

Conflicting Observations Resolved by a Far IR and UV/Vis Study of the NO₃ Radical**

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By codeposition of NO/Ne and O₂/Ne mixtures at 6 K, weakly bound complexes between O₂ and NO are formed. They exhibit a strong, structured charge transfer UV band at $\lambda_{\text{max}} = 275$ nm. The UV band disappears during UV irradiation of the neon matrix, while the visible spectrum of the NO₃ radical appears. Simultaneously, the fundamental ν_4 of the NO₃ radical in the \tilde{X}^2A_2' ground state is observed in infrared absorption for the first time at 365.6 cm⁻¹. Its ^{14/15}N and ^{16/18}O isotopic shifts reveal strong couplings between the two e'-type modes of NO₃, which are both active in a pseudo-Jahn-Teller interaction with the excited \tilde{B}^2E'

electronic state. The dispute on the vibrational fundamentals of the NO₃ radical is now concluded by the unambiguous assignment of combination bands associated with the fundamental ν_4 . Taking into account the observed isotopic shifts and estimated anharmonicities for ν_4 and the most intense IR band of NO₃ at 1492 cm⁻¹ ($\nu_3 + \nu_4$), the frequency of the so far not observed fundamental ν_3 is estimated to be 1100 ± 10 cm⁻¹. A tentative assignment of the vibronic levels in the IR spectrum in the range from 1000 to 3000 cm⁻¹ is given.

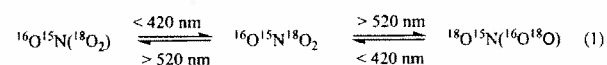
1. Introduction

The free NO₃ radical is an important species in atmospheric chemistry, and the analysis of its electronic and rovibrational spectra is still a great challenge. The strong visible spectrum between 480 and 680 nm was already discovered in the late 18th century,^[1] and was later attributed to the $\tilde{B}^2E' - \tilde{X}^2A_2'$ transition.^[2,3] The discovery of the NO₃ night-time oxidizing properties in the troposphere initiated long-term observations and many kinetic investigations.^[4,5] Numerous spectroscopic studies have sought to obtain the equilibrium symmetry and the assignment of the vibrational transitions in the ground electronic state. Important recent studies include: 1) photoelectron (PE) spectroscopic studies of both the nitrate anion^[6,7] and the NO₃ radical,^[8] 2) laser-induced fluorescence (LIF) spectra of the nitrate radical,^[9,10] as well as a recent reanalysis of the vibronic levels obtained from these spectra, aided by non-adiabatic computations,^[11] 3) the analysis of high-resolution diode laser and FTIR gas phase spectra which were obtained in the region 700 to 1520 cm⁻¹,^[12,13] and later extended to 1300–2800 cm⁻¹,^[14–16] and to the near infrared,^[17] and 4) a neon-matrix FTIR study on NO₃ in the range from 450 to 6000 cm⁻¹.^[18]

From the analysis of the recent spectra, D_{3h} symmetry was determined for the free NO₃ radical in the \tilde{X}^2A_2' ground state.^[11,16,18] However, no consistent assignment of the in-plane ground state vibrational levels exists. The prominent infrared absorption at 1492 cm⁻¹ was thoroughly investigated by high-resolution gas phase spectroscopy almost 25 years ago.^[13,19] Although this band was assigned to the degenerate stretching fundamental, ν_3 ,^[12,13,16] recent calculations^[11] have challenged that assignment. The absorptions above 1100 cm⁻¹ seem to be almost entirely binary or higher combinations of the three fundamentals ν_1 (1053 cm⁻¹),^[9] ν_3 (between 900–1100 cm⁻¹),^[11,18] and ν_4 (around 365 cm⁻¹),^[6,9,20] but none of these fundamen-

als has yet been observed directly. While the ν_1 fundamental is infrared inactive, ν_3 is predicted to be too weak to be detected.^[11] In contrast, ν_4 should be several orders of magnitude stronger than ν_3 , but lies in the far IR region and was not accessible in the recent matrix isolation study.^[18] An extension of this study into the far IR and UV/Vis region is the aim herein. The direct observation of the ν_4 band and of its ^{14/15}N and ^{16/18}O isotopologues would reveal new information either to confirm or to refine the present assignment. Furthermore, as there are two doubly degenerate pseudo-Jahn-Teller (PJT) active fundamentals of e' symmetry in D_{3h} , the experimental isotopic shifts of ν_4 reveal the coupling between these two modes.

NO₃ radicals isolated in solid neon matrices were formed by ultraviolet irradiation of a deposit made from NO/O₂/Ne gas mixtures.^[18] Both photodissociation of NO₃ and ^{16/18}O isotopic exchange according to Equation (1) were investigated.^[18]



The mechanism of the NO₃ formation and its photodecomposition into the diatomic fragments is still under discussion.

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The thermal formation of NO₃ from NO and O₂ and the corresponding reverse reaction along a C_{2v} coordinate are orbital-symmetry-forbidden processes.^[21] Prior to dissociation into NO + O₂ the NO₃ may undergo rearrangement to form a peroxy nitrite intermediate, ONOO. In recent high-level ab initio multireference CASSCF and CI studies^[22] the ONOO radical was predicted to be unbound, while neutralization–reionization studies^[23] and the recent matrix isolation study^[18] support the existence of ONOO.

The present study is directed towards 1) the first measurement of the far IR spectrum of the NO₃ radical and 2) a revised assignment of its vibrational spectrum based on Ne matrix isolation IR spectra observed from 80 to 3000 cm^{−1}. Additional spectral features which can not be assigned to the NO₃ radical, are described only briefly, since they will be elucidated in more detail in a forthcoming study.

2. Results and Discussion

Each matrix sample was investigated by both IR spectroscopy in the region from 700 to 80 cm^{−1} and in the UV/Vis region from 700 to 200 nm. After deposition of an O₂/Ne (1:200) sample at 6 K, no UV absorptions were observed, but the NO/Ne (1:400) matrix yielded bands in the 240–200 nm region. After codeposition of both gas mixtures in a 1:1 ratio at 6.5 to 7 K, weak broad IR absorptions appeared at 639, 488, and 311 cm^{−1}, composed of several closely spaced absorptions (Figure 1, trace A). Simultaneously, a very intense structured UV

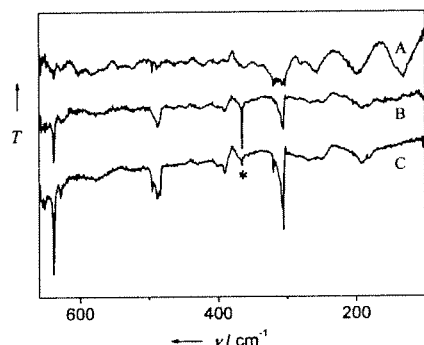


Figure 1. FTIR spectra from 660 to 100 cm^{−1} of a deposit at 6 K using a NO/O₂/Ne (1:2:800) mixture, A) before, B) after UV photolysis (260–400 nm), C) after further irradiation at λ > 495 nm. The ν₄ band of NO₃ is marked by an asterisk. Traces B and C are difference spectra using A as background to remove the interference pattern (present in trace A < 300 cm^{−1}).

band emerged at λ_{max} = 275 nm (Figure 2, trace A). The deposit was subjected to mercury-arc radiation transmitted through a 260 to 400 nm band pass filter (Schott UG11). After 50 min of irradiation, the UV absorption vanished completely and the known structured visible absorption of NO₃^[24] appeared in the 500 to 700 nm region (Figure 2, trace B). At the same time, a new strong sharp IR band developed at 366 cm^{−1} (Figure 1, trace B). The NO₃ visible absorption and the 366 cm^{−1} IR band simultaneously disappeared after exposure of the deposit to

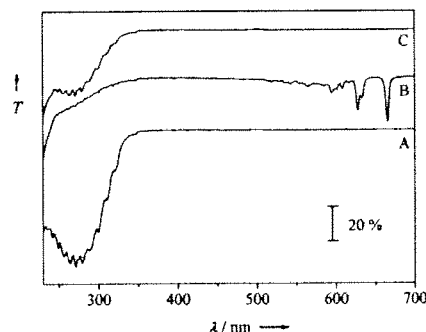


Figure 2. UV/Vis spectra from 700 to 200 nm of a deposit at 6 K using a N¹⁸O/¹⁸O₂/Ne (1:2:800) mixture, A) before, B) after photolysis (260–400 nm), C) after further irradiation at λ > 495 nm.

filtered yellow light of a tungsten lamp (λ > 500 nm, Figure 1, trace C), and the UV band of the NO/O₂ complex was partially regenerated (Figure 2, trace C). As shown in Figure 1, the initially present weak IR absorptions grew strongly during UV irradiation, and increased further during irradiation with visible light of λ > 500 nm.

2.1. UV and Far IR Spectra of NO/O₂ Reaction Products

The origin of the observed UV band is located at 31100 ± 50 cm^{−1} (322 nm). It reveals a vibrational progression with an average spacing of 1220 cm^{−1}, and an ¹⁶/¹⁸O isotopic shift of 60 cm^{−1}. Both the vibrational frequency and the large ¹⁶/¹⁸O isotopic shift are similar to those of the fundamental of the O₂[−] radical anion (1090 cm^{−1}, Δν ¹⁶/¹⁸O = 62 cm^{−1}).^[25] We tentatively assign this band to a charge transfer NO⁺ ↔ O₂[−] transition of a weak van der Waals complex between O₂ and NO, since the transition energy (3.72 eV) is in accord with a π*–π* charge transfer process, in which NO donates electron density to the O₂ moiety. The Coulomb stabilization energy of NO⁺ O₂[−] can be estimated from the ionization energy of NO (9.26 eV),^[26] the electron affinity of O₂ (0.44 eV),^[26] and the transition energy (3.72 eV), to be about 9.26–0.44–3.72 = 5.09 eV, which would correspond to a reasonable distance between the charges of NO⁺ and O₂[−] of about 2.8 Å in the excited complex.

IR absorptions for the weak complex between NO (1874.6 cm^{−1} in Ne matrices) and O₂ (visible in solid Ne at 1554.5 cm^{−1}) have previously been reported in the mid infrared at 1872 and 1530 cm^{−1},^[18] but none of the observed far IR bands can be attributed to this complex. An ab initio study of NO(O₂) van der Waals complexes performed at the UQCISD/6-311 + G(2d) level of theory predicted the interfragment vibrations at well below 100 cm^{−1},^[27] which are outside the spectral limit of our measurement.

Under the experimental conditions used herein and in the previous work,^[18] a considerable amount of (NO)₂ dimer is isolated in the matrix.^[18] They also form weak complexes with O₂ that very probably may contribute to the observed charge transfer band, since oxygen may split the weakly bonded (NO)₂

dimer into $\text{NO}(\text{O}_2)$ and NO . The IR absorptions at 639, 488, and 311 cm^{-1} shown in Figure 1, are attributed to *trans*- ONONO_2 (*asym*- N_2O_4 , *D*-isomer), by comparison of the band positions and their relative intensities with those of an authentic *trans*- ONONO_2 sample produced by UV irradiation of O_2NNO_2 (*sym*- N_2O_4) isolated in a Ne matrix. The corresponding frequencies of the far infrared fundamentals of *trans*- ONONO_2 isolated in O_2 matrices^[28] that have previously been reported at 642, 488, and 304 cm^{-1} agree well with those observed herein. This species is most likely formed from $(\text{NO})_2$ dimer and O_2 that were both trapped in the same matrix cage. As shown in the difference spectra displayed in Figure 3, and obtained from spectra

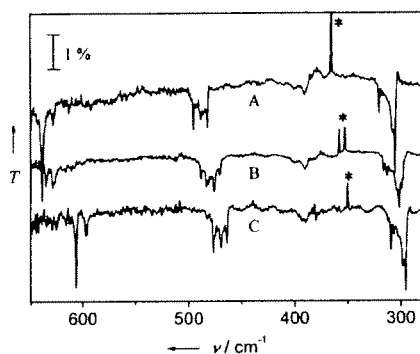


Figure 3. Difference IR spectra prior to and after photodestruction of NO_3 by visible light ($\lambda > 495\text{ nm}$) in the region from 650 to 280 cm^{-1} of natural and ^{18}O isotopic substituted $\text{NO}/\text{O}_2/\text{Ne}$ (1:2:800) mixtures at 6 K . A) $^{14}\text{N}^{16}\text{O}/^{16}\text{O}_2$, B) $^{14}\text{N}^{16}\text{O}/^{18}\text{O}_2$, C) $^{14}\text{N}^{18}\text{O}/^{16}\text{O}_2$. The ν_4 band of the isotopologues of NO_3 is marked by an asterisk.

recorded prior to and after photodecomposition of NO_3 by visible light ($\lambda > 495\text{ nm}$), these bands simultaneously increase (i.e. decrease in transmittance T) as the NO_3 band (marked with an asterisk) decrease in intensity (i.e. increase in T). Figure 3 also reveals significant $^{16/18}\text{O}$ isotopic shifts displayed by these absorptions. Apart from traces of N_2O_3 , the NO_3 radical seems to be the only species in the matrix that absorbs light in the visible range. In the case where at least some of the observed *trans*- ONONO_2 bands are formed by the photodecomposition of NO_3 , the corresponding NO_3 should first be formed from an oxygen complex of a $(\text{NO})_2$ dimer, that by UV photolysis (260 – 400 nm) yield $\text{NO}_3 + \text{NO}$, which finally is converted into *trans*- ONONO_2 by irradiation with visible light.

Further experimental and theoretical work is needed for a full spectroscopic characterization of the NO/O_2 complexes and their photochemistry.

2.2. Far IR Spectrum and Vibrational Fundamentals of the NO_3 Radical

The simultaneous appearance and decrease of the new IR band at 366 cm^{-1} (Figure 1) together with the well-known visible transition of NO_3 (Figure 2, Trace B) unambiguously proves that this IR band belongs to the NO_3 radical. Its position agrees very well with the wavenumber of a hot band observed in the

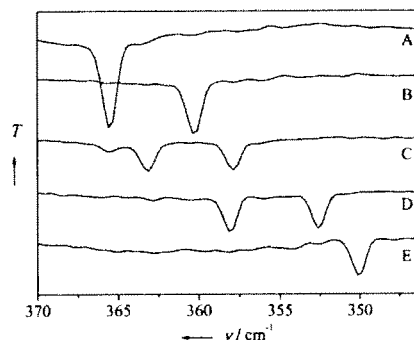


Figure 4. IR spectra of NO_3 in the region from 370 to 346 cm^{-1} after deposition of $\text{NO}/\text{O}_2/\text{Ne}$ (1:2:800) mixtures of several isotopic varieties at 6 K and irradiation through a 260 – 400 nm bandpass filter. A) $^{14}\text{N}^{16}\text{O}/^{16}\text{O}_2$, B) $^{15}\text{N}^{16}\text{O}/^{16}\text{O}_2$, C) $^{14}\text{N}^{18}\text{O}/^{16}\text{O}_2$, D) $^{14}\text{N}^{16}\text{O}/^{18}\text{O}_2$ and E) $^{14}\text{N}^{18}\text{O}/^{18}\text{O}_2$.

cavity ringdown spectrum of the forbidden $\tilde{A}^2E' \leftarrow \tilde{X}^2A_2'$ transition (365 cm^{-1}),^[20] and a similar weak feature with a frequency shift of 368 cm^{-1} has also been observed in the LIF spectrum.^[9] Both of these features were attributed to the fundamental ν_4 . We have investigated four additional NO_3 isotopologues in further experiments (Figure 4). The band splitting of the two mixed species NO_2^{18}O ($363.1, 357.9\text{ cm}^{-1}$) and NO^{18}O_2 ($358.1, 352.6\text{ cm}^{-1}$) proves the degenerate nature of ν_4 . The positions of the fundamentals of NO_3 and their $^{14/15}\text{N}$ and $^{16/18}\text{O}$ isotopic shifts are listed in Table 1. The positions of ν_2 ^[18] and ν_4 were measured for several isotopologues in Ne matrices, and $\nu_1 = 1053\text{ cm}^{-1}$ was obtained in the dispersed LIF study.^[9] The position of ν_1 is supported by the assignment of the $(\nu_1 + \nu_4)$ combination presented in Table 2.

Table 1. Frequencies ν_i (cm^{-1}) and isotopic shifts $\Delta\nu_i$ (cm^{-1}) of the fundamentals and some combination bands of the NO_3 radical.^[a]

ν_i	$\nu_i(^{14}\text{N}^{16}\text{O}_3)$	$\Delta\nu_i(^{15}\text{N}^{16}\text{O}_3)^{[b]}$	$\Delta\nu_i(^{14}\text{N}^{18}\text{O}_3)^{[c]}$
ν_1	1053 ^[d]	(0.0)	(60.4)
ν_2	763.1 ^[e]	19.8 ^[e] (19.9)	9.5 ^[e] (9.7)
ν_3	$1100 \pm 10^{[f]}$	(12.8)	(30.3)
ν_4	365.6 ^[g]	5.3 ^[g]	15.5 ^[g]
$\nu_1 + \nu_4$	1412.5 ^[e]	6.6 ^[e] (5.3)	71.3 ^[e] (75.9)
$\nu_3 + \nu_4$	1491.4 ^[e]	19.4 ^[e] (18.1)	54.2 ^[e] (45.8)

^[a] Values in parentheses represent isotopic shifts calculated according to the Teller–Redlich product rule.^[b] $^{14/15}\text{N}$ isotopic shifts with respect to $^{14}\text{N}^{16}\text{O}_3$. ^[c] $^{16/18}\text{O}$ isotopic shifts with respect to $^{14}\text{N}^{16}\text{O}_3$. ^[d] Gas-phase values from ref. [9]. ^[e] Ne matrix values from ref. [18]. ^[f] This work. ^[g] This work, Ne matrix.

The frequency of ν_3 was recently predicted to be near 1000 cm^{-1} ,^[11,29] but has never been observed experimentally either in absorption or in emission. Due to a pseudo-Jahn–Teller coupling to the excited \tilde{B}^2E' state, the two e' -type modes of NO_3 shift considerably to lower wavenumbers compared to those of the nitrate anion (1383 and 715 cm^{-1}).^[30] This coupling probably also gives rise to the unexpectedly low infrared intensity of the ν_3 fundamental. The reassignment of

Table 2. Ground-state vibrational absorptions in the range of 1100 to 3000 cm⁻¹ obtained from the infrared spectra of the NO₃ radical and their tentative assignments.

Ne matrix ^[1a]	Gas phase ^[a]	Assignment
1173.0	–	3 ν_4
1412.5	–	$\nu_1 + \nu_4$
1491.4	1492 (4.7)	$\nu_3 + \nu_4$
1773.8	–	$\nu_1 + 2 \nu_4$
1925.4	1927 (3.0)	$\nu_3 + 2 \nu_4$
2021.9	2024 (1.5)	5 ν_4
2153.5	2155 (2.0)	$\nu_1 + \nu_3$
2202.0	2200 (0.7)	$\nu_1 + 3 \nu_4$
2246.5	2240 (0.4)	2 ν_3
2375.2	2380 (0.4)	$\nu_3 + 3 \nu_4$
2516.5	2518 (2.1)	$\nu_1 + 4 \nu_4$
2558.7	–	$\nu_1 + 4 \nu_4$ ($\nu_1 + \nu_3 + \nu_4$) ^[b]
2583.4	2585 (1.7)	2 $\nu_3 + \nu_4$
2621.4	–	2 $\nu_3 + \nu_4$
2892.2	–	7 ν_4
2899.0	–	7 ν_4

^[a] Frequencies and relative band intensities (in parentheses) from ref. [16].^[b] Alternative assignment in parenthesis.

the prominent band at 1491.4 cm⁻¹ to the ($\nu_3 + \nu_4$) ($l = \pm 2$) combination (Table 1), and considering a recently predicted unusual positive cross anharmonicity of this combination band of about +25 cm⁻¹,^[11] puts our presently best estimate for ν_3 to 1491–366–25 = 1100 ± 10 cm⁻¹.

^{14/15}N and ^{16/18}O isotopic shifts for ν_1 , ν_2 , and ν_3 of species with D_{3h} symmetry were obtained according to the Teller–Redlich product rule^[31] (Table 1), of which those of ν_3 are estimated from the experimental isotopic shifts of ν_2 and ν_4 for which the product rule reduces to the relationship in Equation (2):

$$\frac{\nu_3 \nu_4}{\nu'_3 \nu'_4} = \sqrt{m_{\text{O}}/m_{\text{O}}'} \frac{\nu_2}{\nu'_2} \quad (2)$$

where quantities referring to the isotopic molecule are marked by a prime and m_{O} are the masses of the oxygen atoms.

2.3. Assignment of Combination and Overtone Bands of NO₃

The isotopic shifts of the fundamentals listed in Table 1 are used in the assignment of the two combination bands ($\nu_1 + \nu_4$) and ($\nu_3 + \nu_4$). For ($\nu_1 + \nu_4$), the ^{14/15}N shift (6.6 cm⁻¹)^[18] should be similar to those of ν_4 (5.3 cm⁻¹; ν_1 displays no ^{14/15}N shift). In general, the isotopic shifts of the two combination bands are expected to be roughly the sum of those of the corresponding fundamentals. The observed shifts are considerably different for the two combination bands, and they agree quite well with the calculated ones (Table 1). From the frequency difference ($\nu_1 + \nu_4$) – ν_4 = 1046.9 cm⁻¹, and the observed value of ν_1 = 1053 cm⁻¹,^[9] a reasonable negative zero order cross anharmonicity $x_{14} \approx -6$ cm⁻¹ can be obtained.

Based on the fundamentals given in Table 1, a tentative assignment of higher vibrational transitions observed previously in neon matrices from 1100 to 3000 cm⁻¹^[18] is outlined in

Table 2. Below 1100 cm⁻¹, only the two fundamentals, ν_4 and ν_2 (365.6 and 763.1 cm⁻¹, respectively) were detected in Ne matrix, and beyond 2000 cm⁻¹ the predicted high density of vibronic states^[11] renders any assignment difficult. Combination bands or overtones which involve excitation of three to five quanta of fundamentals of e' symmetry are split into two sub-levels of that symmetry. This high density of e' levels leads to extensive mixing. In addition to the band positions measured in Ne-matrices (Table 2) gas phase values^[16] are listed for comparison. The agreement of these wavenumbers is excellent—usually better than 2 cm⁻¹. As mentioned in the introduction, all bands listed in Table 2 appeared to be combination bands of the three in-plane fundamentals ν_1 , ν_3 , and ν_4 , and for symmetry reasons only e' -type transitions are allowed for such combinations in the absorption spectrum.

The lowest band listed in Table 2, located at 1173.0 cm⁻¹, was observed for the first time in the recent matrix isolation study,^[18] its frequency is too low for its assignment to any combination of ν_4 with ν_1 , ν_3 , or ν_2 , and it is assigned to $3\nu_4$ ($l = \pm 1$). Assignment to the missing ν_3 fundamental would put the ($\nu_3 + \nu_4$) combination at >1538 cm⁻¹, which does not match the observed spectrum. The assignment to $3\nu_4$ ($l = \pm 1$) implies a reasonable positive anharmonicity of ν_4 of (1173.0–3×365.5)/6 = 12.8 cm⁻¹. The positive anharmonicity of ν_4 is also consistent with the frequency of $2\nu_4$ that was observed in both the low resolution PE spectrum of the nitrate anion at ≈758 cm⁻¹^[6] and in the LIF spectrum of NO₃ (753 cm⁻¹).^[9,11] There is some evidence that the band observed in LIF at 753 cm⁻¹ is the parallel component of $2\nu_4$ ($l = 0$), since both, a_1' and e' transitions are active in the LIF spectrum. The zero-order anharmonicity calculated from the corresponding frequency difference (753.0–2×365.5)/2 = 11.0 cm⁻¹ agrees well with those determined from $3\nu_4$ ($l = \pm 1$).

Several additional combinations ($m\nu_1 + n\nu_4$), $i = 1$ and 3, are assigned in Table 2, but alternative assignments of some of the higher vibrational levels cannot be ruled out. The strong vibronic perturbation is clearly visible in the unusually high intensity of some highly excited vibrational states and in the rather large positive anharmonicity of the PJT active fundamentals. A positive anharmonicity is assumed in the tentative assignment of $2\nu_3$ (2246.5 cm⁻¹), but not for the combination ($\nu_1 + \nu_3$), which is attributed to a strong band at 2153.5 cm⁻¹ (Table 2). The higher vibrational states are clearly not adequately described by zero-order anharmonicities, which do not account properly for the vibronic interaction. Therefore we do not attempt to quote anharmonicity constants quantitatively. Nevertheless, at least in case of low vibrational quantum numbers this approximation still seems to be useful for a rough frequency check.

Experimental Section

Chemicals: NO or ¹⁵NO was made for the experiments in Wuppertal by reaction of sulfuric acid, mercury, and NaNO₃ (Merck) or Na¹⁵NO₃ (>99 atom% ¹⁵N, Isotec Inc, Miamisburg). A 250 mL glass bulb equipped with a 10 mm Young valve was charged with 680 mg of NaNO₃ or Na¹⁵NO₃ (8 mmol) and 15 g of mercury

(75 mmol) and then evacuated. About 10 g of 20 wt% H_2SO_4 aqueous solution was slowly introduced through the valve into the evacuated reaction vessel. The contents were shaken for 1 h at room temperature, and the gaseous reaction products were passed in a vacuum through U-traps held at -100 , -183 and -196°C . Subsequently the trap at -196°C contained 6 mmol of pure NO or ^{15}NO . N^{18}O was obtained by reacting NO with Cl_2 and D_2^{18}O and subsequent reduction of the products with mercury. A dry, evacuated 50 mL glass bulb equipped with a 10 mm Young valve was charged with 220 mg of D_2^{18}O (99% ^{18}O , 10 mmol), 1 mmol of NO and 1 mmol of Cl_2 . The water in the reactor was occasionally heated to reflux using a heat gun. After 1 h heating/cooling treatment, 5 g of mercury (25 mmol) was introduced in vacuum through the valve into the reaction vessel held at -196°C . Following the procedure described for NO and ^{15}NO , 0.8 mmol of N^{18}O (90% enriched) was obtained.

Chlorine (99%, Merck) was purified by fractional condensation prior to use, while oxygen (99.99%, Messer-Griesheim), $^{18}\text{O}_2$ (99% Campro) and neon (99.999% Linde) were used without further purification.

Preparation of the matrices: Details of the matrix apparatus have been described elsewhere.^[32] In all experiments gaseous mixtures $\text{Ne}:\text{NO}=400$ and $\text{Ne}:\text{O}_2=200$ were used. Samples (2 mmol) from the reservoirs were mixed in front of the matrix support at low pressures and deposited on the cold Rh mirror at 6 K at a rate of 2 mmol h^{-1} . Photolysis experiments were carried out using a high-pressure mercury lamp (TQ 150, Heraeus) or a tungsten halogen lamp (250 W, Osram) in combination with a water-cooled quartz lens and different filters. In the UV region a band pass filter to pass radiation in the wavelength range between 260 and 400 nm (Schott, UG11, $d=3\text{ mm}$) and in the visible region a 500 nm cut-off filter was used.

Instrumentation: Matrix IR spectra were recorded in Wuppertal on a IFS 66v FT spectrometer (Bruker) equipped with a special transfer optic for measurement in the reflectance mode. A liquid helium-cooled Si bolometer (Infrared Laboratories), together with a $6\text{ }\mu\text{m}$ Ge coated Mylar beam splitter, were used in the region 700 to 80 cm^{-1} . 32 and 64 scans were coadded for each spectrum using apodized resolutions of 0.3 and 0.6 cm^{-1} , respectively.

UV/Vis spectra were measured with a Perkin-Elmer Lambda 900 UV spectrometer in the range of 200 to 700 nm with a data point separation of 0.5 nm and an integration time of 2 seconds. The radiation of the spectrometer was directed into a 150 cm long optical quartz fiber, through a quartz lens inside the cryostat and twice passed through the matrix deposited on the cold Rh mirror. A second quartz lens and fiber collected the reflected radiation and directed it into the spectrometer.

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Keywords: IR spectroscopy • isomerization • isotopic labeling • matrix isolation • radicals

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