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# Matrix Isolation Infrared Studies of the Reactions of Laser-Ablated Uranium with $N_2$: Reactions beyond Insertion into $N_2$

**K. Sankaran, K. Sundararajan, and K. S. Viswanathan***

*Materials Chemistry Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102 India*

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Uranium was laser-ablated in the presence of $N_2$/Ar mixtures, and the reaction products were studied using matrix isolation infrared spectroscopy. These reactions were studied over a wide range of $N_2$ concentrations in Ar (0.1% to 50%) and also with pure $N_2$. We observed that at low $N_2$ concentrations in Ar (<1%), the reaction product was the insertion product $UN_2$ and its complexes with molecular $N_2$, a result that agreed with an earlier report of Andrews and group. Interestingly, however, as the $N_2$ concentration was increased, we observed the formation of the mononitride, UN. We believe that as the $N_2$ concentration is increased, new reaction channels open up, resulting in the formation of nitrogen atoms and $N_3$ species which then react with laser-ablated uranium atoms to produce UN. The assignment of the infrared feature due to UN in a $N_2$ matrix is also discussed.

## Introduction

In recent times, laser ablation has been employed extensively to study high-temperature species and reactions[1−12] that can be distinctly different from its low-temperature analogue. Andrews and group have studied a number of laser-ablated metal species using matrix isolation infrared spectroscopy.[2−12] In one such work, they reported their results on the laser ablation of uranium in argon, nitrogen and mixed $N_2$/Ar matrixes containing a maximum of 1% $N_2$ in Ar.[10] In their experiments, they observed the insertion product, $UN_2$, and its complexes with $N_2$, as characterized by the infrared absorptions of these species in the region 1050−1000 $cm^{-1}$. Sometime later, the same group studied the reaction of uranium atoms with oxides of nitrogen and reported for the first time in such studies the formation of UN.[11] In a subsequent work, Andrews and group performed detailed isotopic studies and quasirelativistic density functional calculations on these nitrides.[12]

In this work, we have discussed two aspects. First, we have obtained data on the laser ablation of uranium at $N_2$ concentrations in Ar over the range of 0.1−50%. The higher concentrations of $N_2$ were not covered in earlier works, and interesting chemistry appears to occur at these $N_2$ concentrations. At higher $N_2$ concentrations, new reaction channels become operative, leading to the formation of the mononitride, UN. Second, we have discussed the assignment of the infrared feature for UN in pure nitrogen matrixes.

## Experimental Section

The low temperatures required for the matrix isolation work were obtained using a Leybold AG (model RD 210) closed cycle helium compressor cooled cryostat. The minimum temperature obtained with this system was ∼12K. The commercial cryostat was fitted with a home-built laser ablation cell. The details of the laser ablation setup are reported elsewhere.[13]

The laser ablation cell, together with the main body of the cryostat, was pumped using a diffusion pump. The base pressure in the vacuum chamber was $<10^{-6}$ mbar. High-purity Ar and/or $N_2$ (Grade I, Bhoruka Gases Limited, India) were/was used as matrix gases. A Leybold Heraeus variable leak valve was used to control the flow of the matrix gas during deposition. Typical flow rates used for deposition were ∼3 mmol/h.

The second harmonic (532 nm) of a pulsed Nd:YAG laser (Continuum, Model NY61-10), operated in the Q-switched mode, at a repetition rate of 10 Hz was used for ablation. The laser pulse had a temporal width of ∼10 ns. Typically, 20−40 mJ pulses were focused onto the sample, using a 75 mm focal length Suprasil lens. The laser beam was incident on the sample at a near-45° angle. The irradiance of such a focused beam was $\sim10^8$ watts/$cm^2$, resulting in temperatures of >2500 K at the focal point on the sample. The uranium metal was kept at a distance of 60 mm from the cold tip. The position of the laser beam on the sample was varied manually to expose a fresh surface to the laser beam continuously. This arrangement ensured efficient ablation during the entire course of the experiment, as repeated ablation of the same point on the sample lead to a drop in the ablation efficiency.

The laser-ablated species from the sample were trapped in nitrogen or $N_2$/Ar mixed matrixes. In experiments where mixed $N_2$/Ar matrixes were used, the concentration of nitrogen in the mixed matrix was varied from 0.1% to 50%. Typical deposition times were 1 to 2 h. An infrared spectrum of the deposited species was recorded using a BOMEM MB100 FTIR, operating at a resolution of 1 $cm^{-1}$. The matrix was then warmed to 35 K, held at this temperature for 15 min, and then recooled to 12 K. An infrared spectrum of the matrix thus annealed was again recorded. The matrix was then irradiated for 15 min using a broad band Xe UV source (Spectral Energy Inc.) and an infrared spectrum recorded after photolysis. The matrix was again annealed at 35 K, and an infrared spectrum was recorded to follow the reactions in the matrix.

## Results and Discussion

**Uranium in $N_2$/Ar Matrixes.** *As-Deposited Matrix.* Figure 1 shows the infrared spectra of the species produced by laser

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* Corresponding author. E-mail: vish@igcar.ernet.in.

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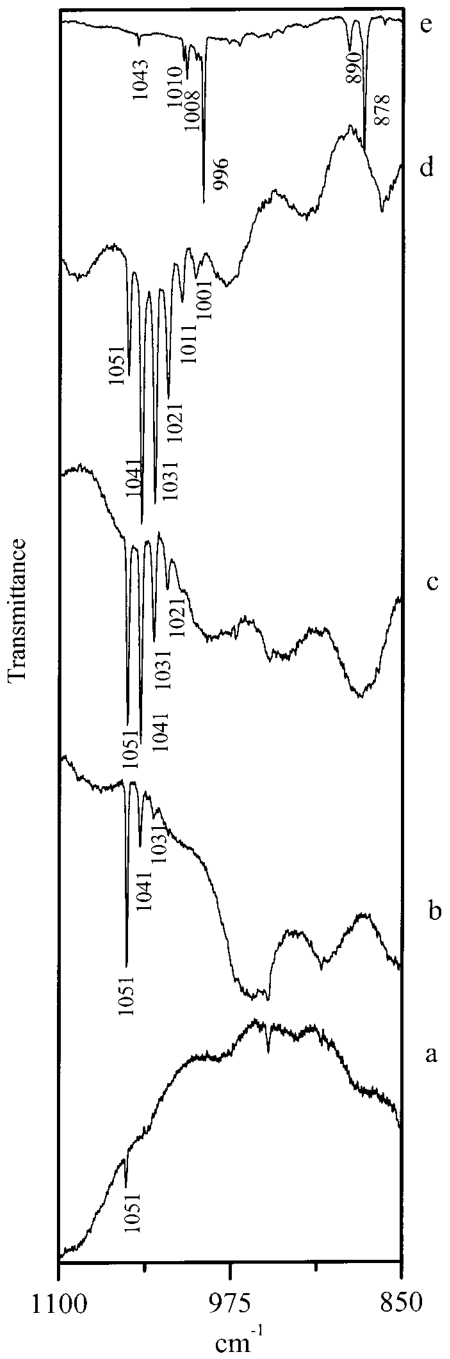

**Figure 1.** Matrix isolation infrared spectra of laser-ablated U in the region 1100−950 cm$^{-1}$ using N$_2$/Ar mixed matrixes and pure nitrogen. Concentrations of nitrogen in the N$_2$/Ar mixed matrixes are (a) 0.1%, (b) 1%, (c) 5%, (d) 10%, and (e) pure nitrogen.

ablation of uranium and trapped in mixed N$_2$/Ar matrixes. In experiments a−d, the concentration of nitrogen in argon was varied from 0.1% to 10%. In experiment e, the matrix was pure nitrogen. All spectra shown in Figure 1 were those recorded before annealing the matrix. Furthermore, only the $^{14}$N$_2$ was used in all the experiments. While experiments with $^{15}$N$_2$ would have been useful, the heavy isotope was not available, and hence, no isotope studies could be performed.

At the lowest concentration of N$_2$ in Ar (0.1%), we observed a single feature at 1051 cm$^{-1}$ (Figure 1a). When the nitrogen concentration was increased to 1%, new features appeared at 1041 and 1031 cm$^{-1}$ (Figure 1b), in addition to the 1051 cm$^{-1}$ feature. Hunt et al. observed similar features when uranium was laser-ablated in the presence of a N$_2$/Ar mixture containing up to 1% N$_2$.[10] They assigned the 1051 cm$^{-1}$ feature to UN$_2$ ($\nu_3$ mode) and the additional features to the N$_2$ complexes of UN$_2$, i.e., the 1041 cm$^{-1}$ feature to UN$_2$$\cdot$N$_2$ and 1031 cm$^{-1}$ to UN$_2$$\cdot$2N$_2$.

Further increase in the concentration of N$_2$ to 5% and 10%, resulted in a progressive increase in the intensities of 1041 and 1031 cm$^{-1}$ peaks and the appearance of additional features at 1021, 1011, and 1001 cm$^{-1}$. Following the assignments of Hunt et al.,[10] these additional features can be assigned to UN$_2$ complexing progressively with increasing amounts of N$_2$. When pure nitrogen was used as the matrix gas, the spectrum shown in Figure 1e was obtained, which was different from those observed when mixed N$_2$/Ar matrixes were used (Figure 1a−d). In the pure N$_2$ experiments, we observed a strong peak at 996 cm$^{-1}$, a weak feature at 1043 cm$^{-1}$, and a doublet near 1008 cm$^{-1}$. The weak absorption at 1043 cm$^{-1}$ was assigned to O$_3$ on the basis of an earlier literature report.[14] The strong feature at 996 cm$^{-1}$ in the N$_2$ matrix was also observed by Hunt et al., and they assigned it to UN$_2$ in a nitrogen cage. While our experimental results generally agree with those of Hunt et al.,[10] it is possible, as we shall see later, that UN$_2$ and its complexes may not be the only species produced in these experiments.

*Matrix Annealed at 35 K.* Figure 2 shows spectra obtained after annealing the matrix at 35 K of the corresponding experiments shown in Figure 1. In the experiment where 0.1% N$_2$ in Ar was used, the 1051 cm$^{-1}$ peak almost disappeared on annealing (Figure 2a). When the N$_2$ concentration was 1% in Ar (Figure 2b), the intensity of 1051 and 1041 cm$^{-1}$ peaks again decreased compared with the intensity of the preannealed spectra (Figure 1b), while the 1031 cm$^{-1}$ feature increased marginally. Of significant interest is the feature that we observed at 997 cm$^{-1}$ on annealing. At the concentrations of N$_2$ employed ($<$1%) in their mixed N$_2$/Ar matrixes, Hunt et al. did not observe this 997 cm$^{-1}$ feature. Furthermore, on annealing, the 997 cm$^{-1}$ peak appears to be produced at the expense of the 1051 cm$^{-1}$ feature and its satellites.

Figure 2c shows the annealed spectrum when 5% N$_2$ in Ar was used as the matrix. Again a decrease in the intensities of the 1051, 1041, 1031, and 1021 cm$^{-1}$ features was observed on annealing. However, each of the above features is more intense than that observed in the 1% N$_2$ experiment. As these features are attributed to UN$_2$$\cdot$$x$N$_2$ complexes ($x = 1-3$), it is not surprising that these features gain in intensity as the nitrogen concentration is increased. Once again, of particular interest was the appearance, on annealing, of the 997 cm$^{-1}$ peak and with a substantial intensity. It must also be noted that the intensity of the 997 cm$^{-1}$ feature was larger than the four features in the 1051−1021 cm$^{-1}$ region (Figure 2c). A peak at 984 cm$^{-1}$, assigned to NUO,[11] appears on annealing, probably produced due to an oxygen impurity.

A similar trend was seen when 10% N$_2$ was used in the N$_2$/Ar mixed matrix (Figure 2d). When pure nitrogen was used as the matrix (Figure 2e), the 996 cm$^{-1}$ peak was the dominant feature, with weak features at 1008 and 1010 cm$^{-1}$.

The above discussion on the intensity changes of the different peaks following annealing is shown graphically in Figure 3 for a typical case where the N$_2$ concentration in Ar was 10%. In this figure, the intensities (computed as areas) of the peaks at 1051, 1041, 1031, 1021, 1011, and 997 cm$^{-1}$ in the as-deposited and annealed spectra are plotted. It can be seen that while the intensity of the peaks between 1051 and 1011 cm$^{-1}$ behaved similarly, i.e., generally decreased on annealing, the 996 cm$^{-1}$ peak alone behaved differently, showing a substantial increase

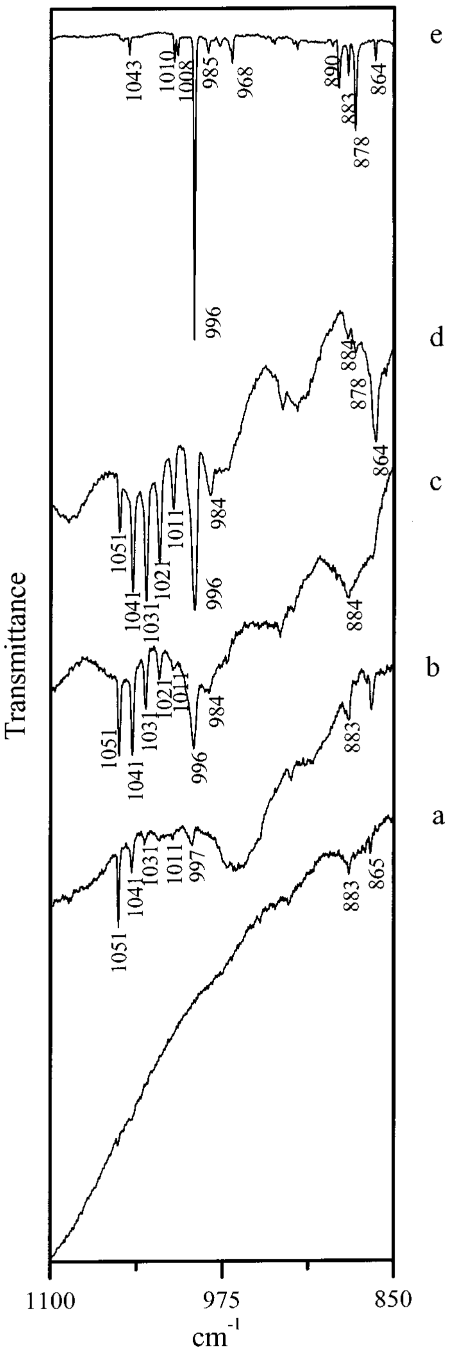

**Figure 2.** Spectra recorded after annealing the matrix at 35 K of the corresponding experiments shown in Figure 1.

on annealing. This observation suggests that the 996 $cm^{-1}$ peak in this experiment may be due to a species different from those responsible for the five peaks in the 1051−1011 $cm^{-1}$ region. A similar behavior in the intensity pattern was observed for other $N_2$/Ar mixtures, though to avoid a repetitive display of data, they are not shown here.

*Photolysis Experiments.* We next considered the effect of photolysis on the spectral features discussed above. Figure 4 shows the infrared spectra recorded under different experimental conditions when uranium was laser-ablated with 5% $N_2$ in Ar.

Panels a and b of Figure 4 correspond to spectra of the as-deposited and 35 K annealed matrixes and are merely reproductions of Figures 1c and 2c, respectively, shown here for completion. It may be recalled that when the matrix was annealed at 35 K, the intensities of the features due to $UN_2$ and its complexes with $N_2$ decreased compared with the intensities in the preannealed spectrum, while that of the 996 $cm^{-1}$ feature increased. After photolysis (Figure 4c), the intensities of all the peaks in this region increased compared with the intensities in Figure 4b. Annealing the matrix after photolysis increased the intensity of the 996 $cm^{-1}$ feature and decreased the intensities of all the other peaks (Figure 4d).

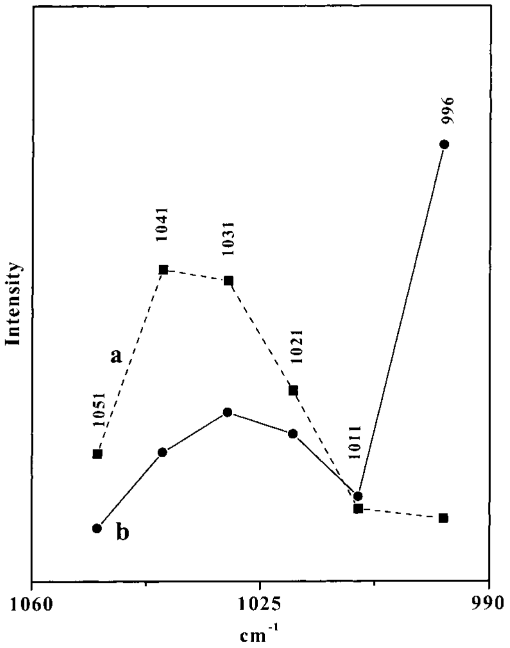

**Figure 3.** Intensities of the different peaks (shown in Figure 1 and 2) in (a) as deposited and (b) 35 K annealed spectra. Concentration of $N_2$ in the $N_2$/Ar matrix was 10%.

Figure 5 displays the intensities (computed as areas) of each of the peaks shown in Figure 4. It can be seen that the intensities of the pentat of peaks in the 1050−1010 $cm^{-1}$ region decreased on annealing, increased on photolysis, and once again decreased on annealing after photolysis. The intensity of the 997 $cm^{-1}$ feature, however, increased progressively during each of these experiments. The above data is also summarized in Table 1, where the intensity changes of each peak in successive experiments are calculated. It can be noticed that the changes in the intensity for the 996 $cm^{-1}$ peak are substantially different in magnitude and sign from the other features, again indicating that this feature may be due to a species different from those responsible for the features between 1051 and 1011 $cm^{-1}$ region.

From the above experimental results the following conclusions are made:

(i) When the concentration of $N_2$ in Ar was <1%, the species formed in the matrix was $UN_2$ and its complexes with $N_2$. This result agrees with that obtained by Hunt et al.[10]

(ii) When the concentration of $N_2$ in Ar exceeded 1%, a feature at 996 $cm^{-1}$ was observed on annealing. This feature behaved differently from the other features in the region 1051−1011 $cm^{-1}$, indicating that the 996 $cm^{-1}$ feature must be due to a different species.

(iii) The intensity of the 996 $cm^{-1}$ feature increases as the $N_2$ concentration in Ar was increased.

The 996 $cm^{-1}$ peak was observed in annealed matrixes containing $N_2$ in concentrations as low as 1% in Ar, which therefore can be considered to be a predominantly argon matrix. A 996 $cm^{-1}$ peak in an argon matrix was attributed by Green and Reedy to UN, which they produced by sputtering uranium metal in the presence of $NO_2$ and trapped in an argon matrix.[15] This assignment of Green and Reedy is also in close agreement with quasirelativistic DFT computations on UN by Andrews

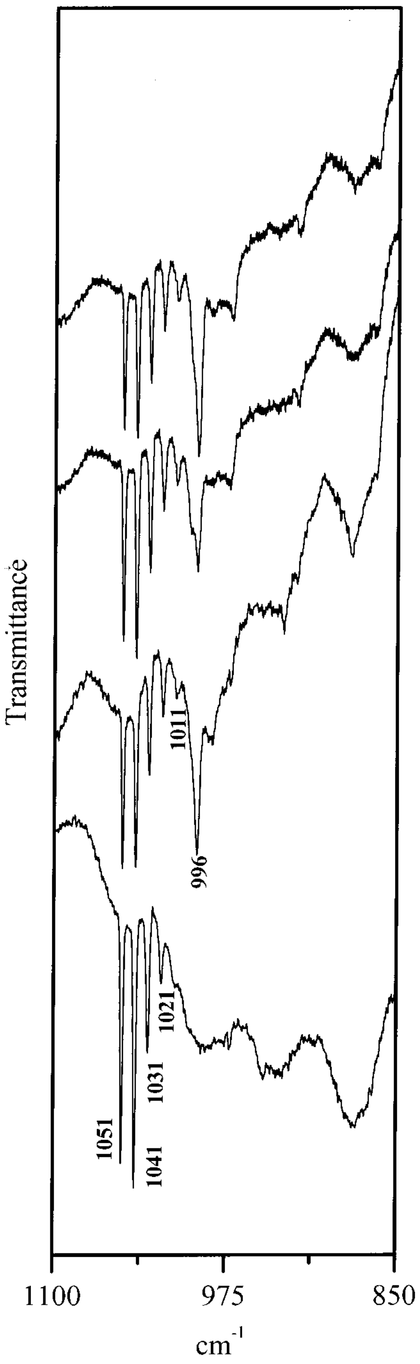

**Figure 4.** Matrix isolation infrared spectra of laser-ablated U in the region 1100−950 $cm^{-1}$ using $N_2$/Ar mixed matrix. Concentration of $N_2$ in the $N_2$/Ar mixed matrix was 5%: (a) as deposited, (b) 35 K annealed, (c) photolyzed, and (d) 35 K annealed after photolysis.

and group.[12] It therefore seems likely that the 996 $cm^{-1}$ feature in the predominantly argon matrix (Figure 2b) is due to UN. (A 996 $cm^{-1}$ feature was also observed in a pure nitrogen matrix; the discussion on its assignment is reserved for a later section.)

The above analysis therefore implies that at low $N_2$ concentrations in Ar, the predominant species is $UN_2$, while as the concentration of $N_2$ in Ar is increased, UN may also be formed. The above hypothesis of different species being formed with changes in nitrogen concentration in a laser ablation process needs an explanation and is considered next.

*Mechanism for the Formation of the Nitrides of Uranium.* It is known that laser ablation of metal surfaces with a power density of $10^8$ watts/$cm^2$ produces metal atoms and ions with high average kinetic energies.[1,7,16,17] When uranium metal is laser-ablated, uranium atoms/ions with high kinetic energies are produced and deposited along with $N_2$. Just prior to deposition, it is possible that collisions of energetic uranium atoms/ions with $N_2$ can produce the insertion product NUN, as was proposed by Hunt et al.[10]

$$\text{U (high KE)} + N_2 \rightarrow \text{NUN} \qquad (1)$$

As the concentration of $N_2$ in the $N_2$/Ar mixed matrix is increased, the concentration of $UN_2$ and its complexes with $N_2$ also increases, which explains the increased intensity of the features due to these species (Figure 1c,d).

Additionally, collisions of energetic uranium atoms/ions with $N_2$ may also produce excited nitrogen (reaction 2)

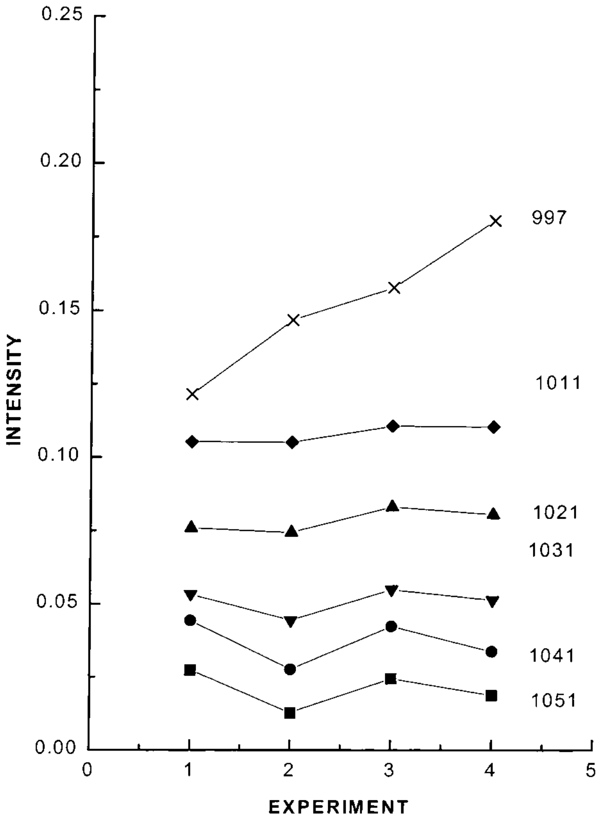

**Figure 5.** Intensities of the different peaks for various experimental conditions: (1) as deposited, (2) annealed at 35 K, (3) photolyzed, and (4) 35 K annealed after photolysis. Concentration of $N_2$ in the $N_2$/Ar mixed matrix was 5%.

**TABLE 1: Changes in the Intensities of the Different Spectral Features during Successive Stages of the Experiment[a]**

| | percentage change[b] in intensity of spectral features | | | | | |
|---|---|---|---|---|---|---|
| | 1051 | 1041 | 1031 | 1021 | 1011 | 996 |
| 35 K (1)[c]−ADM[d] | −53.5 | −50.6 | −46.1 | −19.7 | −5.3 | +324.1 |
| Ph[e]−35 K (1) | +92.0 | +90.3 | +101.1 | +140.8 | +199.0 | +33.1 |
| 35 K (2)[f]−Ph | −23.5 | −27.8 | −17.3 | −17.2 | −2.7 | +51.4 |

[a] $N_2$ concentration in Ar: 5%. Data correspond to spectra in Figure 4. [b] Percentage change in intensity for A−B is calculated as ((A − B)/A)*100. A negative sign indicates a decrease in intensity, while a postive sign an increase. [c] 35 K (1): 35 K annealed after initial deposition. [d] ADM: as-deposited matrix. [e] Ph: after photolysis. [f] 35 K (2): 35 K annealed after photolysis.

$$\mathrm{U\ (high\ KE)} + N_2 \rightarrow N_2{}^* + U \qquad (2)$$

As the $N_2$ concentration is further increased, new reaction pathways now become possible, such as the bimolecular collisions between excited nitrogen molecules which were produced by reaction 2. Provided the energies of the excited $N_2$ are sufficient (see below), they may under go reactions to produce $N_3$ and N radicals, as given below:

$$N_2{}^* + N_2{}^* \rightarrow N^\bullet + N_3{}^\bullet \qquad (3)$$

The N atoms or the $N_3$ radicals thus produced can then react with U atoms to form UN as follows:

$$U + N^\bullet \rightarrow UN \qquad (4)$$

$$U + N_3{}^\bullet \rightarrow UN + N_2 \qquad (5)$$

The products of reaction 3 ($N_3$ + N) have been computed to lie above $N_2 + N_2$ by ~8.6 eV (204.3 kcal/mol).[18] Even though the production of $N_3$ + N is highly endothermic, collision of two exited $N_2$ molecules containing sufficient excitation energy could probably drive reaction 3. Such a scenario is not impossible, as laser ablation of metals produces atoms and ions with average kinetic energies on the order of 8−10 eV.[1,16] When such energetic atoms/ions collide with the $N_2$ molecule, inelastic energy transfer can occur, resulting in possible electronic excitation of $N_2$. Alternatively, excitation of $N_2$ can also proceed in the laser plasma. It may be added that production of N atoms in laser ablation experiments is not unknown; for example, $N_3$ was observed when Fe was laser-ablated in the presence of $N_2$.[7] Production of nitrogen atom in $N_2$/Ar mixtures, containing 50% or above of $N_2$, upon bombardment with 5.4 MeV α-particles was also recently reported.[19]

In the above scheme, the production of the N atoms or $N_3$ species, so imperative to the formation of UN, requires bimolecular collision of $N_2$ molecules, and hence, this process would be favored as the concentration of $N_2$ is increased in the $N_2$/Ar mixture. The above scheme therefore is consistent with the production of UN at relatively high concentrations of $N_2$ in the mixed matrixes (>1% $N_2$).

If the above mechanism for the production of UN (reactions 3−5) is to be substantiated, then reaction 3 demands that the $N_3$ species also be observed in experiments where UN was produced. The infrared features of $N_3{}^\bullet$ and $N_3{}^-$ are well documented in the literature[7,20,21] and are reported to occur at 1657 and 2003 $cm^{-1}$, respectively, in a nitrogen matrix. Figure 6 shows the infrared spectrum over the above regions when uranium was laser-ablated in the presence of pure nitrogen. The occurrence of spectral features at 1657 and 2003 $cm^{-1}$ are clear signatures of the presence of $N_3{}^\bullet$ and $N_3{}^-$ in our nitrogen matrix experiments and provide a strong support for the proposed reaction scheme.

It may be recalled that the intensity of the features due to $UN_2$ and its complexes decreased on annealing while that due to UN increased; at the same time the features due to $N_3$ also decreased in intensity (Figure 6). This observation suggests that $UN_2$ may be unstable with respect to UN, in the presence of nitrogen atoms or $N_3$, as suggested by the following scheme:

$$UN_2 + N^\bullet \rightarrow UN + N_2 \qquad (6)$$

$$UN_2 + N_3{}^\bullet \rightarrow UN + 2\,N_2 \qquad (7)$$

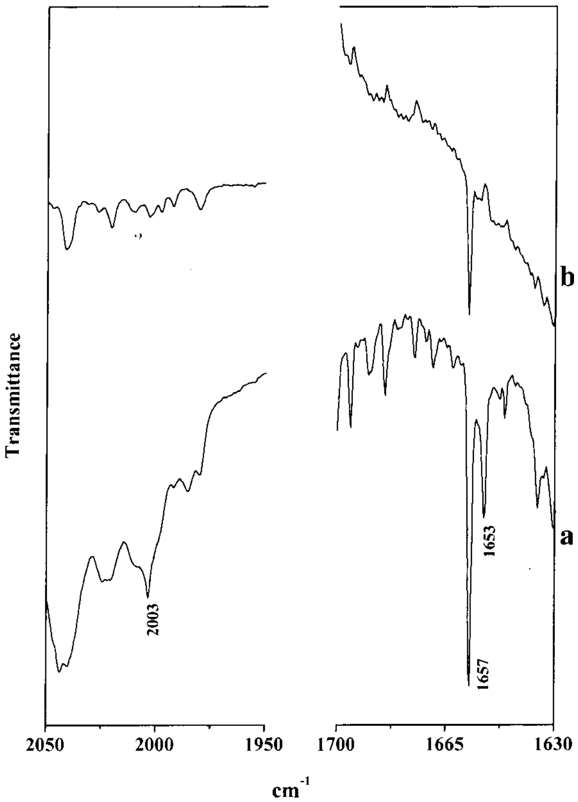

**Figure 6.** Matrix isolation infrared spectra in the region 2050−1630 $cm^{-1}$ when U was laser-ablated in pure nitrogen (a) as deposited and (b) 35 K annealed.

These reactions probably have no significant barrier, as they seem to proceed with relative ease in the low-temperature matrix.

It is therefore clear that the laser ablation of uranium in the presence of $N_2$/Ar mixtures containing low concentrations of $N_2$ produces $UN_2$. As the concentration of $N_2$ in the mixture is increased, the production of UN is favored (on annealing). The above conclusions are valid for all our experiments where the $N_2$ concentration in Ar was varied up to 10%.

*Ablation of Uranium in the Presence of Pure $N_2$.* When uranium was ablated in the presence of pure $N_2$, a strong feature was observed at 996 $cm^{-1}$, in agreement with the observation of Andrews and group.[10,12] On the basis of isotopic shift data, they assigned the 996 $cm^{-1}$ feature in $N_2$ to $UN_2$•s$N_2$, i.e., $UN_2$ complexed to saturation with $N_2$.[12] The corresponding feature in $^{15}N_2$ experiments occurred at 965.6 $cm^{-1}$, yielding an isotopic ratio of 1.031 17, which was found to be consistent with a $\nu_3$ vibration for linear NUN molecule.[12] The feature for UN in a nitrogen matrix was reported to occur at 890.5 and 878.2 $cm^{-1}$ in $^{14}N_2$ experiments and at 862.5 and 850.4 $cm^{-1}$ in $^{15}N_2$. (The doublets in each experiment was explained to be due to site effects.) The isotope ratio was 1.032 46 and 1.032 69, consistent with the shifts expected for a UN diatomic ($\rho$ = 1.03305) and the shifts observed in argon experiments of 1.03270. All the spectral features reported by Andrews et al. in their $^{14}N_2$ experiments was also observed by us, as shown in Figures 1, 2, and 4.

While the above assignments for UN and $UN_2$ certainly appear sound, there are certain questions that need to be addressed.

First, the above assignment implies that UN absorption in an argon matrix occurs at 996 $cm^{-1}$ and shifts to ~890 $cm^{-1}$ in a pure nitrogen matrix. This shift is not unreasonable, as it can be argued that, as in $UN_2$, the UN diatomic complexes with molecular $N_2$, causing this shift. If this were true, one would expect to observe progressively complexes of UN with molecular $N_2$, such as $UN{\cdot}N_2$, $UN{\cdot}2N_2$, ... $UN{\cdot}xN_2$, as the nitrogen concentration in the $Ar/N_2$ mixture was increased, which in turn would have yielded satellites, as was observed with complexes of $N_2$ with $UN_2$. In short, the 996 $cm^{-1}$ feature of UN in argon should have eventually merged to the 890 $cm^{-1}$ feature in pure nitrogen through a series of satellites. However, no such satellites were reported by Andrews, nor do we observe any satellite formation and eventual merger to the 890 $cm^{-1}$ feature in our experiments where we varied the $N_2$ in Ar concentration from <1% to 50%. It may be recalled (Figure 2b−d) that $UN_2$ which absorbs at 1051 $cm^{-1}$ in Ar produced a series of satellites as $N_2$ was added and eventually merges to the 996 $cm^{-1}$ feature in pure $N_2$. Under the same conditions, UN which absorbs at 996 $cm^{-1}$ in Ar does not produce similar satellites. It is therefore intriguing that features due to lower complexes of UN with $N_2$ are not progressively observed. While it is certainly possible that UN would complex with molecular $N_2$, the absence of evidence in our infrared spectra for the lower complexes of UN with $N_2$ raises the question if the UN vibration in the diatomic nitride is sensitive to complexation with $N_2$ at all.

Another experiment that raises a puzzle was the one that we conducted with 50% $N_2$ in Ar. The spectrum recorded when uranium was laser-ablated in the presence of such a gas mixture is shown in Figure 7. It can be seen that the only feature in the spectrum of the as-deposited matrix is that at 996 $cm^{-1}$ (Figure 7a). The 1051 $cm^{-1}$ feature was not observed, which suggests that *no free $UN_2$* was produced in this experiment. Likewise, no features were observed in the 1041−1011 $cm^{-1}$ region, which implies that neither were $UN_2{\cdot}xN_2$ ($x = 1-4$) species produced. On the basis of the Andrews assignment, the 997 $cm^{-1}$ feature can be attributed to $UN_2{\cdot}sN_2$. Given the large concentration of $N_2$ in this experiment, it is not unlikely that almost all the $UN_2$ formed was complexed to saturation and that no lower complexes were observed. However, on annealing, this feature grows in intensity (Figure 7b) by about 40% (computed as area of the peak). This intensity growth is certainly puzzling, as no new $UN_2{\cdot}sN_2$ can be expected to be formed because no lower complexes of $UN_2$ with $N_2$ were observed in the preannealed spectrum that could have served as precursors for the saturated complex. The intensity growth must be therefore due to a species other than $UN_2{\cdot}sN_2$ and which absorbs at the same frequency. (In the same experiments, the features at 878 and 890 $cm^{-1}$ were also observed, though on annealing, the 890 $cm^{-1}$ feature disappeared. Interestingly however, the 890 $cm^{-1}$ feature reappears in pure $N_2$ matrixes.)

If we combine the two above observations, there occurs the possibility that the intensity growth of the 996 $cm^{-1}$ feature on annealing in the 50% $N_2$ experiments may be due to UN. This suggestion is consistent with our earlier suggestion that the UN feature may be insensitive to complexation with $N_2$; i.e., it has the same absorption frequency in both Ar and $N_2$ matrixes. The growth in intensity of the 996 $cm^{-1}$ feature in the 50% $N_2$ experiments on annealing may simply result from $UN_2$ reacting with N or $N_3$ to form more UN. In this nitrogen-rich matrix, the nitrogen atom or $N_3$ species concentration would be high to cause such a reaction. The 996 $cm^{-1}$ feature may therefore have to be doubly assigned to $UN_2$ and UN in a $N_2$ cage.

This dual assignment must, however, be compatible with the isotopic shift data observed by Kushto et al.,[12] which is examined next. If we assume for a moment that the 996 $cm^{-1}$ feature in $N_2$ is due to $U^{14}N$, the $U^{15}N$ would be expected to occur at 964.1 $cm^{-1}$ (computed $\rho = 1.033\,05$) or 964.4 $cm^{-1}$ ($\rho = 1.032\,70$, observed in Ar matrix). The feature at 965.6 $cm^{-1}$ observed by Andrews et al. in their $^{15}N_2$ experiments and assigned to $U^{15}N_2$ can be equally well assigned to $U^{15}N$. The isotope shifts therefore appear to fit well to both assignments; i.e., the 996 $cm^{-1}$ feature can be doubly assigned to both $UN_2$ and UN in a nitrogen cage.

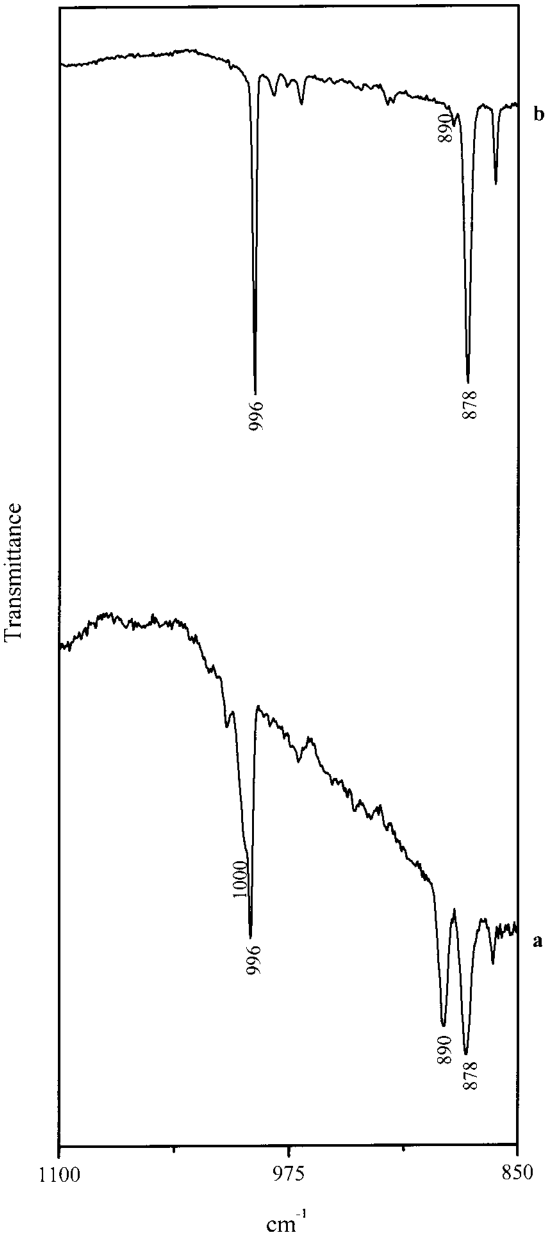

**Figure 7.** Matrix isolation infrared spectra of laser-ablated U in the region 1100−950 $cm^{-1}$ using $N_2/Ar$ mixed matrix. Concentration of $N_2$ in the $N_2/Ar$ mixed matrix was 50%: (a) as deposited and (b) 35 K annealed.

With the data on hand, both the assignment of Andrews et al. and the possibility that we have raised of dual assignment of the 996 $cm^{-1}$ feature appear tenable. We believe that we cannot conclusively decide which of the two assignments are correct. The question may be unambiguously resolved by mass selectively depositing UN and $UN_2$ in a nitrogen matrix and observing the infrared features (as was suggested by one of the referees), a facility which we do not have at present.

The reaction products appear to be similar whether metal or metal oxide was ablated in the presence of $N_2/Ar$ mixtures. Figure 8 shows the infrared spectrum in the region 1060−700 $cm^{-1}$ when $UO_2$ was laser-ablated in the presence of 1% $N_2$ in

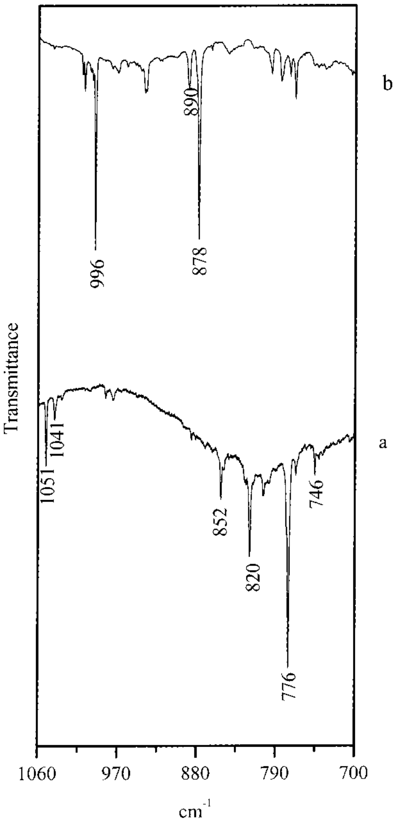

**Figure 8.** Matrix-isolated infrared spectra of laser-ablated $UO_2$ in the region 1060−700 cm$^{-1}$ in (a) 1% $N_2$ in Ar and (b) pure $N_2$. Spectra recorded are those before annealing.

Ar and pure $N_2$. The infrared features in the 1100−900 cm$^{-1}$ region obtained in these experiment were almost identical with that obtained with U metal. This observation is not surprising since U atoms are produced when $UO_2$ is laser-ablated; the products formed with $N_2$ are therefore similar whether U metal or $UO_2$ pellet was used for ablation. Of course, the oxide species of uranium are also observed when uranium oxide is ablated, which are discussed elsewhere.[13]

## Conclusions

The reaction products of uranium and nitrogen was followed for wide range of $N_2$ concentrations when uranium was laser-ablated in the presence of $N_2$/Ar mixtures. When the nitrogen concentration was low (<1%), the reaction product was uranium dinitride (NUN), and its complexes with $N_2$ were in agreement with an earlier report of Hunt et al. However, as the $N_2$ concentration was increased, new reaction channels become available, which result in the formation of uranium mononitride (UN). This observation has been explained based on a reaction scheme involving collisions of nitrogen with uranium atoms or ions with high kinetic energies, leading to the formation of nitrogen atoms and $N_3$ species. The possible alternate assignments for the infrared features of UN in a nitrogen matrix has also been discussed.

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