A matrix isolation FTIR investigation of laser-ablated uranium oxide in argon and nitrogen matrices

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Abstract. Uranium oxide was laser-ablated using the second harmonic of a Nd : YAG laser, and the products studied after trapping them in Ar and N_2 matrices. The species obtained in the Ar matrix were UO, UO_2 and UO_3, which represent the primary products of laser ablation. Charge transfer complexes, (UO_2^+) (O_2^-) and (UO_2^{2+}) (O_2^{2-}) were also observed. In the N_2 matrix, in addition to the primary ablation products, reaction products with nitrogen were also observed; the prominent among them being UN_2 and NUO, together with their complexes with N_2. Charge transfer complexes were also seen in these experiments. Features due to NO, N_3 and N_3^- were identified, which clearly point to the role of nitrogen in these reactions.

Keywords. Uranium oxide; matrix isolation; laser ablation; high temperature.

1. Introduction

Studies on high temperature chemistry have important applications in space and nuclear technology. In recent times, high temperature studies have received a further impetus due to the effective use of lasers to generate high temperatures. In combination with a variety of spectroscopy techniques, laser-ablation has been used to study high temperature behaviour of materials and their associated chemistry. One such technique is laser ablation matrix isolation spectroscopy, which in recent times has gained popularity for such studies (Vala *et al* 1990; Andrews *et al* 1992; Hunt and Andrews 1993; Hunt *et al* 1993; Andrews *et al* 1994; Kushto *et al* 1997).

In the matrix isolation technique, the species of interest is trapped along with a large excess of an inert gas, at low temperatures ($\approx$ 12 K). The concentration of the species of interest (S) in the matrix (M) is typically about 1 : 1000 ($S : M$), which ensures that the species, S, is surrounded only by the inert matrix atoms. Reactive molecules, such as those produced in a laser ablation process, when isolated in inert gas matrices, have extended lifetimes, simply for want of a reaction partner. The spectroscopy of these reactive species can then be studied leisurely.

Conventional high temperature studies have employed the Knudsen effusion methods (Gabelnick *et al* 1973a, b; Green and Reedy 1976; Green *et al* 1976). In this method, the material is heated in a Knudsen cell (K-cell) and species effusing out of the orifice are then studied using techniques, such as mass spectroscopy, torsion methods and infrared spectroscopy. While the Knudsen effusion method has met with unqualified success, one of its major

constraints has been its upper temperature limit. Experiments at temperatures above 2500 K pose serious problems with regard to production of high temperatures and associated sample-container reactions at these temperatures. For studies above 2500 K it is well nigh impossible to select an inert and stable container. Laser ablation offers an elegant solution to these problems. High intense laser beams when focused down to spot sizes of a few tens of microns generate temperatures in excess of 2500 K (Joseph *et al* 1997). Generation of high temperatures (> 2500 K) using laser pulses is therefore experimentally trivial. Furthermore, the sample itself acts as its container and hence the container problem is also alleviated.

A number of studies have been reported where laser ablation has been combined with matrix isolation infrared spectroscopy to study the reactions of metal vapours produced at high temperatures (Vala *et al* 1990; Andrews *et al* 1992; Hunt and Andrews 1993; Hunt *et al* 1993; Kushto *et al* 1997). In particular, a number of studies by Andrews and coworkers have been made on the reactions of laser-ablated uranium with O_2, N_2, NO, NO_2 and N_2O (Hunt and Andrews 1993; Hunt *et al* 1993; Kushto *et al* 1997). Various reaction products were observed with each of the reactant gases. With O_2, the major species were UO, UO_2 and UO_3, together with complexes of UO_3 with O_2; with N_2, the major product was UN_2 formed by an insertion of U into N_2; while with NO, NO_2 and N_2O, products such as NUO, $[NUO]^+$ $[NO]^-$, and NUO_2 were observed. In each case, the major reaction was the insertion of uranium atom in the respective reactant molecule, such as O_2, N_2, etc. While K-cell matrix isolation studies have been performed on UO_2 in argon matrices, no laser ablation

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study of this material has been reported. We have therefore undertaken the present work to study the species formed over uranium oxide following laser ablation. Our study was motivated by two questions: First, how do the species produced by the laser ablation of UO_2 compare with those obtained using K-cell evaporation? Secondly, what are the reaction products of the laser-ablated species of UO_2 with N_2? Would these reactions yield the mixed nitrogen–oxygen species of uranium, such as those observed by Andrews and coworkers in their laser ablation experiments with NO_x?

2. Experimental

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 ≈ 12 K. The commercial cryostat was fitted with a home-built laser ablation cell. The laser ablation cell made of aluminum had the following provisions: a 40 mm flange fitted with a home-made veeco type coupling for holding the solid samples, a 40 mm port carrying a quartz window through which the laser beam was focused on the samples and two ports coaxial with substrate on the cold tip, each port being fitted with a KBr window for coupling the infrared beam of the FTIR into the cryostat. The laser ablation cell was connected to the main body of the cryostat through an 'O' ring seal. The schematic of the laser ablation matrix isolation setup is shown in figure 1.

The laser ablation cell together with the main body of the cryostat was pumped using a 300 L·s^{-1} diffusion pump (Edwards Diffstak MK2), backed by a 200 L·min^{-1} rotary pump (Hind Hivac ED12). The base pressure in the vacuum chamber, measured using a Hind Hivac STP 4 M penning gauge, was $< 10^{-6}$ mbar.
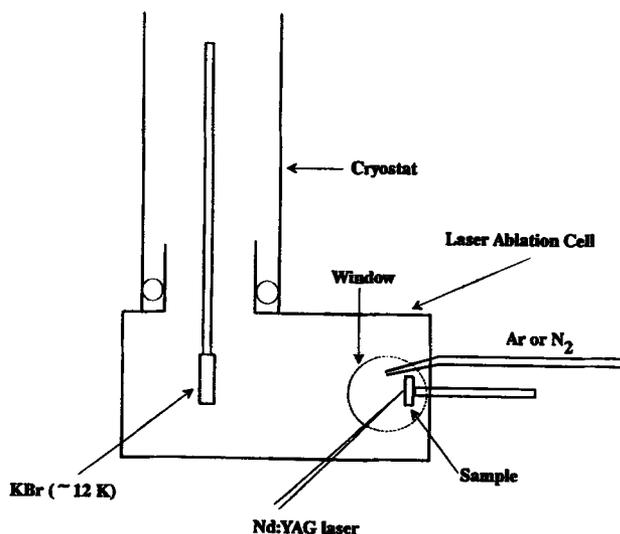

Figure 1. Schematic of the laser ablation cell.

High purity Ar and N_2 (Grade I, Bhoruka Gases Limited, India) were 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 to 40 mJ pulses were focused onto the sample, using a 75 mm focal length suprasil lens. The irradiance of such a focused beam was $\approx 10^8$ watts/cm^2, resulting in temperatures > 2500 K at the focal point on the sample. The uranium oxide sample used in these experiments was a single-phase, well-sintered pellet (Nuclear Fuel Complex, Hyderabad). The sample pellet 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 was mixed with a large excess of an inert gas and deposited on the cold KBr substrate placed at the cryotip (≈ 12 K); a typical deposition lasting for ~ 30 min to an hour. An infrared spectrum of the deposited species was recorded using a BOMEM MB100 FTIR, at a resolution of 1 cm^{-1}. The matrix was then warmed to 35 K, held at this temperature for 15 minutes, recooled to 12 K and an infrared spectrum again recorded. Infrared spectra of such annealed matrices served to identify spectral features due to multiple trapping sites and also to drive reactions in the matrix.

We made no attempt to measure the temperature at the focal spot of the laser in our laser ablation matrix isolation experiments. A companion group in our laboratory using laser ablation mass spectroscopy had estimated the temperatures produced in these experiments, by measuring the time-of-arrival of the ablated species, from the point of ablation to the ionization source in the mass spectrometer. At the typical irradiances we had employed, they estimated the temperatures to be in excess of 2500 K (Joseph *et al* 1997).
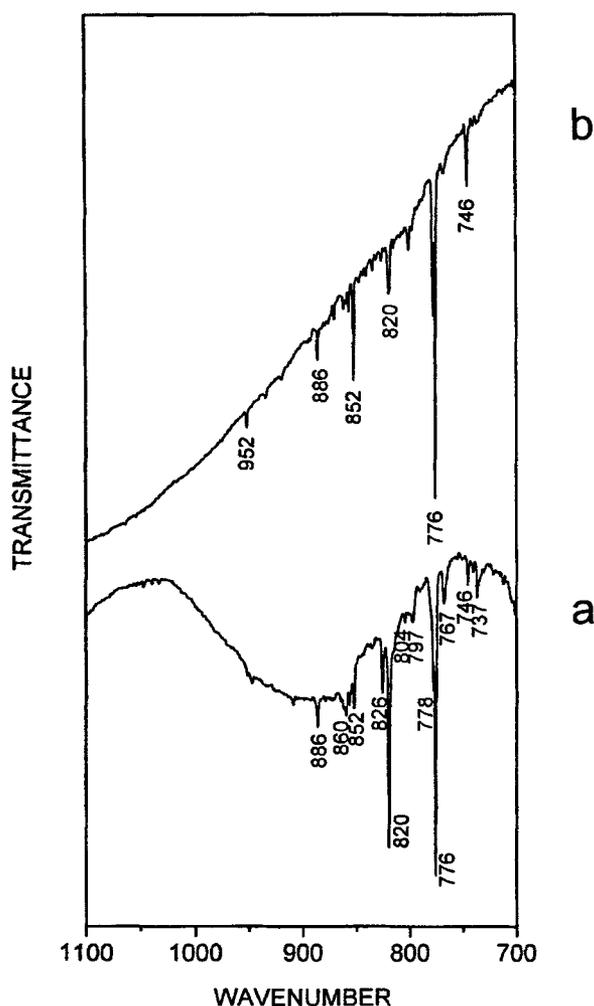
3. Results and discussions

3.1 *Experiments using an argon matrix*

Figure 2a shows the infrared spectra of the laser-ablated species of uranium oxide, trapped in an argon matrix. The major peaks in this spectrum appeared at 776 and 820 cm^{-1}. In addition, we also observed a number of peaks with moderate to weak intensities at 737, 746, 767,

778, 797, 826, 852, 860, 886 and 952 cm^{-1}. The intense spectral features are due to UO and UO_2; the 820 cm^{-1} peak being due to UO and the 776 cm^{-1} peak being due to the v_3 vibration of UO_2. The relatively weaker features at 746 and 852 cm^{-1} are due to the v_2 and v_4 vibrations of UO_3. These assignments are based on the earlier K-cell matrix isolation work, where the vapour phase species over uranium oxide at a maximum temperature of 1900 K, were trapped in an argon matrix (Gabelnick *et al* 1973b). The laser ablation process in which the temperatures at the sample were in excess of 2500 K has therefore yielded principally the same vapour phase species as the K-cell work. However, in the laser ablation of UO_2, features due to UO and UO_2 were dominant, while in the K-cell experiments, the major spectral features were due to UO_2 and UO_3. In experiments where uranium was laser-ablated in the presence of oxygen, the major reaction products were UO_2 and UO_3 (Hunt and Andrews 1993).

Figure 2b shows the infrared spectrum recorded after the matrix was annealed at 35 K. The most intense feature

Figure 2. Matrix isolation infrared spectra of the laser-ablated species of uranium oxide trapped in an argon matrix; (a) before annealing; (b) matrix annealed at 40 K.

in figure 2a at 776 cm^{-1} corresponding to UO_2 gained marginally, while the 852 cm^{-1} and 746 cm^{-1} peaks of UO_3 gained somewhat more substantially in intensity. However, the intensity of the 820 cm^{-1} UO peak reduced drastically. This change in the intensity pattern on annealing was at variance with the observation made by Hunt and Andrews (1993). In their experiment, annealing the matrix at 30 K caused a marginal reduction in intensity of all the oxide peaks of uranium; namely UO, UO_2 and UO_3. The reduction in the intensity of the UO peak in our experiment is probably due to the reaction of at least part of the UO with atomic oxygen to form higher oxides; a reaction that probably needs little activation energy, as it appears to occur in the cryogenic matrix. As atomic and molecular oxygen are produced in the laser ablation of uranium oxide (Joseph *et al* 1997), atomic oxygen is expected to be available in the matrix.

The spectral features at 737, 767, 797, 826 and 860 cm^{-1} almost disappeared on annealing, indicating that these features may be due to uranium oxide species trapped in unstable sites. The 778 cm^{-1} feature persisted even on annealing and was probably due to UO_2 trapped in a secondary site, in addition to the one corresponding to the 776 cm^{-1} feature. A similar satellite was also reported by Hunt and Andrews (1993).

The 886 and 952 cm^{-1} features had been assigned earlier by Andrews and Hunt to charge transfer complexes of (UO_2^+) (O_2^-) and (UO_2^{2+}) (O_2^{2-}) respectively, in their laser ablation experiments of uranium metal with molecular oxygen (Hunt and Andrews 1993). Such species are likely to be formed in our experiments, because as mentioned earlier, laser ablation of uranium oxide does produce molecular oxygen. The reaction of molecular oxygen with UO_2 is likely to lead to the formation of charge transfer complexes. In the experiments of Andrews, multiplets were observed, associated with these complexes, and the multiplets were suspected to arise from the different orientations of the ion pair. However, in our experiments only the 886 and 952 cm^{-1} features were observed.

3.2 Experiments using a nitrogen matrix

Figure 3a shows the infrared spectrum of the laser-ablated species of uranium oxide trapped in a N_2 matrix. The major features were at 878 and 996 cm^{-1}. Features were also observed at 768, 774, 785, 795, 846, 890, 938, 939 and 1008 cm^{-1}. This spectrum is substantially different from that observed when an Ar matrix was used, indicating that N_2 either induces severe matrix perturbations or reacts chemically with the laser-ablated species.

Our experiments using Ar as the matrix indicated that UO, UO_2 and UO_3 were the major species produced in the laser ablation of uranium oxide. The same species must be produced in the experiments when N_2 was used as the matrix. The features at 795, 785, 774 and 768 can be

attributed to UO and UO$_2$ in the N$_2$ matrix, as these features appear close to the Ar values of 820 and 776 cm^{-1} for these species. The exact assignments of these features will be discussed later.

Figure 3b shows the infrared spectrum recorded after the matrix was annealed at 35 K. The intense 996 cm^{-1} absorption gained further, but the other major feature at 878 cm^{-1} reduced marginally in intensity. The 890 cm^{-1} product absorption also gained in intensity. A feature at 960 cm^{-1} (which was not discernible in the pre-annealed spectra) picked up in intensity after annealing. For all other peaks, changes in intensities were moderate.

3.2a *Reactions in the nitrogen matrix*: The absorption at 996 cm^{-1} in the nitrogen matrix is one evidence of reactions in this matrix. This feature was observed by Andrews and coworkers in their experiments where
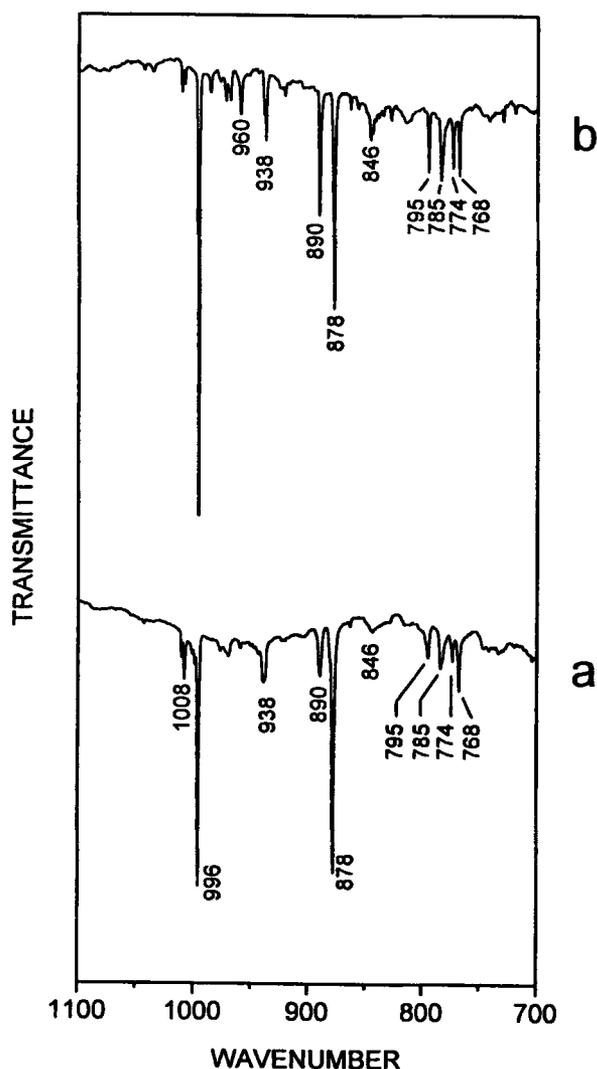
Figure 3. Matrix isolation infrared spectra of the laser-ablated species of uranium oxide trapped in a nitrogen matrix; (a) before annealing; (b) matrix annealed at 35 K.

uranium vapours were deposited in the nitrogen matrix and was assigned to UN$_2$ in a nitrogen cage (Hunt *et al* 1993). The 996 cm^{-1} feature in our spectrum can also be attributed to UN$_2$ which is produced in the nitrogen matrix as a result of the reaction of the primary products of ablation (i.e. U, UO, UO$_2$ and UO$_3$) with reactive nitrogen. The dinitride is probably formed by an insertion of U into N$_2$, or by a reaction of UO$_x$ with reactive nitrogen species, such as N$_3$ or N$_3^-$. The presence of these azide species in the nitrogen matrix experiments was indicated by the absorptions at 1658 cm^{-1} and 2003 cm^{-1} due to N$_3$ and N$_3^-$ respectively (Tian *et al* 1988; Chertihin *et al* 1996).

Nitric oxide (NO) was another reaction product in our nitrogen matrix experiments identified by its absorption at 1875 cm^{-1}. With atomic oxygen produced in the laser ablation process, and reactive nitrogen species such as N$_3$ present in the matrix, it is not surprising to observe NO in these experiments. Please note that the spectra shown in figures 2 and 3, span only the region where the uranium species absorb; the region where the features of NO, N$_3$ and N$_3^-$ occur have not been shown.

3.3 Experiments using mixed matrix (N$_2$/Ar)

To identify the species responsible for the features at 938, 890, 878 cm^{-1} and the quartet near 780 cm^{-1} observed in the nitrogen matrix, we performed experiments using mixed N$_2$/Ar matrices. In these experiments, the concentrations of N$_2$ in the matrix gas mixture were varied over the range 1% to 50%. The corresponding spectra are shown in figure 4. Due to the complexity of these spectra, we will separately discuss the features of each product in different matrices, albeit at the expense of being repetitious.

UO$_2$: The feature for this product occurred at 776 cm^{-1} in pure Ar and in Ar matrices containing up to 3% N$_2$. With further increase in N$_2$, this feature splits and is probably responsible for at least some of the peaks in the quartet observed near 780 cm^{-1} in pure N$_2$.

UO: This product is evidenced by a feature at 820 cm^{-1} in pure Ar. As the N$_2$ concentration was increased the features due to these products decreased in intensity. A later discussion will serve to identify the feature due to this species (and also that due to UO$_2$) in the N$_2$ matrix.

UO$_3$: The features due to this product are observed at 852 and 746 cm^{-1} in pure Ar. As the N$_2$ concentration was increased, it was difficult to discern features due to this species. It appears that UO$_3$ is unstable in the conditions existing when trapped in a N$_2$ matrix.

UN$_2$: Not surprisingly, this product was not observed in pure Ar for want of N$_2$ to form the nitride. In matrices containing less than 1% of N$_2$, a feature was observed at 1051 cm^{-1}, which was assigned to UN$_2$. As the N$_2$ concentration was increased, new features appeared at

1040, 1032, 1021, 1012, in excellent agreement with the earlier report of Andrews (Hunt *et al* 1993). These features were attributed to UN_2 complexing progressively with increasing amounts of N_2; the 1040 cm^{-1} feature to $(UN_2)(N_2)$ and the 1012 cm^{-1} peak to $(UN_2)(4N_2)$. In pure nitrogen, UN_2 was reported to occur at 996 cm^{-1}, in agreement with our observations; though alternate explanations appear possible.

NUO: In matrices containing 1% N_2, this product was observed by its spectral feature at 984 cm^{-1}, with a satellite at 974 cm^{-1}. As with UN_2, NUO is also probably

formed by the reaction of UO_x with reactive nitrogen species. As the N_2 concentration was increased, new features appeared at 964, 956, 948 and 940 cm^{-1}, very similar to the structure observed with UN_2. We therefore infer, that $(NUO)(xN_2)$ complexes are formed similar to the $(UN_2)(xN_2)$ complexes. Each of the features from 964 to 940 cm^{-1} can be assigned to complexes with progressively increasing amounts of N_2; the 964 cm^{-1} feature to $(NUO)(N_2)$ and the 940 cm^{-1} peak to $(NUO)(4N_2)$. The 938 cm^{-1} feature in the N_2 matrix can therefore be assigned to NUO in a N_2 cage.

The feature at 984 cm^{-1} (Ar matrix) was assigned to UN stretch in the NUO molecule, while the UO vibration in this species was believed to occur near 820 cm^{-1}, at exactly the same position where the diatomic UO absorbed (Kushto *et al* 1997). The question now arises as to where the UO absorption occurs in the nitrogen matrix. We examined the possibility that one (or more, if site effects come into play) of the quartet of peaks in the nitrogen matrix near 780 cm^{-1} may be due to the UO stretch in the NUO molecule or diatomic UO. We calculated the intensity ratios of the 938 cm^{-1} feature with each of the peaks in the 780 cm^{-1} quartet, for four sets of repeat experiments in the nitrogen matrix, performed on four different days. The values are shown in table 1. It can be seen that while the 938/795 ratio remains fairly constant in the different experiments, the other ratios show a scatter. This data suggests that the intensity of the 938 and 795 cm^{-1} features is correlated and must belong to the same species. We therefore believe that the 795 cm^{-1} feature must be due to the UO stretch in the NUO molecule (or in the UO diatomic), while the 938 cm^{-1} feature (which had been assigned to the NUO species earlier), must be due to the UN stretch. The three other features in the '780 quartet' may be assigned to UO_2, the triplet arising possibly due to multiple site effects.

It may be relevant to note that in the experiments of Andrews *et al* where laser-ablated uranium vapour was reacted with NO, the NUO molecule was produced by the insertion of U into the NO molecule (Kushto *et al* 1997). In our experiments, where solid UO_2 was laser-ablated in the presence of N_2, the NUO molecule could probably
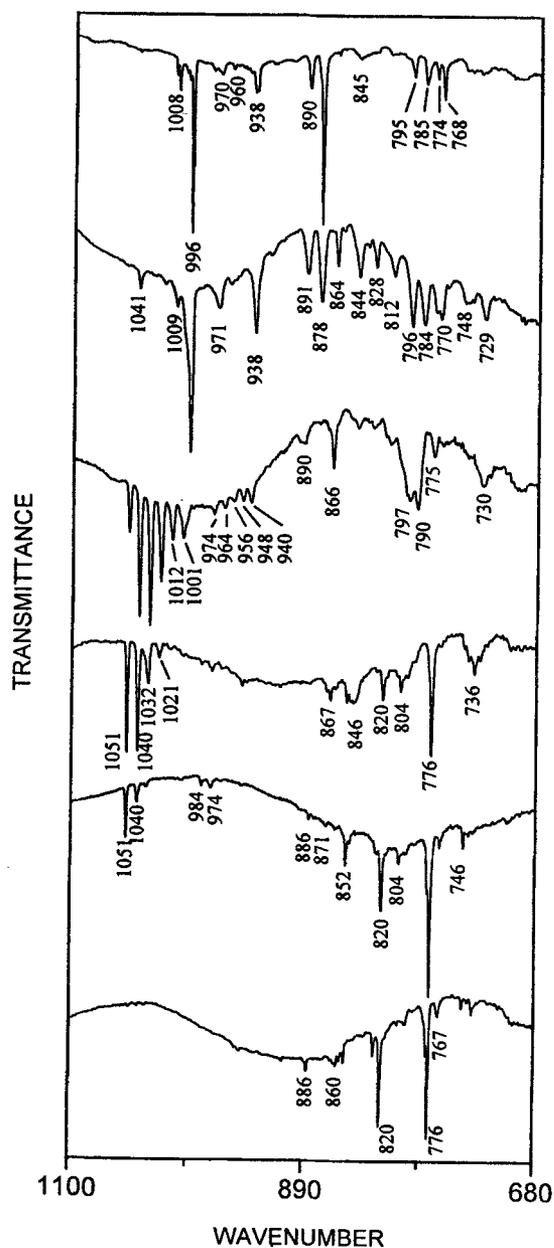
Figure 4. Matrix isolation infrared spectra of the laser-ablated species of uranium oxide trapped in mixed nitrogen/argon matrices. Concentrations of N_2 in the Ar/N_2 mixture were (**a**) 0%; (**b**) 1%; (**c**) 3%; (**d**) 12·5%; (**e**) 50%; (**f**) 100%. All spectra were recorded before annealing the matrix.

Table 1. Intensity ratios of the 938 cm^{-1} feature with each of the feature in the quartet near 780 cm^{-1}, in four different repeat experiments in the nitrogen matrix.

Experiment	I_{938}/I_{795}	I_{938}/I_{785}	I_{938}/I_{774}	I_{938}/I_{768}
1. Before annealing	1·23	1·20	2·95	1·32
After annealing	1·54	0·95	1·95	1·65
2. Before annealing	0·96	0·47	0·97	1·17
After annealing	1·25	0·82	0·68	3·01
3. Before annealing	1·09	0·55	0·94	0·59
After annealing	1·13	0·65	0·53	1·13
4. Before annealing	1·15	0·42	1·18	0·46
After annealing	1·56	0·88	0·79	0·81

have been produced by the reaction of UO with nitrogen atoms, in the matrix; in keeping with the observation that the intensity of the UO peak decreased with increase in the N_2 concentration.

(UO_2^+) (NO^-): In experiments containing 1% N_2 in the matrix gas mixture, features appeared at 886 and 871 cm^{-1}, which agree quite well with the values (880 and 869 cm^{-1}) reported for (UO_2^+) (NO^-) in an Ar matrix (Kushto *et al* 1997). On increasing the N_2 concentration, the 871 cm^{-1} feature increased in intensity and finally appeared as a strong peak at 878 cm^{-1} in the pure N_2 matrix. The 886 cm^{-1} feature that appeared in the Ar rich matrix, appeared at 890 cm^{-1} in N_2. The 890 and 878 cm^{-1} features in the N_2 matrix are therefore most likely due to (UO_2^+) (NO^-) in N_2. The charge transfer complexes involving NO are possible since as mentioned earlier NO is one of the reaction products in these experiments. It must be mentioned that the 878 cm^{-1} feature was also observed by Hunt *et al* (1993), though no assignment was proposed in that work.

Based on the work of Kushto *et al* (1997), (UO_2^+) (N_2^-) may also be considered as a likely candidate for the spectral features near 880 cm^{-1}. Electron attachment to N_2 is endothermic by 1·6 eV ($\pm$ 1·0 eV) (Chase *et al* 1985) and the overall reaction

$$UO_2 + N_2 \rightarrow (UO_2^+)(N_2^-), \tag{1}$$

is endothermic and has a ΔH of 164 kcal/mol, compared with a value of 126 kcal/mol for (UO_2^+) (NO^-) (Green *et al* 1976). Both the endothermic reactions are expected to be stabilized in the matrix by Coulombic attraction. Assuming a point charge model and a cation–anion distance of 3·5 Å, typical of adjacent sites in an inert matrix, the Coulombic stabilization would amount to $\approx$ 95 kcal/mol. Though this value appears insufficient to stabilize either of these complexes, the point charge model should only be considered to provide an estimate for the interaction energy, and it is more likely that the Coulombic interaction would aid the formation of the (UO_2^+) (NO^-) rather than (UO_2^+) (N_2^-). However, given the rather large uncertainty in the electron affinity of N_2, we draw this conclusion with caution. (In the above calculation, the ionization potential of UO_2, reported by Mann (1964) was used).

It may be noted that the spectra became complex when the concentration of N_2 in Ar was > 10%, probably due to multiple trapping sites that may be produced in mixed matrices.

While N_2 has been employed in a number of matrix isolation experiments as an inert matrix, this matrix has thrown up a variety of interesting reactions in laser ablation experiments. The inert matrix manifesting reactivity is a feature of laser ablation experiments, where ablated species with high kinetic energies can induce hyperthermal reactions (Friichtenicht 1974; Kang and Beauchamp 1985).

4. Conclusions

This study reports for the first time the matrix isolation infrared spectra of laser-ablated uranium oxide species trapped in Ar and N_2 matrices. The species obtained in the Ar matrix, UO, UO_2 and UO_3, represent the primary products of laser ablation. In the nitrogen matrix, in addition to the primary laser-ablated species, reaction products of these ablated species with reactive nitrogen were also observed. UN_2 and NUO, together with their complexes with N_2, were the dominant reaction products. Charge transfer complex (UO_2^+) (NO^-) was also observed in these experiments, as also features due to NO, N_3 and N_3^-.

It may be interesting to note that all the species observed in this single study, where uranium oxide was laser-ablated in the presence of Ar and N_2, represent the products observed in a collection of separate experiments reported previously, where uranium metal was laser vapourized in the presence of O_2, N_2, NO, NO_2 and N_2O.

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