FINE DEFINITION OF IR SPECTRA FOR CERTAIN METALLIC OXIDE SPECIES

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THE REACTIONS BETWEEN U, UO OR UO(2) + reactants in Ar matrices at 14 K. IR spectra were recorded with a Fourier transform spectrophotometer. Several new species were identified. An ion was produced by three different reactions of uranium, UN and UN(2). We expect it to be linear. The species UO+ could not be observed by any of the following reactions.
DEFINITION OF IR SPECTRA FOR CERTAIN METALLIC OXIDE SPECIES.

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AL COMPOUNDS, INFRARED SPECTRA, NITROGEN OXIDES, URANIUM COMPOUNDS.

AL OXIDES, WU29, WU39

REATIONS BETWEEN U, UO OR UO(2) HAVE BEEN STUDIED BY COCONDENSATION OF THE GENTS IN AR MATRICES AT 14 K. INFRARED SPECTRA OF THE SPECIES IN THE MATRICES E RECORDER WITH A FORIR TRANSFORM SPECTROMETER. THE VIBRATIONAL MODE FREQUENCIES SEVERAL NEW SPECIES WERE IDENTIFIED BY USE OF ISOTOPIC SUBSTITUTION. THE UO(+) WAS PRODUCED BY THREE DIFFERENT REACTIONS AND WAS FOUND TO BE LINEAR. THE IDES OF URANIUM, UN AND UN(2), WERE PRODUCED BY TWO METHODS; UN(2) WAS FOUND E LINEAR. THE SPECIES UO+ COULD NOT BE PRODUCED IN SUFFICIENT QUANTITIES TO BE SERVED BY ANY OF THE FOLLOWING REACTIONS: U + NO(2) , U + NO OR UO + I.
The reactions between U, UO or UO₂ and NO or NO₂ have been studied by cocondensation of the reactants in Ar matrices at 14°K. Infrared spectra of the species in the matrices were recorded with a Fourier transform spectrometer. The vibrational mode frequencies of several new species were identified by use of isotopic substitution. The U₃⁺ ion was produced by three different reactions and was found to be linear. The nitriles of uranium, UN and UN₂, were produced by two methods; UN₂ was found to be linear. The species...
UO₂ could not be produced in sufficient quantities to be observed by any of the following reactions: U + NO₂, U + NO or UO + I.
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I. INTRODUCTION

The matrix-isolation technique has been successfully applied in our laboratory to the study of the $\text{UO}_2^+$ ion (Reference 1). The basic objective of the work undertaken in FY1976 and FY7T was to complete and extend these studies to obtain the infrared spectra of other metal oxide ions. Particular emphasis was placed on the observation of the species $\text{UO}^+$.

The associative ionization reactions (1) and (2) have been observed (References 2–4) in gas-phase crossed-beam studies using mass spectrometers,

\[ \text{U} + \text{O} \rightarrow \text{UO}^+ + \text{e}^- \]  
\[ \text{U} + \text{O}_2 \rightarrow \text{UO}_2^+ + \text{e}^- \]  

In addition, other reaction channels for $\text{U} + \text{O}_2$ were detected:

\[ \text{U} + \text{O}_2 \rightarrow \text{UO}^+ + \text{O} + \text{e}^- \]  
\[ \text{U} + \text{O}_2 \rightarrow \text{U}^+ + \text{O}_2 + \text{e}^- \]

Observation of the infrared spectra of the ions produced in a cross-beam experiment is difficult, due, in part, to the low particle densities in the beams and the predominance of neutral species among the reaction products (Reference 2). Consequently, no infrared spectrum of $\text{UO}^+$ or of $\text{UO}_2^+$ has been previously reported.

The matrix-isolation technique provides a suitable method for studying the spectra of such ionic species by trapping the ions in concentrations sufficient for spectroscopic observation. Recombination reactions, such as reaction (5),

\[ \text{UO}_2^+ + \text{e}^- \rightarrow \text{UO}_2 \]

which would readily neutralize cations in a matrix, can be minimized by the presence of an electronegative molecule or atom, such as NO$_2$ or I. This approach has been used to study a variety of anions and cations.
Ions have been produced both by cocondensation of reactive species and by photolysis of appropriate precursors in the matrix.

Spontaneous ion pair formation from a charge-transfer reaction between two species in a matrix can occur if the gain in energy due to the Coulomb attraction of the ions is sufficient to compensate for the energy input required to form the anion and cation. For the specific cases of the reactions between U, UO or UO₂ and NO₂ or NO, the necessary thermodynamic data are available (Reference 6 for NO and NO₂; Reference 7 for U, UO, and UO₂). The ionization potentials of U, UO and UO₂ have been measured (Reference 8) as well as the electron affinities of NO₂ (Reference 9) and NO (Reference 10). These data show that several of the reactions to form ion pairs in an Ar matrix are thermodynamically favorable (Reference 1).

It is important to note that reaction energy barriers could prevent significant reaction even in cases that are thermodynamically favorable. Furthermore, competitive reactions to form products other than the desired ones, for either kinetic or thermodynamic reasons, may prevent the formation of sufficient amounts of the desired products for spectroscopic observation. This problem may be particularly important for the study of UO⁺ because both reactions (6) and (7) are thermodynamically favorable and will be competitive:

\[
\begin{align*}
U + NO₂ &\rightarrow UO + NO \\
U + NO₂ &\rightarrow UO⁺\cdot NO⁻
\end{align*}
\]

Thus, the thermodynamic data alone are not sufficient to predict the occurrence of a charge-transfer reaction, but they can serve to indicate reasonable possibilities for study and they can exclude other possibilities.

Two different reactions were attempted in Ar matrices to see if the UO⁺ species could be produced and its infrared absorption spectrum observed. The first was reaction (7) above. The second was reaction (8) in which iodine atoms generated by in situ photolysis of HI, reaction (9), were used:
\text{Reactions:}

\begin{align*}
\text{UO} + \text{I} & \rightarrow \text{UO}^+ \cdot \text{I}^- \\
\text{HI} & \xrightarrow{hv} \text{H} + \text{I} 
\end{align*}
II. EXPERIMENTAL

Figure 1 shows a schematic diagram of the matrix-isolation apparatus used for most of the studies discussed in this report. An Air Products Displex closed-cycle helium refrigerator, model CSW-202, was used to cool a gold mirror substrate to the operating temperature. Most matrices were deposited at 14 K (± 1 K) by using a temperature controller consisting of a proportional resistance heater and a chromel vs Au – 7% Fe thermocouple. Matheson research grade argon gas was used with $^{16}$N$^{18}$O$_2$ (Miles-Yeda Ltd., 92.8% $^{18}$O), $^{14}$N$^{16}$O (Matheson) and $^{15}$N$^{16}$O (Stohler Isotopes, 99% $^{15}$N) to prepare mixtures which entered the auxiliary gas line shown in Fig. 1 and were deposited on the gold mirror.

The species $^{235}$U, $^{238}$U and $^{238}$UO$_2$ were produced either by vaporization from a Knudsen cell (Reference 1) or by sputtering, using the device shown in Fig. 2. This sputtering device, which is similar to one described previously (Reference 11), consists of a uranium screw cathode with a 2-mm-diameter hole in which a platinum wire anode is positioned. Argon or O$_2$/Ar mixtures flow into the hollow cathode where a discharge is initiated. The Ar$^+$ ions produced are accelerated into the cathode with sufficient energy to cause U atoms to be sputtered from the surface. If oxygen is present in the sputtering gas, oxides of uranium are produced. The device was particularly useful for those studies in which the reactions of U atoms were studied because the high reactivity of liquid uranium made Knudsen-cell vaporization impractical.

After deposition of a matrix, the refrigerator and attached deposition mirror were rotated 180° to face the spectrometer. Infrared spectra in the range 3000–300 cm$^{-1}$ were recorded with a Digilab FTS-14 Fourier transform
Fig. 1. Schematic diagram of the experimental arrangement used for infrared spectroscopy of low-temperature matrices.
Fig. 2. Sputtering device used to produce high-temperature atoms and molecules.
spectrometer. Maximum instrumental resolution, better than 0.5 cm$^{-1}$, was used for most spectra and a frequency measurement to ± 0.05 cm$^{-1}$ was made, although the line breadth of some observed absorption peaks limited the reproducibility to 0.1 cm$^{-1}$. The spectrometer's infrared beam was reflected from the spectrometer to the gold mirror substrate and back to the spectrometer's TGS detector by a mirror system (Reference 12). As many as 4096 interferograms of each sample were coadded and transformed to improve the signal-to-noise ratio although 256 interferograms were generally adequate. All recorded spectra were transferred to magnetic-tape storage so that the ratio of any two spectra could be readily obtained. In most cases the background spectrum was a pure Ar matrix.
III. RESULTS AND DISCUSSION

A. UO$_2^+$ and NO$_2^-$

During FY1976 the study of matrix-isolated UO$_2^+$ was completed and a manuscript entitled "Infrared Spectra of Matrix-Isolated UO$_2^+$ and NO$_2^-$ was prepared and published (Reference 1). The abstract of that paper is given below.

"The reactions of UO and UO$_2$ with NO and NO$_2$ have been studied by infrared spectroscopy using the matrix isolation technique. Codeposition of vaporized UO and UO$_2$ with NO and with NO$_2$ gases in an argon matrix at 14 K resulted in the production of the UO$_2^+$ molecular ion paired with either a NO$_2^-$ or NO$^-$ anion. Three different reactions have been observed to yield a UO$_2^+$ cation product: (1) UO$_2$ + NO$_2$, (2) UO$_2$ + NO, and (3) UO + NO$_2$.

Infrared absorption frequencies in the range 1150-1190 cm$^{-1}$ have been measured and interpreted as the stretching modes of bent (bond angle = 109°) N$^{16}$O$_2^-$, N$^{16}$O$^{18}$O$^-$, and N$^{18}$O$_2^-$ ions paired with UO$_2^+$. Infrared absorption frequencies in the range 770-900 cm$^{-1}$ have been measured and interpreted as the stretching modes of linear U$^{16}$O$_2^+$, U$^{16}$O$^{18}$O$^+$, and U$^{18}$O$_2^+$ paired with either NO$^-$ or NO$_2^-$." 

B. UN and UN$_2$

During the course of the studies of reactions between uranium atoms and NO$_2$ in Ar matrices, several peaks were observed which could be assigned to products of a reaction involving U and NO$_2$. These peaks were not observed with U alone in Ar matrices nor with NO$_2$ alone in Ar matrices. Peaks other than those assigned to uranium nitrides will be discussed in Section III C of this report.

One group of peaks that was observed in the range 1060-980 cm$^{-1}$ attracted special attention because they appeared without additional peaks irrespective
of whether $^{14}\text{N}^{16}\text{O}_2$ or $^{14}\text{N}^{18}\text{O}_2$ was used as a reactant. Experiments were completed to identify the absorbers responsible for these peaks.

Several matrices were formed using various $\text{N}^{16}\text{O}_2/\text{N}^{18}\text{O}_2$ mixtures; a typical spectrum is shown as (A) in Fig. 3. The results of these experiments may be summarized as follows: (1) none of the peaks is due to an absorber containing oxygen (no $^{18}\text{O}$-isotope shifts were observed); (2) the three peaks between 1001 and 991 cm$^{-1}$ are probably due to the same species because their relative absorbances remained constant in different experiments; and (3) the peak at 983.7 cm$^{-1}$ is due to a different species because of its variable relative absorbance in different experiments and its substantial growth when the matrix was annealed to 30 K.

The possibility that uranium nitrides might be responsible for some of the observed peaks was examined by sputtering the U hollow cathode with a mixture of 0.05% $^{14}\text{N}_2$ in Ar, with NO$_2$ absent. The resultant spectrum was similar to spectrum (A) in Fig. 3, except that the X-UN peak was much weaker and the NUN peak was not detected within the noise. The U hollow cathode was then sputtered with a mixture of $^{14}\text{N}_2/^{15}\text{N}_2$ in Ar (0.13% total N$_2$ in Ar) to form a matrix which produced spectrum (B) in Fig. 3.

The triplet observed with $^{14}\text{N}$ alone (1001-991 cm$^{-1}$) has a single corresponding triplet at lower frequencies in the presence of $^{15}\text{N}$ [compare spectra (A) and (B) in Fig. 3]. The measured frequencies for the lower-frequency triplet are in excellent agreement with those calculated from the higher-frequency triplet if the observed peaks are assigned to the matrix-isolated UN molecule as shown in Table 1. The calculated $\omega_e$ and $\omega_x$ values are reasonable for the UN molecule, as judged from the corresponding values (Reference 13) for matrix-isolated UO. The annealing behavior of this triplet, as shown in spectrum (C) of Fig. 3, is reproducible irrespective of whether UN is produced by U + NO$_2$.
Fig. 3. Infrared spectra obtained from an Ar matrix at 14 K. (A) The products of cocondensation of U atoms with NO₂; (B) the products of sputtering U with a 1:1:800 ¹⁴N₂:¹⁵N₂:Ar mixture; (C) the same matrix as (B) after annealing to 30 K and recooling to 14 K.
TABLE I. Comparison of the observed and calculated frequencies (cm$^{-1}$) assuming four sites for UN.

<table>
<thead>
<tr>
<th>Site $^a$</th>
<th>Obs $\tilde{v}^b$ $^{14}$U</th>
<th>Obs $\tilde{v}^b$ $^{15}$U</th>
<th>Calc $\tilde{v}^c$ $^{14}$U</th>
<th>Calc $\tilde{v}^c$ $^{15}$U</th>
<th>Calc $\omega^d$</th>
<th>Calc $\omega^e$</th>
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<tr>
<td>1</td>
<td>1000.97</td>
<td>969.25</td>
<td>969.04</td>
<td>1007.7</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>995.52</td>
<td>963.97</td>
<td>963.77</td>
<td>1002.1</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>991.90</td>
<td>960.50</td>
<td>960.26</td>
<td>999.6</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>983.70</td>
<td>953.37</td>
<td>952.32</td>
<td>...</td>
<td>...</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Only sites 1, 2, and 3 can be assigned to matrix-isolated UN.
$^b\pm0.05$ cm$^{-1}$
$^c$From $\tilde{v}$ of $^{14}$U assuming the harmonic oscillator approximation with $\rho=0.968103$.
$^d\pm1.6$ cm$^{-1}$.
$^e\pm0.8$ cm$^{-1}$.
or U sputtered with N$_2$/Ar. A comparison of spectra (B) and (C) shows that the peak at 1001 cm$^{-1}$ grows slightly upon annealing, whereas the other two peaks of the triplet diminish. This behavior suggests the presence of one stable and two unstable sites for the UN molecule in the Ar matrix.

The peak observed at 1050.93 cm$^{-1}$ [spectrum (A) in Fig. 3] has two counterparts (1040.71 and 1019.39 cm$^{-1}$) in the presence of $^{15}$N [spectrum (B)]. The number of peaks and their frequencies are consistent with their assignment to the $v_3$ modes of linear N-U-N isotopomers (force constants $f' = 8.215$ mdyn Å$^{-1}$, $f'' = 0.062$ mdyn Å$^{-1}$).

These preliminary results have been published in more detail (Reference 14) in a Note entitled "The identification of UN in Ar matrices."

Additional experiments were done in Kr matrices which confirmed the assignments given for linear N-U-N in Ar matrices. The results for both Ar and Kr matrices are given in Table II.

C. Reactions of U atoms

A number of heavy-metal oxides have been studied in low-temperature matrices in our laboratory; these oxides include UO and UO$_2$ (Reference 13), UO$_3$ (Reference 15), PuO and PuO$_2$ (Reference 16), UO$^{18}$ (Reference 1), and several actinide and lanthanide monoxides and dioxides including ThO and ThO$_2$ (Reference 17).

In all cases, the stretching-mode frequencies were observed between 600 and 1000 cm$^{-1}$; thus UO$^+$ was expected to absorb in this range. For the monoxides previously studied, the observed frequencies were found to deviate only slightly from the harmonic oscillator approximation. Thus, in the case of UO$^+$, the observed frequency ratio should be well approximated by the following expression,

$$ \frac{\mu (U^{18}O^+)}{\mu (U^{16}O^+)} = \sqrt{\frac{\mu (U^{16}O^+)}{\mu (U^{18}O^+)}} = 0.94639 $$

(10)
TABLE II. Observed and calculated frequencies of linear N–U–N in Ar and Kr matrices at 14 K.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Mode</th>
<th>Ar Matrix</th>
<th>Kr Matrix</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>Obs cm(^{-1})</td>
<td>Calc(^{a}) cm(^{-1})</td>
</tr>
<tr>
<td>U(^{14})N(_{2})</td>
<td>(\nu_1)</td>
<td>1001.66</td>
<td>1040.28</td>
</tr>
<tr>
<td></td>
<td>(\nu_3)</td>
<td>1050.93</td>
<td></td>
</tr>
<tr>
<td>U(^{14})N(^{15})N</td>
<td>(\nu_1)</td>
<td>979.11</td>
<td>1030.26</td>
</tr>
<tr>
<td></td>
<td>(\nu_3)</td>
<td>1040.74</td>
<td></td>
</tr>
<tr>
<td>U(^{15})N(_{2})</td>
<td>(\nu_1)</td>
<td>967.80</td>
<td>1009.05</td>
</tr>
<tr>
<td></td>
<td>(\nu_3)</td>
<td>1019.39</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)\(f = 8.215, f' = 0.062\) mdyn Å\(^{-1}\) in Ar; \(f = 8.058, f' = 0.070\) mdyn Å\(^{-1}\) in Kr.
where \( \mu \) represents reduced mass. Because of expected small anharmonic contributions to the \( \text{UO}^+ \) vibration, the frequency ratio should be slightly greater than the theoretical harmonic value given by Eq. (10). For example, in the cases of \( \text{UO} \) (Reference 13) and \( \text{PuO} \) (Reference 16), the measured frequency ratios are 0.03 and 0.04% higher, respectively. Thus, the identification of \( \text{UO}^+ \) from its infrared spectrum should be possible with the Fourier transform spectrometer which has a frequency accuracy of about 0.006% in this range.

Because of the success of the methods used to obtain the infrared spectrum of \( \text{UO}^+ \) (Reference 1), analogous methods to produce \( \text{UO}^+ \) were attempted. The energy relationships shown in Fig. 4 suggest that the \( \text{UO}^+ \) product from the reaction between \( \text{U} \) and \( \text{NO}_2 \) may not be the only product or even the principal product. To obtain the numerical values in Fig. 4, a Coulomb stabilization energy of 88 kcal mol\(^{-1}\) was used (see Reference 1); this value is an estimate based on a point-charge separation corresponding to the nuclear spacing in the solid Ar lattice. Because of the uncertainty in the value for the Coulomb stabilization energy and the uncertainties involved in the use of gas-phase thermodynamic data for reactions on a low-temperature matrix surface, the data in Fig. 4 serve only to indicate possibilities. The reaction of \( \text{U} \) atoms with \( \text{NO}_2 \) seems, from these considerations, to be a possible method to produce \( \text{UO}^+ \).

Several experiments were completed in which \( \text{U} \) atoms, vaporized from a Knudsen cell or sputtered from the device shown in Fig. 2, were cocondensed in Ar matrices at 14 K with either \( ^{14}\text{N}^{16}\text{O}_2 \), \( ^{14}\text{N}^{18}\text{O}_2 \) or mixtures of the two. Portions of three infrared spectra from two experiments with \( ^{14}\text{N}^{16}\text{O}_2 \) are shown in Fig. 5. Infrared spectra were also taken of most
Fig. 4. Energy relationships (in kcal mol$^{-1}$) for various reaction pathways of the $U + NO_2$ reaction.
matrices after annealing them to approximately 30 K to allow diffusion to occur. Absorption peaks that are due to reaction products generally increase in absorbance after annealing whereas reactant peaks decrease. A pair of spectra similar to (B) and (C) in Fig. 5 are shown in Fig. 6 for an experiment in which a mixture of $^{14}\text{N}^{16}\text{O}_2$ and $^{14}\text{N}^{18}\text{O}_2$ was used. In addition, experiments were completed in which approximately 85% $^{18}\text{O}$-enriched NO$_2$ was used. The results of these experiments may be summarized as follows:

1. It is concluded that the reaction $\text{U} + \text{NO}_2 \rightarrow \text{NO}$ occurs; this conclusion is based on the observation of both the known $\text{U}^{16}\text{O}$ peak (Reference 13) and the $\text{N}^{16}\text{O}$ peak (Reference 1), as well as the corresponding peaks that resulted from the $^{18}\text{O}$-substituted isotopomers when $^{14}\text{N}^{18}\text{O}_2$ was used as a reactant.

2. The reaction $\text{U} + \text{NO}_2 \rightarrow \text{UO}_2 + \text{N}$ is also believed to occur because the peak attributable to the known $\text{U}^{18}\text{O}_2$ stretching mode was seen whenever $^{14}\text{N}^{18}\text{O}_2$ was a reactant. The fate of the N-atom product of this reaction is not known and other reactions—for example, nitride formation—may occur.

3. Uranium nitrides, UN and UN$_2$, as well as some other uranium-nitrogen species, X-UN, are produced by an unknown mechanism, as has been discussed in Section III-B of this report.

4. The peak for the previously-observed (Reference 18) "free" NO$_2^-$ species was observed (see Fig. 5 and 6) in all of the experiments with U atoms and NO$_2$ and is hypothesized to be the result of the capture by NO$_2$ of free electrons produced by the sputtering device.

5. The species UO$_2^+$ was observed in small amounts (Reference 1) in the form of a UO$_2^+$-NO$^-$ ion pair. Presumably, the UO formed in the reaction of U with NO$_2$ reacts with additional NO$_2$ to form the observed ion pair.
Fig. 5. Infrared spectra of U + NO₂ reaction products in Ar matrices at 14 K. (A) 1% ¹⁴N¹⁶O₂ in Ar; (B) 0.1% ¹⁴N¹⁶O₂ in Ar; (C) annealed matrix containing 0.1% ¹⁴N¹⁶O₂.
Fig. 6. Infrared spectra of an Ar matrix at 14 K made by cocondensing U atoms with 50% $^{18}$O-enriched NO$_2$ (0.1% in Ar). Bottom - the original matrix; and top - after annealing the matrix to 30 K and recooling to 14 K.
6. The species labeled $E_1$ in Fig. 5 has lower-frequency counterparts in the presence of $^{18}O$ that suggest the possibility that the absorber is $U$-$O$-$O$ and that the mode responsible for $E_1$ is primarily a $U$-$O$ stretch. However, no definitive assignment was made from this work.

7. The peak labeled "$F_1$" in Fig. 5 had no corresponding peak at lower frequency in the presence of $^{18}O$ and cannot, therefore, be assigned to $U^{16}O^+$. No assignment for "$F_1$" was possible from these studies.

8. Many of the weaker peaks observed in the experiments shown in Figs. 5 and 6 could not be assigned to particular absorbing species in the matrix; however, it is clear that none of the observed peaks are due to $UO^+$. We conclude that either the desired reaction, reaction (7), to produce the $UO^+$ cation does not compete favorably with other reactions shown in Fig. 4 or that $UO^+$ is a very weak absorber. Our experience with NO/NO$_2$, UO/UO$_2$ and other monoxide/dioxide systems suggests that the monoxide generally has a smaller absorption coefficient than the dioxide. Thus, we expect that $UO^+$ may be a weaker absorber, perhaps by a factor of 2 to 10, than the observed species $UO_2^+$. This expectation alone does not seem sufficient to explain the absence of $UO^+$ in the spectra. Its absence in these studies seems best explained by the preferred occurrence of reactions between U and NO$_2$ other than reaction (7), particularly since some of the competing reactions shown in Fig. 4 have been observed directly.

Some additional experiments were completed in which U atoms were co-condensed in Ar matrices with either $^{14}N^{16}O$ or $^{15}N^{16}O$. Although these studies provided useful data for understanding the reactions of matrix-isolated U atoms, no observed peaks could be assigned to $UO^+$ from any of the observed infrared spectra.
An alternative method of producing UO$^+$ was studied. This method involved the use of HI. Matrix-isolated HI had been previously used as a source of hydrogen atoms in matrix studies (Reference 19) with the H being produced by in situ ultraviolet photolysis [reaction (9)]. In our study, interest was focused on the iodine atoms produced by this photolysis, because they represented a potential electron trap. Thus, reaction (8) could occur to give UO$^+$ as a result of a charge exchange between UO and I in the solid Ar matrix. Also, a possible advantage of this approach, relative to the U$^+$ -NO$_2$ approach, is that side reactions such as those of Fig. 4 should be less likely to occur. One a priori disadvantage is that the H atoms in the matrix could participate in reactions to produce species other than UO$^+$. 

A 200-W Hg arc was employed for the photolysis, the sputtering device was used to produce UO, and Matheson HI was used. Experimental difficulties were encountered with the HI/Ar mixtures because of the following facts: (1) HI decomposes readily in metal vacuum lines; (2) HI is an unusually weak infrared absorber (Reference 20); and (3) HI tends to polymerize in matrices (Reference 21). These difficulties prevented completion of a definitive experiment, but in no case was a peak observed which could be assigned to UO$^+$ in a UO$^+$·I$^-$ complex.
IV. CONCLUSIONS.

The reactions of U, UO, and UO$_2$ with NO and NO$_2$ in low temperature Ar matrices result in the production of a number of interesting new species that can be identified and characterized by infrared spectroscopy. Many of these species are potentially important reaction products in high temperature or other reactive gaseous systems. In addition to UO$_2^+$, UN, UN$_2$, NO$_2^-$ and possibly U-O-O, whose infrared spectra were observed, studied, and discussed in this report, other reaction products were also produced, but were not identified. Isotopic substitution was used to characterize UO$_2^+$, UN, UN$_2$ and NO$_2^-$. Additional reactions occur to form previously observed neutral products including UO, UO$_2$, and NO. In none of the experiments could a peak be assigned to UO$_2^+$. 
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6. JANAF Thermochemical Tables, Dow Chemical, Midland, MI, 1960.
