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THE INFRARED SPECTRA OF UO AND UO₂ VAPOR CONDENSED
IN RARE-GAS MATRICES*

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Abstract:

The molecules UO and UO₂ were vaporized from tantalum and tungsten Knudsen cells containing variously a urania-uranium mixture, solid urania of natural isotopic composition, and solid urania, 60% enriched in oxygen-18, in the temperature range 2300° - 2500°K. The molecules were trapped in argon and krypton matrices at 20°K and studied spectroscopically from 4000 cm⁻¹ to 100 cm⁻¹.

Positively identified vibrational frequencies in argon matrices are 773 cm⁻¹ for UO¹⁶, 734 cm⁻¹ for UO¹⁸, and the frequencies 869, 853, and 825 cm⁻¹ for one of the stretching modes of the UO₂ molecule of respective isotopic composition UO₂¹⁶, UO¹⁶O¹⁸, and UO₂¹⁸. The second stretching frequency and the bending frequency of UO₂ were not observed.

INTRODUCTION

In order to obtain accurate thermochemical data for gaseous UO and UO₂ and to aid in understanding their bonding, we have undertaken an infrared spectroscopic study of these molecules trapped in matrices of solid argon and krypton. The matrix isolation technique was chosen because the molecules can be produced only by the vaporization of refractory compounds at high temperatures; conventional absorption spectroscopic techniques are not applicable. No spectroscopic data on gaseous UO or UO₂ were available at the time this work was begun; current studies with which we have become acquainted during this present work are mentioned in a later section.

Several authors¹⁻⁷ have studied vaporization processes which produce the UO and UO₂ as predominant species. In the vaporization of mixtures of urania and liquid uranium metal, Ackermann *et. al.*¹ report the relative partial pressures of UO₂, UO and U at 2100°K. Their equations extrapolate to give $UO_2/UO/U = 1/5.4/0.2$ at 2400°K. The urania phase sublimes congruently below 2200°K,^{2,7} with UO₂ the predominant species; the partial pressures at 2200°K, are $UO_3/UO_2/UO/U = 1/8/1/4 \times 10^{-4}$. Above 2200°K, in a tungsten cell, urania sublimes congruently at progressively more substoichiometric compositions⁷ with UO becoming more abundant in the vapor. Gaseous UO₃ should not be detectable mass spectrometrically from samples of atomic ratio O/U < 2.0. Thermochemical calculations based on reported thermodynamic data for the equilibria in the U-O system and for gaseous TaO and TaO₂⁹ indicate that tantalum should not reduce solid UO_{2.00} with the production of observable amounts of gaseous Ta oxides. Equations from which the partial and total vapor pressures in the uranium-oxygen system can be calculated are given in Table I.

Ackermann, et. al.¹ have calculated thermodynamic properties of gaseous UO by using the symmetric stretching frequency, 860 cm^{-1} , of the aqueous uranyl ion as the estimated vibrational frequency of UO. Kaufman, Muentner, and Klemperer⁸ have shown by electric deflection studies that the UO_2 molecule has a permanent dipole moment and is thus nonlinear.

EXPERIMENTAL SECTION

Apparatus.

The water-jacketed, stainless steel vacuum assembly containing the Knudsen cell from which the molecules of interest are vaporized is shown in Fig. 1. It was designed so that it can be attached either to the ion source of a time-of-flight mass spectrometer or to the tail of two different cryostats for spectroscopic studies. The mass spectrometer has previously been employed in this laboratory for the study of high temperature vaporization processes and related gaseous equilibrium studies.^{10,11} The ability to perform both mass and spectral analyses of the vapor from the same sample in the same effusion cell is of considerable advantage.

The temperature of the tantalum or tungsten Knudsen cell, heated by electron bombardment, was measured with an optical pyrometer by sighting through a shuttered window into a blackbody hole in the cell cap. The measured temperatures include corrections for the transmissivity of all optical components between the blackbody hole in the cell and the pyrometer. The molecular beam effused horizontally from an orifice in the side of the cell. Argon or krypton gas for the matrix passed through a calibrated flowmeter and entered the vacuum chamber coaxially with the molecular beam through a stainless steel capillary tube. A detachable pumping system utilizing a

30 $\text{\AA}$ /sec. oil diffusion pump maintained pressures below 10^{-4} torr during the depositions and below 10^{-6} torr after deposition. Spectral observations on a given film could be made successively with Perkin-Elmer Model 421 and Beckmann Model IR-11 infrared spectrophotometers by moving the evacuated apparatus.

The supporting structure of the Knudsen cell is shown in Fig. 2. Although there was some doubt as to the feasibility of using boron nitride in the hot region of such an assembly, we have found that it can be sufficiently well outgassed by maintaining the Knudsen cell at 800-1000°C overnight before an experimental run. Adequate radiation shielding between the Knudsen cell and the boron nitride supports is required so that the latter remains below about 1500°C. Otherwise the surfaces of the boron nitride parts become conductive when nitrogen is lost, and electrical shorts occur.

For the infrared experiments the matrix gas and effusing molecular beam were simultaneously deposited on cooled optical windows which could be rotated by 90° to face either the molecular beam or the optical beam. For the frequency range 4000 to 300 cm^{-1} CsBr and CsI optical windows were used; for the 500 to 50 cm^{-1} range, the matrix was deposited on a single crystal silicon window, and the outer windows were high density polyethylene. The temperature of the matrix window was measured with an uncalibrated copper-constantan thermocouple attached to it by Stycast resin; the reference junction was either on the helium well of one cryostat or an external liquid nitrogen bath in the other. An Andonian Associates three-liter liquid helium cryostat equipped with a variable-temperature tail was used during experiments in which the Knudsen cells were made of tantalum. In later experiments in which, coincidentally, a tungsten cell was used, an Air Products

and Chemicals, Inc. Model AC-3L Cryotip refrigerator was employed to produce liquid hydrogen. In both cryostats the optical window was firmly clamped to the cold block by means of an ETP copper frame with indium gaskets.

Experimental Materials.

For experiments in which a urania-liquid uranium mixture was desired, 20 mg samples of acid-cleaned metal were placed in each of two sintered-urania cups weighing approximately 4 g each. Each cup had previously held liquid uranium during its use by Ackermann, et. al.¹ for vapor pressure and phase studies, so a two-phase equilibrium at high temperatures was assumed.

For experiments in which urania of natural isotopic composition was to be vaporized, the samples of very slightly superstoichiometric UO_2 , obtained from Argonne National Laboratory, were sintered at 2000°K for 30 min. under high vacuum in a previously outgassed tungsten crucible to remove any adsorbed gases and to assure stoichiometry.

Isotopically enriched uranium dioxide containing a ratio $\text{O}^{18}/\text{O}^{16} = 1.5 \pm 0.2$ was prepared by oxidizing finely divided metal to $\text{U}_3\text{O}_8(\text{s})$ with 18-enriched $\text{O}_2(\text{g})$, followed by vacuum reduction at 1900°C in a previously outgassed tungsten Knudsen cell. The finely divided metal was prepared by reacting metal foil with hydrogen to produce $\text{UH}_3(\text{s})$, then reducing the UH_3 by vacuum heating at 350°C. The isotopic composition of the enriched UO_2 was determined by measuring the ratio of ion currents due to $(\text{UO}^{18})^+$ and $(\text{UO}^{16})^+$ in the mass spectrometer when the solid was vaporized from a tantalum cell in the temperature range 2300 - 2500°K. For convenience we designate the enriched solid as "UO₂-18" in this paper.

Various urania samples were subjected to x-ray powder diffraction analysis using $\text{CuK}\alpha$ radiation. Table II lists the samples and conclusions from these analyses.

MASS SPECTRAL OBSERVATIONS

In general our mass spectrometric measurements confirmed the earlier studies mentioned in the Introduction. Only a few observations need be noted here. When a tantalum Knudsen cell was used to vaporize the liquid uranium in urania cup samples at 2400°K , UO^+ predominated over UO_2^+ and U^+ in the mass spectrum ($\text{UO}_2^+/\text{UO}^+/\text{U}^+ = 1/5/0.4$) at 15 ev ionizing energy, an energy too low to produce UO^+ by fragmentation of $\text{UO}_2(\text{g})$ or U^+ by fragmentation of $\text{UO}(\text{g})$. These ratios agree well with those extrapolated from the data of Ackermann, *et. al.*¹. When stoichiometric urania was sublimed from tantalum at 2400°K , UO_2^+ was observed at three times the intensity of UO^+ at ionizing electron energies below 15 ev. During several hours at temperatures from 2300 to 2500°K , the ion current ratio changed until it finally equilibrated in the range $\text{UO}^+/\text{UO}_2^+ = 1.2$ to 1.6 in experiments at various temperatures. This is taken as strong evidence that urania becomes substoichiometric, but does not reach the lower phase boundary observed in the U-UO_2 mixtures. From the work of Edwards, *et. al.*⁷ and the observed ratio of $\text{UO}^+/\text{UO}_2^+$, we estimate this composition to be approximately $\text{UO}_{1.97}$.

No TaO^+ , TaO_2^+ or UO_3^+ was observed. Under the experimental conditions, the detection limits for these ions was approximately 1% of the intensity of UO^+ or UO_2^+ .

Electron bombardment heating of the Knudsen cell was accompanied by ionization of some of the molecules in the effusing molecular beam. When

the cell was heated to 2400°K by a bombardment current of 0.9 amp, with the emitting filament grounded and the cell at +630 volts, broad peaks due to U^+ , UO^+ , and UO_2^+ could be observed in the absence of an electron beam in the mass spectrometer's ion source. These peaks were of about 12 percent of the intensity of, and were centered about four mass units lower than, their counterparts formed in the ion source. They could be detected by careful adjustment of the deflection plates in the flight tube of the mass spectrometer, and contributed less than 1% of the ion current when the normally formed ions were properly focused. Presumably the spurious ions were trapped in the matrix along with neutral molecules; since only a fraction of a percent of the effusate should have been ionized in this way, their effect on the spectra should be small even if they remain as ions in the matrix.

INFRARED STUDIES

Typical experimental conditions used throughout these studies involved vaporizing the samples through orifices of 0.020 and 0.025 cm² area at temperatures of 2200 to 2600°K; deposition times ranged from 20 to 60 min. These conditions correspond to partial pressures of UO in various experiments; the amounts of UO and UO_2 striking the matrix window located 10 cm from the orifice were calculated to be 6×10^{-7} to 3×10^{-5} moles. From the observed flow rates of the inert gas and if half the inert gas is assumed to condense on the window, the calculated mole ratio of rare gas to UO or UO_2 ranged from 500 to 30,000.

Several representative spectra are shown in Figs. 3 to 6. Fig. 3 shows a spectrum of the vapor from the UO_2 - U mixture trapped in krypton. The main feature at 765 cm⁻¹ was reproduced quite well in other experiments,

but the bands near 818 were quite variable relative to the 765 cm^{-1} band. A spectrum of the trapped vapor from the UO_2^{16} sample is shown in Fig. 4. This spectrum is somewhat atypical in that it shows more bands and greater changes upon annealing than most of our spectra from similar samples. In particular, the band at 818 cm^{-1} is relatively much more intense than in most cases; the growth of the bands at 850 and 799 cm^{-1} after annealing the argon matrix at about 35° for fifteen minutes is also much more dramatic than in most of our other spectra. A spectrum obtained with the "UO₂-18" sample is shown in Fig. 5. The UO_2 was sublimed from a tantalum cell and apparently only a small amount of UO_2 was trapped in the matrix. As will be discussed later, the bands at 869, 853, and 825 will be ascribed to ν_3 of UO_2 isotopic species. No absorption bands due to vaporized molecules were observed between 700 and 100 cm^{-1} . In one experiment in which "UO₂-18" was vaporized from a tantalum cell, total absorption was observed between 100 and 55 cm^{-1} ; since the absorption due to UO_2 at 869 cm^{-1} was quite weak when similar samples were studied, it is not probable that the absorption we observed was due to the bending mode of UO_2 .

As indicated above, we observed neither TaO^+ nor TaO_2^+ in the mass spectrometric studies, and no bands ascribable to TaO, TaO_2 or tungsten oxides¹² appeared in our spectra. Weltner and Thompson¹³ reported observing electronic but not vibrational bands of TaO when urania was vaporized from a tantalum cell into matrices of argon and neon. Kaufman, Muentert, and Klemperer⁸ reported observing TaO in mass spectra when urania was vaporized from tantalum. Our outgassing of the Knudsen cell prior to use precluded TaO(g) from being emitted from the tantalum itself; despite the fact that no TaO was observed in our spectra and that available thermochemical

data suggest that the reactions to produce gaseous TaO or TaO₂ from Ta and solid or gaseous UO₂ should reduce only a small fraction of the UO₂, it is obvious from our spectra that relatively much more UO₂ was produced when urania samples were vaporized from a tungsten cell rather than a tantalum cell.

A summary of the bands observed in the 900-700 cm⁻¹ region is shown in Table III; the data shown represent the results of 19 different experiments. These data will be discussed in the next section. The mass-spectral and thermochemical data yield the following criteria for assigning the observed infrared spectra:

- (1) The vapor phase over the U-UO₂ mixture should be primarily UO.
- (2) If a UO₂(s) sample is kept at 2400 - 2500°K for an appreciable time, it should become more substoichiometric and yield a vapor phase with increasing UO/UO₂ relative partial pressures.
- (3) The relative intensities of the O¹⁸ species should be close to those calculated from the mass ratios observed in the mass spectral measurements made immediately before the matrix isolation experiments.

DISCUSSION

Vibrational frequency of UO

The band at 773 cm⁻¹ in argon, with a shoulder at 776 cm⁻¹, is identified as the UO fundamental for the following reasons:

- (1) The 773 cm⁻¹ band was always the most intense band in the spectrum from U-UO₂ mixtures.
- (2) The ratio of frequencies 734/773 = 0.949 is that expected for the isotopic species UO¹⁶/UO¹⁸ (calculated ratio is 0.946).

- (3) The ratio of peak absorptivities for the bands (734/ 773 ratio of 1.6) is in agreement with that found in the mass spectrum ($\text{UO}^{18+}/\text{UO}^{16+}$ ratio of 1.5 ± 0.2).
- (4) The 773 cm^{-1} band was always the strongest band when urania was sublimed from a tantalum cell, which evidently reduces the urania at high temperatures. This band was initially less intense than the 869 cm^{-1} band when urania was sublimed from tungsten; however, the 773 cm^{-1} band grew from about one-third to about twice the intensity of the 869 band as a UO_2^{16} sample was exhaustively sublimed from a tungsten cell at 2500°K as shown in Fig. 6.
- (5) The 773 band appeared as one of the major features in the matrix spectrum of an oxygen-contaminated sample of uranium monosulfide. Cater, et. al. have shown¹⁴ that $\text{UO}(\text{g})$ is the predominant vapor species in the early stages of such a vaporization.

Vibrational frequencies of UO_2

The band at 869 cm^{-1} is identified as either ν_1 or ν_3 of UO_2^{16} for the following reasons:

- (1) This band was the most intense feature of the spectrum when stoichiometric $\text{UO}_2(\text{s})$ was sublimed from a tungsten cell. See statement (4) above and Fig. 6.
- (2) The intensities of the bands at 869 ($\text{UO}^{16}\text{O}^{16}$), 853 ($\text{UO}^{16}\text{O}^{18}$), and 825 ($\text{UO}^{18}\text{O}^{18}$) were appropriate for the known isotopic ratios of our samples. The frequency ratio (see discussion below) for the species UO_2^{18} and UO_2^{16} , $825/869 = 0.949$, is within the range 0.946-0.950 calculated for the asymmetric stretch, ν_3 , for bond angles from 90° to 180° with the assumption that the bending frequency, ν_2 , is much lower than ν_3 .

We believe that none of the other bands can be assigned to monomeric UO or UO_2 . A band frequently was observed at 818 cm^{-1} , but the ratio of the intensity of this band to the intensity of either the 869 or 773 band varied dramatically in different experiments. Furthermore, there was no appropriately shifted band when the UO_2 -18 sample was vaporized.

Several weak bands were also observed in the vicinity of 800 cm^{-1} , with a band of 799 cm^{-1} usually being quite sharp. These bands also showed variable intensities relative to the UO or UO_2 bands.

Finally, the most curious feature of the " UO_2 -18" spectra was the appearance of two strong bands at 769 and 726 cm^{-1} . Although the 773 , 769 , 734 , and 726 cm^{-1} quartet might be appropriate for a UO_3 band, there are strong arguments against such an assignment.

First, there should never be an appreciable concentration of UO_3 in the vapor phase of any of our samples, particularly in the U-UO_2 mixtures; we were never able to detect any UO_3 in the mass spectrometer. Secondly, the $^{16}\text{O}/^{18}\text{O}$ abundance ratio as determined by the observed UO^+ and UO_2^+ species in the mass spectrum would predict an intensity ratio of about $1/6/11/7$ for the UO_3^{16} , $\text{UO}_2^{16}\text{O}^{18}$, $\text{UO}^{16}\text{O}_2^{18}$, and UO_3^{18} species. The observed ratio of integrated band areas was $1/1.5/1.6/0.7$ for the 773 , 769 , 734 , and 726 cm^{-1} quartet. To verify these ratios, we prepared a second " UO_2 -18" sample which had an $^{18}\text{O}/^{16}\text{O}$ ratio of ≈ 1 . Spectra obtained from this sample showed the four bands discussed above; the four were all of about the same intensity. There is no way to obtain an equilibrium UO_3 isotopic mixture containing equimolar amounts of UO_3^{16} , $\text{UO}_2^{16}\text{O}^{18}$, $\text{UO}^{16}\text{O}_2^{18}$, and UO_3^{18} . It is tempting to ascribe the four bands to weakly interacting UO dimers, but then the splittings observed when only UO^{16} was present should have been larger than observed.

CONCLUSIONS

The UO vibrational frequency is concluded to be at 773 cm^{-1} in an argon matrix and at 765 in krypton. The isotopic shift data do not allow an unambiguous assignment of the 869 cm^{-1} band to ν_1 or ν_3 of UO_2 . If the 869 cm^{-1} band is taken to be ν_3 , the UO_2^{18} band should be between 822 and 825 cm^{-1} (bond angle of 90 and 180° , respectively). The accuracy of our frequency measurements ($\pm 1\text{ cm}^{-1}$) does not allow an accurate estimate of the bond angle. If the 869 cm^{-1} band is assigned as the symmetric stretch, ν_1 , and if ν_2 is assumed to be at a very low frequency, then the ν_1 band of UO_2^{18} should be between 822 and 819 cm^{-1} . Since ν_3 would be expected to be more intense than ν_1 and since the calculated isotopic shifts for ν_3 agree more closely with those observed, we believe it is probable that the 869 cm^{-1} band (864 in krypton) is ν_3 of UO_2 .

Although we have not observed a band assignable as the symmetric stretch, ν_1 , of UO_2 , it is possible to estimate its frequency using the values of ν_3 for the three isotopic species. Since the bending mode, ν_2 , is probably below 200 cm^{-1} , the degree of the secular equation can be reduced by assuming the bending force constant equal to zero. Then by assuming values of ν_1 and the bond angle along with the measured value of ν_3 for UO_2^{16} , values of the two force constants, k_1 and k_{12} , can be calculated. The assumed values of ν_1 which lead to a predicted value of ν_3 of $\text{UO}^{16}\text{O}^{18}$ at $853 \pm 1\text{ cm}^{-1}$ are shown in Table IV as a function of assumed bond angle. While this calculation is not very precise, it does seem reasonable to expect ν_1 to be in the range 775 - 810 cm^{-1} . We did observe weak bands at 799 cm^{-1} and 757 cm^{-1} in the " UO_2 -18" experiments, but the intensity of the 799 cm^{-1} band

in UO_2^{16} experiments was somewhat variable relative to the intensity of the 869 cm^{-1} band.

For the calculation shown in Table III at 160° , for example, the force constants for UO_2 are:

$$\begin{aligned}k_1 &= 6.08 \pm 0.1 \text{ mdyne/\AA}^\circ \\k_{12} &= -0.21 \pm 0.1 \text{ mdyne/\AA}^\circ\end{aligned}$$

where $V = \frac{1}{2}k_1r_1^2 + k_{12}r_1r_2 + \frac{1}{2}k_1r_2^2$. The force constant for UO using $\nu = 773 \text{ cm}^{-1}$ is $5.27 \text{ mdyne/\AA}^\circ$.

Thermochemistry of UO

The use of the present vibrational frequency 773 cm^{-1} rather than the estimated 860 cm^{-1} for the UO molecule makes relatively little change in the thermochemical values calculated by Ackermann, et. al.¹ even at the high temperatures of interest. However, it alleviates the uncertainty associated with the use of an estimated vibrational frequency. Thus the entropy, enthalpy, and free energy function increase by 0.21 e.u. , 0.16 e.u. , and 102 cal/mole respectively at 2000°K . At 2500°K the increases are respectively 0.21 e.u. , 0.17 e.u. and 104 cal/mole respectively. The resulting entropy exclusive of the electronic contribution and standard free energy of formation of UO(g) at 2000°K are 73.5 e.u. and -35.8 kcal/mole , respectively. These corrections are far less than the error due to neglect of the electronic contributions, which in the case of the entropy may add approximately 5 e.u. according to Ackermann, et. al.¹

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Table I. Vapor Pressure Equations for the U-O System

For U-UO₂ mixtures^a, 1600-2400°K

$$p_{\text{UO}_2}(\text{atm}) = -(30,180 \pm 300)/T + (7.74 \pm 0.14)$$

$$p_{\text{UO}}(\text{atm}) = -(26,880 \pm 300)/T + (7.11 \pm 0.14)$$

$$p_{\text{U}}(\text{atm}) = -(25,620 \pm 300)/T + (5.21 \pm 0.14)$$

For stoichiometric UO₂^b, 1600-2200°K

$$p_{\text{UO}_2}(\text{atm}) = -(32,196 \pm 893)/T (9.150 \pm 0.390)$$

a. Ackermann, Rauh, and Chandrasekhariah, ref. 1.

b. Ackermann, Gilles, and Thorn, ref. 2.

Table II. Lattice Parameters of UO_2 Samples

Sample ^a	Lattice Parameter
1	5.4713 ± 0.0009
2	5.4710 ± 0.0013
3	5.4705 ± 0.0007
Lit. ^b	$5.469 - 5.472$

a) Samples 1 and 2 were used in UO_2^{16} experiments; sample 3 in "UO-18" experiments.

b) C. Holley, Ed., Thermodynamic and Transport Properties of Uranium Dioxide and Related Phases, Technical Reports Series No. 39, International Atomic Energy Agency, Vienna (1965).

Table III. Vibrational Frequencies of Matrix
Isolated UO and UO₂.^a

Molecule	Argon Matrix	Krypton Matrix
UO ₂ ¹⁶	<u>869</u> ; 872	864
UO ¹⁶ O ¹⁸	853	
UO ₂ ¹⁸	825	
--	818	
--	799	
UO ¹⁶	<u>773</u> ; 776	<u>765</u> ; 767
--	769 ^b	
	757 ^b	
UO ¹⁸	<u>734</u> ; 736	
--	726 ^b	

a) All values in cm⁻¹. The more intense member of a doublet is underlined.

b) Appeared only in "UO₂-18" spectra.

Table IV. Calculated Values of ν_1 of UO_2^a

θ^b	UO_2^{16}		$\text{UO}^{16}\text{O}^{18}$		UO_2^{18}	
	ν_1	ν_3	ν_1	ν_3	ν_1	ν_3
120°	798 ± 12	869.0	769 ± 11	853 ± 1	753 ± 12	823.9
140°	793 ± 13	869.0	764 ± 12	853 ± 1	748 ± 12	824.6
160°	791 ± 13	869.0	762 ± 12	853 ± 1	746 ± 12	825.1
180°	790 ± 14	869.0	761 ± 13	853 ± 1	745 ± 12	825.3
OBS	---	869 ± 1	---	853 ± 1	---	825 ± 1

a) All values in cm^{-1} .

b) Assumed bond angle.

Vacuum Chamber-Knudsen Cell Assembly

Figure 1

Figure 2

Knudsen Cell Assembly

Figure 3

IR Spectrum (Krypton Matrix) of Vapor from UO_2 -U Mixture

Figure 4

IR Spectrum (Argon Matrix) of Vapor from UO_2^{16}

IR Spectrum (Argon Matrix) of Vapor from Oxygen-18-Enriched Urania

Figure 6

IR Spectrum (Argon Matrix) of Vapor
from UO_2^{16} (Tungsten Cell)