussian basis of the same size.¹ The results of subsequent test calculations on the helium atom are reported in this note.

After preliminary calculations with cardinal splines we changed to *B* splines because they offered the following advantages: the roundoff error is smaller and local potentials are represented by band matrices rather than full matrices. Cubic cardinal splines gave essentially the same error as *B* splines for 11 mesh points, but for 21 mesh points the error for a cardinal spline basis was about 7 times as large as for a *B* spline basis. The band structure of the matrices, a

consequence of the fact that *B* spline basis functions are identically zero outside a range of four mesh intervals, permitted a large reduction in the number of operations.

TABLE I. Relative error $\delta E/E$ in the total energy of the ground state of a helium atom for cubic *B* splines. Logarithmic meshes with $N+1$ mesh points and an outermost point at $r_N \approx 11.5 B$ were used. The “exact” energy is $E = 2.8616800 \text{ H.}^a$

N	$\delta E/E$
5	2.6×10^{-3}
10	4.6×10^{-5}
15	3.1×10^{-6}
20	1.4×10^{-6}
25	2.3×10^{-6}

^aReference 2.