SENSITIVITY OF CESIUM CHEMISTRY TO THE O/U RATIO IN UO_{2+X}

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ABSTRACT

The effect of O/U ratio on chemical reactivity was investigated in a cesium-iodide/urania/tungsten system at temperatures up to 2200 K. It was found that slight changes in the oxidation of the urania had a large effect on reactivity. Crushed fresh fuel samples showed little reaction with CsI; however, slightly hyperstoichiometric fuel showed considerable reaction. The tungsten participated in the reaction by removing excess oxygen from the urania, eventually leading to a cesium tungstate species that was analyzed by Fourier Transform Infrared (FTIR) and X-ray diffraction (XRD) techniques.

INTRODUCTION

Reactor safety analysis for a hypothetical loss of coolant accident (LOCA) scenario requires an understanding of high-temperature interactions between fuel, fission products, and structural materials. In the event of large-scale fuel failure and subsequent fission product release, in-core temperatures would likely exceed 1000 K, a temperature regime where reactions occur very quickly and the chemistry of the system is bounded by thermodynamic, rather than kinetic, constraints. There are numerous chemical species involved, and a large effort is required to acquire quantitative data; thus, the thermodynamic database used in modelling fission-product release from fuel is continually being appended and revised. We are involved in this effort, studying the interaction of UO_{2+x}, fission products, and structural materials at temperatures up to 3000 K. Several oxide-fuel reactor designs share many of the same safety concerns, so international collaboration is very productive and worthwhile. However, there are significant differences between CANDU[*] and light water reactor (LWR) fuel that may affect fission product chemistry. Some data on the operating conditions and properties of typical CANDU fuel and various LWR fuels of particular importance to reactor safety are presented for comparison in Table 1.

Physical properties of uranium-oxide fuel, such as thermal conductivity and oxygen-diffusion coefficients, are highly dependent on the O/U ratio, to the extent that the former can be used as an analytical measure of the extent of oxidation of urania (e.g., Lucuta et al. [1]). In addition, the chemistry of the fuel should also be sensitive to O/U ratio. This was investigated in a chemical system comprising CsI and UO_{2+x} in a tungsten vessel. The reactivity of the system

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[*] CANada Deuterium Uranium, registered trademark of Atomic Energy of Canada Limited

was found to change dramatically with the O/U ratio of the UO_{2+x}, which was varied over the small range 2.00 ± 0.01 ≤ 2+x ≤ 2.01 ± 0.01. At the higher O/U ratio the tungsten scavenged excess oxygen from the urania, and formed a cesium tungstate. Iodine vapour was liberated from the mixture at low temperatures.

EXPERIMENTAL

Samples of CsI and UO_{2+x} in a tungsten cell were heated to 2200 K in an evacuated Knudsen cell apparatus described previously [2], as shown in Figure 1. The Knudsen-cell cavity had a diameter of 10.0 mm, a depth of 12.7 mm and an orifice diameter of 0.7 mm. The ratio of orifice size to sample surface area was 0.005. Mass spectra of the vapour phase effusing from the cell were collected using a Finnigan quadrupole mass spectrometer and PC-based Shrader data acquisition software. Temperatures were measured using a pyrometer focussed into the blackbody cavity in the Knudsen cell. The pyrometers included a single-wavelength Ircon from 623 to 1073 K, and two dual-wavelength Ircon pyrometers, ranging from 973 to 1673 K and 973 to 2200 K respectively. Details on the calibration procedures will be published elsewhere [3].

The CsI, 99.999% pure, was purchased from AESAR. One of the uranium-oxide starting materials was a crushed fresh fuel pellet analyzed gravimetrically as having O/U = 2.00 ± 0.01. A slightly oxidized starting material was made by heating the crushed pellet to 673 K for 3 d, resulting in a powder with O/U = 2.01 ± 0.01, as measured by bulk analysis. Stoichiometric uranium dioxide powder purchased from Cerac, which was found to have oxidized in storage to $UO_{2.29\pm0.01}$, was used for the infrared experiments. Cesium diuranate, $Cs_2U_2O_7$, synthesized according to the procedure of Cordfunke and co-workers [4] was analyzed by X-ray diffraction to be composed of a mixture of the α and β phases, in a ratio of 1.8 ± 0.7.

Experiments comprised measurement of the ion signal as a function of either temperature or ionizing-electron energy. The vapour pressure of silver was used to calibrate the apparatus for the measurement of absolute vapour pressures. Compensation for daily variations in mass spectrometer sensitivity was achieved by monitoring a calibrated leak of perfluorotributylamine (FC43), also used to determine the mass dependence of the quadrupole analyzer and electron multiplier. Personal computer programs written in Labview were used to analyze data from temperature ramps to compute second-law heats of vaporization and vapour pressures. Ion intensity was plotted as a function of electron energy, and appearance potentials (AP) were determined by extrapolation of the linear portion of the curve to the baseline. These data were used in combination to deduce speciation as a function of temperature.

Fourier-transform infrared (FTIR) spectroscopy was performed on the cesium-tungsten compound evolved from a mixture of CsI and $UO_{2.29\pm0.01}$ in contact with tungsten plates. The volatiles were trapped in an argon matrix deposited on a KBr window cooled to 10 K on an APD202 cryostat. A Bomem DA3 FTIR spectrometer with a mercury-cadmium-telluride (MCT) detector and KBr beamsplitter was used to collect spectra between 500 and 4000 cm^{-1} at a resolution of 4 cm^{-1}. In addition, layers crystallized on the tungsten plates used in the infrared experiments were analyzed by X-ray diffraction (XRD), sampled after heating to 1073 and to 1696 K.

RESULTS

The samples of CsI/urania and cesium uranate, when heated in a tungsten Knudsen cell, gave qualitatively similar results. The ions observed as the samples were heated as a function of temperature are displayed in Table 2, and their second-law heats of vaporization computed from integrated Clausius-Clapeyron plots in Table 3.

Little reaction was observed in the system with the unoxidized fuel. The main signal arose from the volatilization of cesium iodide from 700 to 1000 K. In addition, a small release of cesium was observed between 1000 and 1250 K, as shown in Figure 2. The condensed phase compound giving rise to this signal depleted rapidly above 1250 K. The heat of vaporization of ions belonging to Cs and CsI determined from the slope of the integrated Clausius-Clapeyron plot was 155 ± 8 $kJ\bullet mol^{-1}$ in agreement with the literature value, 154 $kJ\bullet mol^{-1}$ at 1000 K [5]. The appearance potential of the cesium ions was 7.6 ± 0.1 eV (Table 3), suggesting a molecular parent such as CsI. The appearance potential for cesium ions from atomic cesium is much lower, reported as 3.894 eV [6].

In contrast to the stoichiometric UO_2, the oxidized fuel sample released large amounts of cesium when heated between 1000 and 1600 K, Figure 2. The high-temperature cesium ion appearance potential of 7.1 ± 0.1 eV again suggested a molecular parent. The cesium ion was observed along with $CsWO_2^+$, $Cs_2WO_4^+$, as well as tungsten-oxide ions, and this indicated that the Cs^+ signal arose from the volatilization of a cesium tungstate parent. The oxidized sample showed at least 20 times more reaction than the fresh urania, as shown in Figure 3.

The heating of cesium uranate produced low temperature cesium release between 769 and 1000 K, perhaps because of volatilization of a cesium hydroxide residue remaining from the cesium uranate synthesis but more likely from the reaction of cesium uranate and tungsten, Reaction (2), discussed later. High-temperature cesium species were observed between 1024 and 1724 K, as shown in Figure 2. As in the case of oxidized urania, tungsten-oxygen ions were also observed in the high temperature region, suggesting the signals were from the volatilization of a cesium tungstate. The deviation between the data for CsI + UO_{2+x} and $Cs_2U_2O_7$ on Figure 2 above 1300 K was attributed to the amount of cesium tungstate present in the sample. Cesium signals were converted to partial pressures using the parameters listed in Table 4. A non-linear least squares fit was used to obtain the following relationship between P(Pa) and T(K):

$$\ln\left(\frac{P}{Pa}\right)=21.0-2.7x10^{4}\left(\frac{K}{T}\right)$$

This equation yields a second-law heat of vaporization of -224 $kJ\bullet mol^{-1}$, comparable to those reported in rows 2, 3, and 5 of Table 3. In addition, the fit can be used to compute third-law heats of vaporization, when free energy functions of the gas-phase cesium tungstate become available. We plan to calculate the latter from structural information, bond lengths and vibrational frequencies, derived from semi-empirical or *ab initio* models and spectroscopic evidence.

The sample of highly oxidized $UO_{2.29}$ heated with CsI in the presence of tungsten, produced a volatile compound that gave infrared absorptions at 892 and 831 cm^{-1}, characteristic of W-O stretching frequencies [7]. The peak was first observed at 1265 K, and grew until 1696 K, in agreement with the Knudsen cell results, as shown in Figure 4.

X-ray diffraction analysis identified major phases as being tungsten metal and UO_2. At 1073 K, small amounts of ternary phases involving cesium-uranium-oxygen, cesium-tungsten-oxygen, and tungsten-uranium-oxygen were observed. Definite phase identification was not possible because signal levels were very low. At the higher temperature, 1696 K, at which point all the reaction product was expected to have vaporized, no ternary phases were observed.

DISCUSSION

Ternary cesium-transition metal-oxygen phases are of interest in reactor safety because they would be the product of the reaction of cesium with structural materials in the primary heat transport system. For instance, Cs_2SnO_3, arising from a reaction between fission product cesium and the tin alloying element in Zircaloy-4 cladding, may be important in the deposition of vapour phase cesium as it is transported from the fuel into containment. The thermodynamic properties, vapour pressure and reactivity of cesium stannate are quite different from those of CsI, the most abundant cesium vapour phase species. In this current study, we have examined the formation of cesium tungstate. Although tungsten is only a minor component of Zircaloy-4, $0.1 mg \cdot g^{-1}$ [8], it is easily oxidized and hence was chosen to demonstrate the formation of ternary alkali metal-transition metal-oxygen compounds that may play a role in mitigating fission product release in a reactor accident scenario.

Cesium-tungsten-oxygen compounds exhibit a variety of stable phases, some of which are of interest to the electronics industry. For instance, Cs_xWO_3 ($0.16 \leq x \leq 0.33$) has been found to show superconducting properties [9], and electrochromic devices may be prepared that take advantage of ion diffusion through hexagonal-tungsten-bronze (HTB) lattices formed by certain cesium tungstates [10]. Hence, the chemical literature has several detailed accounts of research into cesium-tungsten-oxygen phases and their characterization. A phase diagram, Cs_2O-WO_2-WO_3 was published by Cava and co-workers [9], showing the relationship between a number of stoichiometries. Tungsten is in the +6 oxidation state in many of these compounds, such as Cs_2WO_4 and $Cs_6W_{11}O_{36}$ [11]. However, reduced compounds also occur, spanning a series of a crystal structures, ranging from HTB to pyrochlore [12].

In general, cesium tungstates can be produced by the reaction of cesium salts (often Cs_2CO_3) and WO_3 between 973 and 1173 K [10]. For instance, a reaction between CsI and WO_3 at 973 K was observed elsewhere to give HTB crystals corresponding to reduced $Cs_{0.29}WO_3$ [13]. Cesium tungstates melt at moderately high temperatures, similar to those at which the ion signal was observed in the Knudsen cell apparatus. The melting point of Cs_2WO_4 was reported as 1235 K [12]. In another study, a tri-tungstate and a tetra-tungstate were observed to decompose upon melting, at 1133 and 1161 K respectively [14]. The same authors found a di-tungstate that melted congruently at 1033 K. High-temperature transitions between cesium-tungsten-oxygen phases have been studied by differential scanning calorimetry and differential thermal analysis [7,15].

From the observation of the ions of cesium, tungsten oxides and ternary cesium-tungsten-oxygen species in the Knudsen cell experiments, it is evident that a cesium tungstate forms by reaction between CsI and tungsten in the presence of UO_{2+x}. The reaction involving CsI begins at temperatures as low as 623 K, and continues until either the excess oxygen is depleted or CsI is volatilized, Reaction (1). Iodine is volatilized below 700 K, Table 2; however, because the system was not in chemical equilibrium, thermodynamic information such as heats of vaporization could not be derived from the Knudsen cell data for this species.

(1) $2CsI + W + 4/(x-y)\ UO_{2+x} \rightleftarrows Cs_2WO_4 + 4/(x-y)\ UO_{2+y} + I_2(g)$

Formation of a cesium tungstate also appears possible by a process involving cesium diuranate and tungsten, such as Reaction (2). Vapour pressures derived from thermodynamic equilibrium calculations indicate Cs_2O would be volatilized in amounts observable in the Knudsen-cell apparatus above 800 K, in agreement with current results. Direct observation of Cs_2O is difficult because of fragmentation of the oxide in the ionizer and overlap with of CsO^+ with a prominent FC43 ion at m/z = 149.

(2) $2Cs_2U_2O_7 + W \rightleftarrows Cs_2WO_4 + 4UO_2 + 2Cs_2O(g) + \frac{1}{2}O_2(g)$

In both Reactions (1) and (2), the product cesium tungstate has a significant vapour pressure at its melting point, which would account for observation of ions from the volatilized tungstates, shown in column 4 of Table 2, in the mass spectrometer.

CONCLUSIONS

The present experiment demonstrates the importance of O/U ratio in high temperature uranium-oxide chemistry. Tungsten, being more easily oxidized that other cell materials, such as tantalum, was shown to extract excess oxygen from UO_{2+x} and form a cesium tungstate. Cesium tungstates and cesium uranates are similar in that they represent stable phases on a ternary phase diagram involving oxides of the metal in the (IV) and (VI) oxidation state and Cs_2O, i.e., WO_2-WO_3-Cs_2O and UO_2-UO_3-Cs_2O respectively. Although no example of a quaternary cesium-tungsten-uranium-oxygen phase diagram was found in the literature, it is likely that tungsten oxides are soluble in the fluorite UO_2 lattice, as is the case for rare earth and alkaline earth oxides. Participation of tungsten in the reaction between CsI and UO_{2+x} may be considered an example of how metal structural materials could influence the fission product-fuel chemistry in the primary heat transport system.

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TABLE 1
TYPICAL OPERATING CONDITIONS FOR CANDU VERSUS LWR FUEL

Operating Conditions	CANDU	LWR
Centreline temperature	$1073 \leq T_c \leq 1973$ K	$1073 \leq T_c \leq 1473$ [16]
Linear power ($kW \cdot m^{-1}$)	20 to 55	15 to 33 [17]
Average burnup ($MWh \cdot kgU^{-1}$)	144 to 288	192 to 960
Oxygen potential ($kJ \cdot mol^{-1}$)	-379 to -358 (481 to 642 K) [Elder 1994, private communication]	<-350 [18] -550 to -400 at 1023 K [19]
Stoichiometry after average burnup ($UO_{2\pm x}$)	$0.0005 \leq x \leq 0.001$	$-0.005 \leq x \leq 0.001$ [19]
Fission product abundances in fuel as a whole (10^{-4} mol/kg U)	46.4 cesium 4.80 iodine burnup of 190 $MWh \cdot kgU^{-1}$ calculated from ORIGEN [8]	58.1 cesium 5.60 iodine burnup of 240 $MWh \cdot kgU^{-1}$ calculated from ORIGEN [20]

TABLE 2
MAJOR IONS OBSERVED AS A FUNCTION OF TEMPERATURE

$CsI + UO_{2+x}$ + W	I_2^+	Cs^+, CsI^+, Cs_2I^+, I^+, Cs^{++}, I^{++}	Cs^+, W^+, WO^+, $[(WO_2)_x(WO_3)_y]^+$ $0 \leq x \leq 1$ and $0 \leq y \leq 3$, $CsWO_2^+$, $Cs_2WO_4^+$,	UO_2^+, UO^+, U^+, UO_2^+, UO^{++}, U^{++}
$Cs_2U_2O_7$ + W		Cs^+, Cs^{++}, $(CsOH)_2^+$		
300 K	●			
500 K	●			
700 K		●		
900 K		●		
1100 K		●	●	
1300 K			●	
1500 K			●	
1700 K			●	
1900 K				●

TABLE 3
ENTHALPIES OF VAPORIZATION AND APPEARANCE POTENTIALS

Sample	Temperature (K)	Appearance Potential (eV)	Average Heat of Vaporization ($kJ \cdot mol^{-1}$)
$CsI(g)$ from 4% $CsI + UO_{2.29\pm0.01}$	746	7.9 ± 0.1	not measured
$Cs(g)$ from 4% $CsI + UO_{2.00\pm0.01}$	1248	7.1 ± 0.1	251
$Cs(g)$ from 5% $CsI + UO_{2.00\pm0.01}$	1146	7.6 ± 0.1	222
$(CsOH)_2$ or Cs_2O from $Cs_2U_2O_7$	845	8.3 ± 0.1	188
$Cs(g)$ from $Cs_2U_2O_7$	1127	3.3 ± 0.1 8.6 ± 0.1	226

TABLE 4
PARAMETERS USED TO COMPUTE VAPOUR PRESSURES

$$P=kIT$$

$$k=\frac{1}{\sigma\eta\gamma f s k_{Ag}}$$

Symbol	Description	Value
P	pressure	calculated (Pa)
I	ion intensity	measured (counts)
T	temperature	measured (K)
σ	ionization cross section	3.2×10^{-16} cm^2
η	isotopic abundance of ion	1 for cesium
γ	mass sensitivity correction	1.44 for Cs^+
f	orifice correction	0.81
s	analyzer drift correction	2.954
k_{Ag}	silver calibration constant	1.26×10^{21} counts K cm^{-2} Pa^{-1}

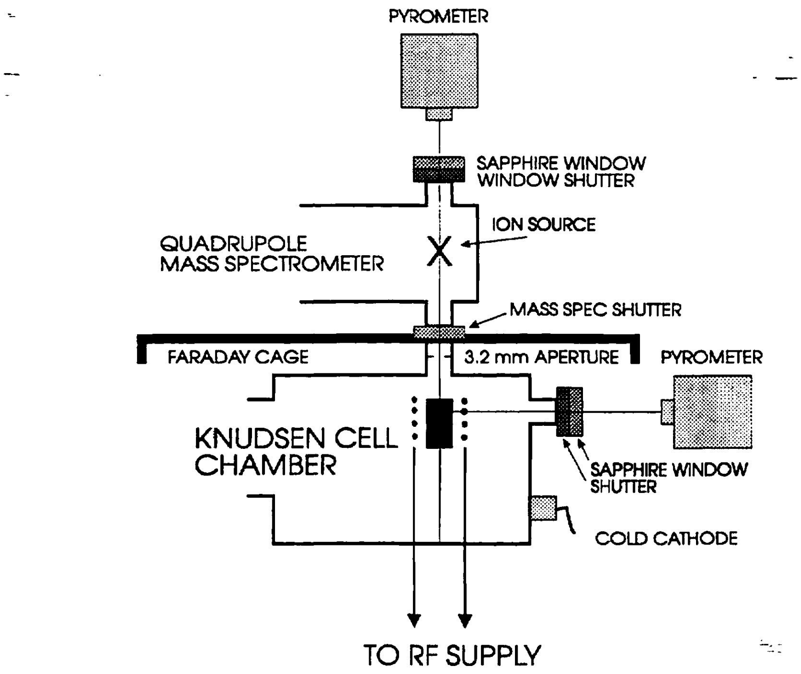

FIGURE 1: SCHEMATIC OF KNUDSEN CELL APPARATUS

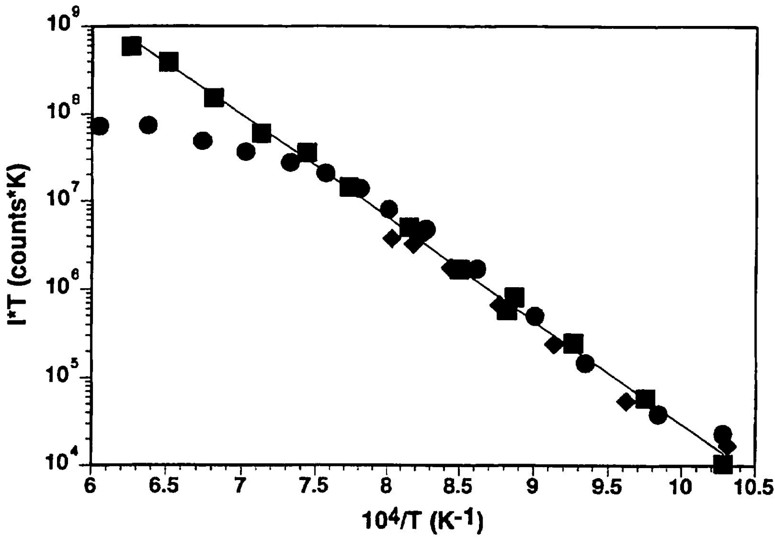

FIGURE 2: PLOT OF THE PRODUCT OF CESIUM ION SIGNAL (COUNTS) AND TEMPERATURE (K) AS A FUNCTION OF RECIPROCAL TEMPERATURE (K^{-1}). DATA FROM $Cs_2U_2O_7$ ■, CsI + $UO_{2.01\pm0.01}$ ●, AND CsI + $UO_{2.00\pm0.01}$ ◆, ALL FALL ON THE SAME LINE PRODUCED FROM A NON-LINEAR LEAST SQUARES FIT OF THE DIURANATE RESULTS.

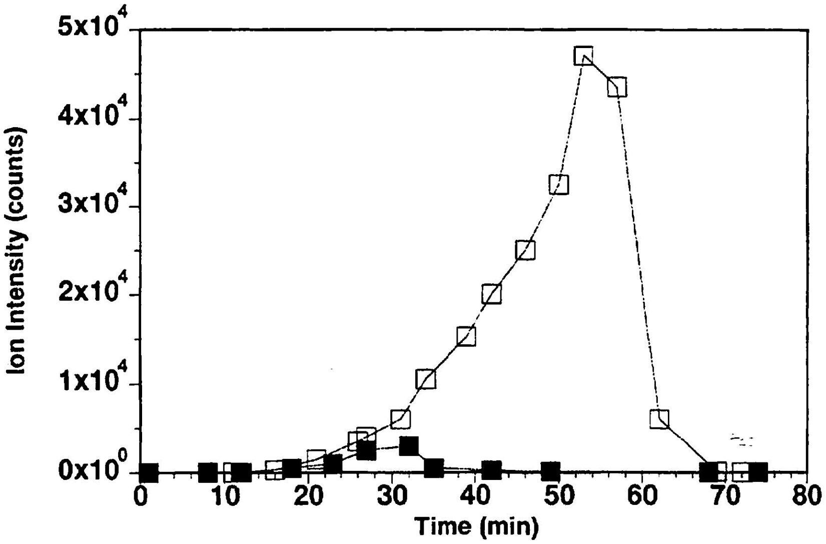

FIGURE 3: PLOT OF CESIUM ION INTENSITY (COUNTS) AS A FUNCTION OF TIME (MIN), AS HEATED ABOVE 950 K. A 20 FOLD INCREASE IN CESIUM SIGNAL WAS OBSERVED WITH THE OXIDIZED FUEL, □, AS COMPARED TO THE FRESH FUEL, ■.

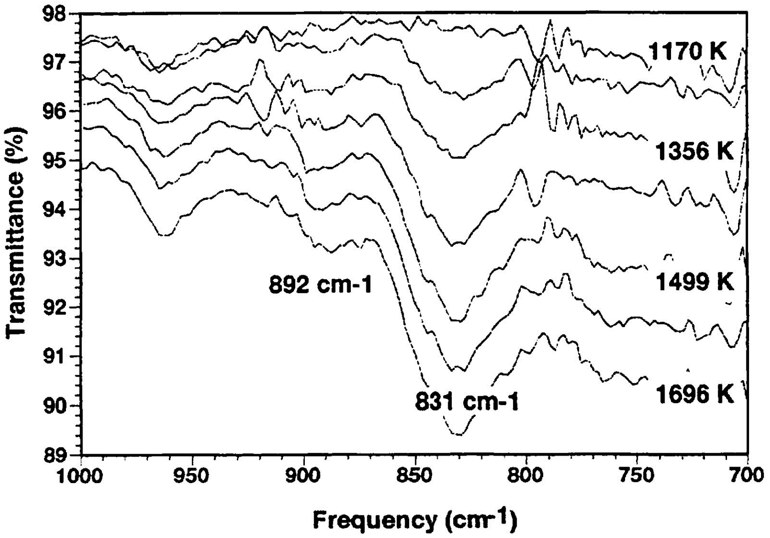

FIGURE 4: PLOT OF TRANSMITTANCE AS A FUNCTION OF FREQUENCY. DATA WERE TAKEN AS CsI, $UO_{2.29\pm0.01}$, AND W WERE HEATED BETWEEN 1170 AND 1696 K. PEAKS ATTRIBUTED TO THE W-O STRETCHING VIBRATION ARE IDENTIFIED.

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