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INFRARED STUDIES OF METAL OXIDES UPPER LIMITS OF THE
INFRARED OSCILLATOR STRENGTHS OF UO AND UO₂

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INFRARED STUDIES OF METAL OXIDES UPPER LIMITS OF
THE INFRARED OSCILLATOR STRENGTHS OF UO AND UO2

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THE INFRARED OSCILLATOR STRENGTHS OF UO AND UO₂

Milton J. Linevsky

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SUMMARY

Attempts to obtain infrared absorption spectra for UO and UO₂ were carried out using a high temperature furnace technique in which these molecules were produced by heating mixtures of uranium and uranium oxide. No observable absorption was obtained in the region of the vibrational fundamentals of these molecules, i.e., 1200 cm⁻¹ to 700 cm⁻¹. Based on these negative observations upper limits for the oscillator strength of UO and UO₂ were estimated to be 2×10^{-5} and 8×10^{-5} , respectively.

INTRODUCTION

In several previous reports (refs. 1-3), spectroscopic measurements were described in which both visible and infrared spectra were obtained for the oxides of uranium. The visible work was carried out (ref. 1) using a high temperature furnace technique in which both absorption and emission spectra were measured over a mixture of uranium metal and uranium dioxide. Under these conditions the vapor consisted primarily of UO and UO₂. In the temperature range of approximately 2100°C to 2400°C a complex system of bands was observed in the region of 4800Å to 7000Å. No complete analysis was carried out; however, preliminary indications pointed to UO₂ as the most likely species giving rise to the observed spectra.

Seeded flame studies were also carried out in the visible (ref. 2) in which UF₆ was introduced into one atmosphere cyanogen-oxygen and nitrous oxide-hydrogen flames supported on a water-cooled Meker type burner. Spectra of these flames were completely different in nature from those obtained in the furnace, being dominated by a strong continuum-like emission from 2400Å to 8000Å. Under the flame conditions, assuming equilibrium, the concentration of uranium oxides was distributed such that UO₃>UO₂>UO. Typically, these ratios at 3600°K for UO₃:UO₂:UO are approximately 0.77:0.23:0.0015. It was concluded that the continuum emission was due to recombination processes involving O atoms and UO₂ and/or UO₃.

The UF₆ seeded flame studies were extended into the infrared (ref. 3). A single 150 cm⁻¹ (FWHM) wide feature centered at 800 cm⁻¹ was observed in a one atmosphere cyanogen-oxygen flame and was shown to be due to a uranium oxide species. By a comparison with the known spectral intensity of CO₂ (a known component in the flame), it was possible to obtain the absolute band intensity for the uranium oxide feature. This value was found to be approximately 2.7×10^{-20} w/SR/particle at 3600°K. Based on the calculated equilibrium concentrations of UO₃, UO₂, and UO present in the flame it was shown that: if the emitter were UO₃ then its oscillator strength would be $\sim 8 \times 10^{-5}$, if the emitter were UO₂ then its oscillator strength would be $\sim 3 \times 10^{-4}$, and if the emitter were UO its oscillator strength would be

$\sim 4 \times 10^{-2}$ in order to account for the observed emission intensity. It was impossible to determine which oxide species was responsible for the observed emission.

In the present study infrared observations in absorption were carried out on the vapors over mixtures of uranium/uranium oxide generated in the high temperature furnace. Under these conditions the diatomic oxide, UO, is favored in concentration over UO₂ with very little UO₃ being present. If, indeed, the emitter observed in the flame studies were UO and therefore implying a very large infrared oscillator strength ($\sim 4 \times 10^{-2}$), a sizeable infrared absorption should be observable in the present furnace studies. No large absorptions were observed.

EXPERIMENTAL

Details of the high temperature carbon-tube King furnace have been given elsewhere (ref. 4). The procedure used was similar to that used previously for the visible studies (ref. 1).

Approximately equal amounts of uranium metal (depleted), cut into small strips, and uranium dioxide (obtained from K and K Laboratories) were mixed together and loaded into a tantalum boat contained in a tantalum-lined cylindrical carbon cell. The inside length of the cell was approximately 4 1/2 inches. Tantalum lined carbon end pieces with rectangular openings approximately 1/4 inch wide by 5/8 inch high were fitted into the ends of the cell and served to allow light to pass through the cell.

The light source from the absorption studies consisted of a standard Perkin-Elmer globar and chopper contained in a housing in which a flat and a spherical mirror allowed the focussing of the light through the furnace and onto the collecting optics of a light gatherer. The light gatherer which also consisted of a second set of flat and spherical mirrors brought the image into focus onto the entrance slit of a Perkin-Elmer monochrometer. This was equipped with a grating blazed at 12 microns and order sorter filters to pass the 8.5 to 15 micron region. The furnace was fitted with KBr windows. A schematic of the experimental setup is given in Figure 1. Through the use of the chopped source it was possible to discriminate between the high d.c. radiation from the furnace and any possible absorption of the globar radiation.

A determination consisted of observing the globar radiation with and without a loaded cell in the furnace so that any possible absorption spectra could be obtained by difference. Typically, the cell was placed in the center of the carbon tube furnace and thoroughly degassed under vacuum at approximately 1500°C. After several hours of degassing, helium gas (O₂ impurities removed by passing over red-hot titanium metal) was admitted to the furnace to a pressure of 1 atm. The furnace temperature was gradually raised to the desired temperature. Attempts to obtain absorption spectra were carried out from approximately 1900°K to 2700°K in

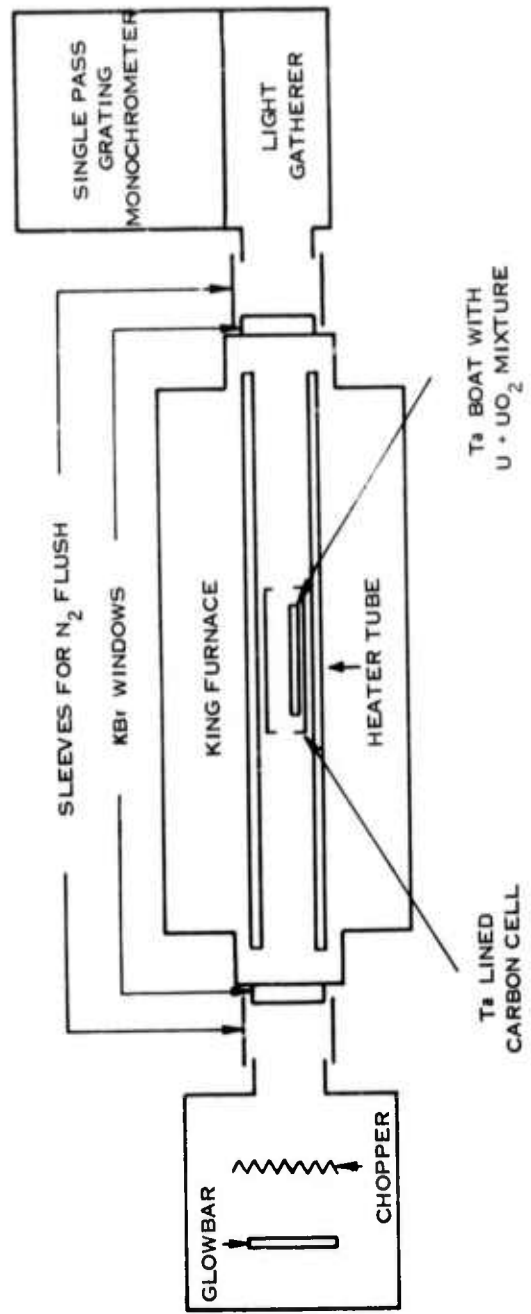


Figure 1. High Temperature Furnace and Infrared Optical Set-Up.

a series of eight different determinations. In no case was any evidence for absorption in the region between 1200 cm^{-1} and 700 cm^{-1} found.

RESULTS AND CONCLUSIONS

Based on the negative observation of absorption under the experimental conditions, several conclusions can be drawn as to the upper limits of the infrared oscillator strength for UO and/or UO₂.

The concentrations of UO and UO₂ were estimated from the vapor pressure results reported by Ackermann, et al (ref. 5) for these species over mixtures of uranium and uranium oxide. At the highest temperature (2700°K) at which spectral measurements were attempted the concentration of UO was found to be approximately 4×10^{15} molecules/cc, and that of UO₂ approximately 1×10^{15} molecules/cc.

Very crude estimates as to the upper limit of the corresponding oscillator strengths were made in the following manner. The total absorption (ref. 6) was taken as:

$$\frac{I_0 - I}{I_0} \Delta\nu = 8.85 \times 10^{-13} Nf\ell \quad (1)$$

where: I_0 and I are the incident and transmitted intensities,
 $\Delta\nu$ the effective slit width,
 N the number of absorbers,
 ℓ the path length, and
 f the oscillator strength.

It was assumed that a 2% change in signal could be detected and that the effective slit width of the spectrometer under the experimental conditions was approximately 1 cm^{-1} . Since no rotational constants were available for UO, the constants for the ground state of ThO were used (ref. 7) in order to estimate the rotational partition function and an approximate line spacing for UO at 2700°K. Concentrations of UO at J values around $J = 60$ (maximum population) were then calculated and an upper limit for the oscillator strength of UO was obtained from equation (1) assuming all vibrational and electronic levels contributed to the absorption. This value was found to be approximately 2×10^{-5} . In a similar manner the upper limit for UO₂ was found to be approximately 8×10^{-5} .

Although these estimates should be taken as very crude approximations, nevertheless their magnitudes are typical of vibrational oscillator strengths. The very large value for U_0 ($\sim 4 \times 10^{-2}$), which was a possibility based on the seeded flame work, now appears to be completely unrealistic.

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