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Reactions of ground state Ti atoms with NO: insertion versus complexation. An IR matrix isolation study

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Dedicated to the memory of Christophe Prot

Abstract

The reaction of ground state Ti atoms with NO during condensation in solid argon has been reinvestigated. The NTiO molecule, already characterized in reactions of laser-ablated Ti, is the only product observed for the reaction between one Ti atom and one nitric oxide molecule. Isotopic data on v_1 , v_2 , v_3 , $2v_1$ and $2v_2$ have been measured in the mid- and far-infrared regions. This enables a complete harmonic force-field calculation based on a bent geometry, in agreement with the conclusions of the previous study. No evidence is found, however, of a metastable nitrosyl complex intermediate, as previously proposed. This study confirms that the insertion reaction proceeds directly from the ground electronic state reagents, with no or very little activation energy. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

The reactivity of transition metal atoms in the gas phase or in isolated conditions is a challenging object of study, due to the difficulty of carrying out structural spectroscopic studies in very dilute media, and to the presence of numerous low-lying electronic configurations. For reactions involving titanium atoms, oxidation by O_2 , NO_2 , N_2O and O_3 has been studied by chemiluminescence from the excited TiO^{*} product, in flames by Gole and coworkers [1,2], in crossed-beam studies by Parson et al. [3], and more recently, the Ti + NO \rightarrow

 $TiO^* + N$ reaction was studied in the single collision regime using pulsed, crossed molecular beams by Naulin et al. [4]. The Ti + NO, O_2 and N_2O reactions have also been the object of several kinetic studies in fast flow reactors at room temperature, probing the kinetics of disappearance of Ti atoms in the ground [5,6] or excited states [7] or the TiO product concentrations. These studies vielded effective rate constants of the bimolecular reactions and concluded the existence of low activation energy (2-4 kcal/mol) to the oxygen atom abstraction reaction $Ti + XO \rightarrow TiO + X$. Interestingly, this barrier was found to be the lowest for X = N [5,6]. In analogy with the mechanism involved in the alkaline-earth-metal atom abstraction reactions with oxygen-containing molecules, harpooning or electron-jump mechanisms were assumed as the onset of the metal-molecule

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interaction. Another investigation explored the temperature and pressure dependence of $Ti + O_2$, N_2O , NO, CO_2 , SO_2 or NO_2 oxidation reactions in a fast flow reactor [8]. The observed pressure dependences of the Ti + NO and $Ti + CO_2$ reaction rates indicate a contribution from a termolecular association channel, in addition to the abstraction reactions already documented. For NO, the evolution of the effective rate constants with temperature for the reaction,

$$Ti + NO \leftrightarrow [TiNO] \rightarrow TiO + N$$

suggested exothermicity for the first step, while the abstraction activation energy remains globally slightly positive. Until recently, however, nothing was known about the chemical nature or electronic structure of TiXO (X = N, O, N₂) intermediates. Also, as discussed in Ref. [6], the reason for the increase in rate constants in Ti + NO vs. Ti + O₂ reaction remains unclear and inconsistent with simple electron-transfer mechanisms, which suggests that the nature and bonding of these intermediates are important in that respect.

Recently, in a theoretical systematic study of the NO interaction with first row transition metal atoms, using density functional theory, predictions were made of the binding energies, structures and spectroscopic properties of a TiNO, titanium nitrosyl species [9]. This study predicted the existence of a linear, nitrogen-bound nitrosyl complex with a fairly large Ti–NO binding energy (\approx 50 kcal/ mol) in the ² Σ ground state, fairly short Ti–N (\approx 1.7 Å) and elongated N=O (\approx 1.228 Å) distances.

Even more recently, Kushto and coworkers investigated the reaction of laser-ablated Ti atoms with nitric oxide in rare-gas matrices, and found two reaction products of the lowest stoichiometry, Ti + NO, along with ionic reaction products and larger neutral species. Based on their experimental findings and on further DFT calculations, they identified these species as a titanium nitrosyl species, TiNO, characterized by an NO stretching mode near 1615 cm⁻¹, and a titanium oxonitride species, NTiO, characterized by the two valence stretching vibrations in the 900–700 cm⁻¹ region [10]. From atomic or molecular diffusion experiments proceeding by slight warming of the argon matrix up to 25 K *after* Ti atom deposition, it was concluded that this species could be formed with very little or no activation energy from the ground state reagents. This left, however, the existence of a second, metastable titanium nitrosyl species, predicted some 36 kcal/mol higher in energy, more difficult to account for. The ability of titanium atoms to insert spontaneously into an O=X multiple bond has been documented before in matrix isolation studies of the Ti + CO₂ reaction [11,12], and investigated theoretically [13].

In the course of parallel studies of the reactivity of ground state, thermally produced transition metal atoms with various diatomic molecules in solid argon [15–18], the reaction of NO molecule with ground state Ti has been reinvestigated. In this article, we show that the oxonitride insertion product is the only product observed in the reaction of a ground state Ti atom with a nitric oxide molecule in an argon matrix. Our results completely confirm the assignments of the v_1 and v_2 fundamentals by Kushto et al. [10], but the larger product yield with the thermal effusion technique enables us to detect the lower frequency fundamental, the bending vibration v_3 , and the $2v_1$ and $2v_2$ overtones. A quadratic harmonic force field is also presented, based on the isotopic data obtained on all fundamentals for the ⁴⁶Ti/⁴⁷Ti/⁴⁸Ti/⁴⁹Ti/⁵⁰Ti, ¹⁶O/¹⁸O, ¹⁴N/¹⁵N, isotopic species of NTiO. These data (bond force constants and interaction force constants) are interesting for the discussion of the bonding within transition metal-containing molecules [18], and give precious reference points for testing the various theoretical modelling methods [19].

2. Experimental

The Ti + NO samples were prepared by cocondensing Ti vapour and NO/Ar mixtures (0.2– 2% molar ratios) onto a cryogenic metal mirror maintained around 10 K. The experimental methods and set-up have been previously described [20]. Briefly, here, Ti was vapourized from a 1 mm diameter TiMo alloy wire (Goodfellow, UK) heated resistively to ~1700°C. Metal deposition rates, monitored with a microbalance, were typically of the order of $0.10-0.40 \text{ }\mu\text{g/min}$.

Argon gas (L'Air liquide, France, 99.995%) was used without further purification, NO (L'Air Liquide, 99.9%) and ¹⁵NO gas (Isotec, USA, with an isotopical purity of 97.8%) were purified, in order to remove N₂, N₂O and NO₂, by using trap-to-trap vacuum distillations. ¹⁴N¹⁸O was prepared in the laboratory by addition of ¹⁸O₂ onto ¹⁴N¹⁶O gas to form ¹⁴N⁽¹⁶⁺¹⁸⁾O₂ which was subsequently reduced to ¹⁴N¹⁸O and ¹⁴N¹⁶O by reaction with mercury [21]. The resulting gas is a mixture containing approximately 52% ¹⁴N¹⁶O and 48% ¹⁴N¹⁸O. The purity of the samples was confirmed spectroscopically. For experiments performed with O₂ and N₂, 99.998% purity gases from Air Liquide, France, were used without purification.

In general, after 2 h deposition time, infrared spectra of the resulting sample were recorded in the transmission-reflection mode between 5000 and 70 cm⁻¹ using a Bruker 120 FTIR spectrometer and suitable combinations of CaF₂/Si, KBr/ Ge or 6 µm Mylar beamsplitters with either liquid N₂-cooled InSb or narrow band HgCdTe photodiodes or a liquid He-cooled Si-B bolometer, fitted with cooled bandpass filters. The resolution was varied between 0.1 and 0.5 cm⁻¹. Bare mirror backgrounds, recorded at 10 K from 5000 to 70 cm^{-1} prior to sample deposition, were used as references in processing the sample spectra. Also, absorption spectra in the near-, mid- and farinfrared were collected on the same samples through either CaF₂, CsI or polyethylene windows mounted on a rotatable flange separating the interferometer vacuum (10^{-2} mbar) from that of the cryostatic cell (10^{-7} mbar). The spectra were subsequently subjected to baseline correction to compensate for infrared light scattering and interference patterns.

The sample could be next irradiated using a 200 W mercury–xenon high pressure arc lamp and interference or broadband filters as it was found that some of the products could be photolysed or converted by UV–visible light. Infrared spectra of the photolysed samples or next after sample annealing to 35 K in several steps were recorded between 5000 and 70 cm⁻¹ as outlined above.

3. Results

In samples where Ti atoms were codeposited with NO in an argon matrix, both in relatively diluted conditions, infrared spectra presented no absorption in the metal nitrosyl N-O stretching region (1500–1900 cm⁻¹) apart from those attributed to unreacted NO, (NO)₂ and their isotopomers [22,23]. The contrast with the results obtained with a typical late first-row transition metal such as Ni is striking. Fig. 1 presents the spectra obtained in equivalent conditions (M/NO/Ar $\approx 0.5/1/100$) depositing either Ti or Ni ground state atoms with NO. With Ni atoms, the reaction products were identified mainly by absorptions in the 1600-1900 cm⁻¹ region, characteristic of metal-nitrosyl complexes [14,22] (Fig. 1). Under the same experimental conditions, the reaction of Ti with NO does not lead to the formation of any nitrosyl complex, but only to the appearance of new bands in the 700–920 cm⁻¹ region, described recently by Kushto et al., and attributed to the primary oxonitride insertion product, NTiO. Our experiments presented no sign of a band at 1614.7 cm⁻¹ attributed to a titanium mononitrosyl species, TiNO, as discussed in Ref. [10]. This species, was calculated as stable or metastable in Refs. [9,10]. In diluted conditions (Ti/NO/Ar = 0.2/0.2/100), the only



Fig. 1. Comparison of infrared absorption spectra in the nitrosyl (1500–2000 cm⁻¹) and oxonitride regions (700–950 cm⁻¹) for argon matrices containing NO + Ni, NO + Ti, and NO only at 10 K; from bottom to top: NO/Ar = 1/100, Ti/NO/Ar = 0.5/1/100 and Ni/NO/Ar = 0.5/1/100.

signals which could be detected were due to water, present as an impurity in the vacuum system. The band located at 1614.7 cm⁻¹, assigned in Ref. [10] to a linear TiNO complex, is detected only when the matrix is heated up to 35 K or when the NO molar ratio is increased. This band thus belongs to a larger nitrosyl complex.

Other species could be observed, which present a second-order dependence in NO, such as the one responsible for absorptions at 1488, 1208 and 977 cm⁻¹ and assigned to a OTiNNO structure in Ref. [10]. Interestingly, upon UV-visible photoexcitation, this species could be converted into OTiO or N₂-perturbed OTiO [10], while the amount of NTiO remains constant (Fig. 2). This shows that this species is formed only by addition of NO to NTiO and could be compared to the secondary reaction of Ti with CO₂: after an initial insertion step leading to OTiCO, Mascetti et al. showed that further reaction with CO₂ proceeds through a complexation channel only to yield OTi(CO)(CO₂) [11,13]. Experiments were run using $Ti + O_2 + N_2$ ternary mixtures in argon, which resulted in the production of N₂-perturbed OTiO after Ti photoexcitation, but no trace of OTiNNO could then be detected. From this, we can conclude that the OTiNNO \rightarrow N₂-perturbed OTiO isomerization is thermodynamically favoured. The OTiNNO product yield was too low in our experiments to observe more than the three most intense fundamentals, thus, precluding a serious structural discussion for this species.



Fig. 2. Comparison of infrared spectra in the Ti–O stretching region for Ti + NO and Ti + O_2 reactions in solid argon at 10 K, before and after broad band UV–visible photoexcitation.

Experiments were run replacing NO by O_2 to compare the reactivity of ground state Ti with these two molecules under the very same experimental conditions. Our results for the Ti + NO and Ti + O_2 reactions are contrasted in Fig. 2. In the related insertion reaction Ti + $O_2 \rightarrow OTiO$, the product yield after deposition of ground state Ti and O_2 is relatively low but dramatically enhanced upon Ti atom photoexcitation. This shows that, at the difference of the Ti + NO reaction, the insertion reaction in O_2 presents a small energy barrier, which is not readily overcome at a low temperature (≈ 10 K here).

In this paper, we shall focus our study on additional information relative to the oxonitride primary insertion product, NTiO. Spectra obtained with different concentrations of NO and Ti in argon matrices show two sharp bands located at 718.3 and 900.7 cm⁻¹ (Figs. 2 and 3) previously observed and assigned by Kushto et al. [10] to Ti–N and Ti–O stretching modes, respectively, for the NTiO species. Their relative infrared intensities remain constant when the sample is photolysed or after warming the matrix up to 35 K. Sharp satellite features near these bands are due to the natural titanium isotopes (⁴⁶Ti 7.9%, ⁴⁷Ti 7.3%,



Fig. 3. Comparison of experimental and simulated infrared spectra in the v_2 region of NTiO trapped in argon matrix at 10 K. The simulations assume lorentzian band shapes. For both the stable (- - -) and unstable (\cdots) trapping sites, the relative intensities are supposed to follow the population of naturally occurring Ti isotopes. The dotted-dashed line represents the total simulated profile.



Fig. 4. Infrared spectra of v_2 and v_3 of ²A' NTiO for various isotopic precursors at 10 K in solid argon, 690–730 and 200–300 cm⁻¹ regions, Ti/NO/Ar = 0.5/1/100. The dotted lines correspond to blank samples with NO/Ar = 1/100.

⁴⁸Ti 74.0%, ⁴⁹Ti 5.5% and ⁵⁰Ti 5.3%), see Fig. 3. Near each of these sharp bands, a weaker blueshifted band at 726 and 910 cm⁻¹ can be observed, which correlate with the main bands when the Ti or NO concentrations vary, and appear as doublets in the spectra obtained with NO isotopic mixtures ($^{14}N^{16}O/^{15}N^{16}O$ or $^{14}N^{16}O/^{14}N^{18}O$). They remain unaffected by the photolysis effects but disppear completely when the matrix is heated. These bands are thus probably due to a site effect of NTiO in the matrix (Figs. 3–5). The absorptions observed for the different isotopic species of NTiO are listed in Table 1, for the main, stable trapping site.

Two new, weaker bands at 1430.7 and 1791.5 cm^{-1} can be observed (Fig. 6), which correlate with the two strong bands at 700 and 900 cm^{-1} , over any change in experimental conditions (temperature, concentrations, NO isotopic effects). From the observed isotopic effects and relative intensities, these bands correspond to overtones of the bands located in Ti-N and Ti-O stretching spectral region, respectively. Their integrated intensities are much smaller than those of the fundamental bands $(I_{vTi-N}/I_{2vTi-N} = 350 \text{ and } I_{vTi-O}/$ $I_{2vTi-O} = 200$), and their isotopic shifts (¹⁴N/¹⁵N, ¹⁶O/¹⁸O) are nearly twice those observed for the corresponding fundamental bands. From a knowledge of fundamental and overtone frequencies, anharmonicity corrections ($\omega_e x_e$) have been



Fig. 5. Infrared spectra in the TiO stretching region (v_1 of NTiO and v_3 of OTiO) for various precursors of NO reacting with ground state Ti atoms in solid argon.

evaluated at -2.9 and -5.0 cm⁻¹ only for the Ti–N and Ti–O modes, respectively.

In the far-infrared region, one absorption band has been observed at 248.2 cm⁻¹ (Fig. 4) which correlated with the NTiO bands, and could be attributed to the bending mode NTiO. The bands are broadened by inhomogeneous effects (FWHM ≈ 2 cm⁻¹), and no titanium isotopic structure could be observed for this band, even with spectra recorded at a 0.1 cm⁻¹ resolution.

When the matrix is annealed, the NO dimerizes readily, and several bands are associated with titanium reactions with (NO)₂. The secondary reaction (Ti + 2NO) products such as TiO₂, TiO₂ (N_2) formed in these experiments do not originate from sample contamination by molecular oxygen, but from secondary insertion and recombination, as shown by isotopic labelling of these species when ¹⁸O-labelled NO is used (see the triplet isotopic structure of TiO₂ when a N¹⁶O/N¹⁸O mixture is used, which is indicated by dotted lines in Fig. 5). In addition to $OTiN_2O$, which has been discussed earlier, bands located at 1125.1 and 1581.5 cm⁻¹ could not be attributed to Ti-(n²-NO)₂ and Ti– $(n^1$ -NO)₂ products, respectively, as suggested in Ref. [10]. These bands were only observed as traces in some of our experiments, and their relative infrared intensity grew markedly when O_2 was added voluntarily in the samples.

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Ti isotopic structure ^a	¹⁴ NTi ¹⁶ O	¹⁵ NTi ¹⁶ O	¹⁴ NTi ¹⁸ O	Assignment			
Ti ^b	248.2	244.8	243.0	$v_3(0.3)$ bending mode			
⁴⁸ Ti	718.3	701.4	716.1	v_2 (0.96) "Ti–N" stretching mode			
⁴⁶ Ti, ⁴⁷ Ti	722.2, 720.2	705.4, 703.3	720.1, 718.3				
⁴⁹ Ti, ⁵⁰ Ti	716.5, 714.7	699.5, 697.7	714.1, 712.4				
⁴⁸ Ti	900.7	898.2	865.8	$v_1(1)$ "Ti–O" stretching mode			
⁴⁶ Ti, ⁴⁷ Ti	904.9, 902.7	902.4, 900.4	870.1, 867.9				
⁴⁹ Ti, ⁵⁰ Ti	898.7, 896.9	896.3, 894.3	863.8, 861.8				
Ti ^b	1430.7	1397.0	1426.4	$2v_2 (2.7 \times 10^{-3})$			
Ti ^b	1791.5	1785.9	c	$2v_1 (5.4 \times 10^{-3})$			

Observed frequencies in cm⁻¹ of ¹⁴NTi¹⁶O, ¹⁵NTi¹⁶O and ¹⁴NTi¹⁸O molecules isolated in argon matrix (relative intensities are in parentheses)

^a The natural titanium isotopic distribution is ⁴⁶Ti: 7.9%, ⁴⁷Ti: 7.3%, ⁴⁸Ti: 74.0%, ⁴⁹Ti: 5.5% and ⁵⁰Ti: 5.3%.

^bTitanium isotopic effects are unresolved.

^cOverlap with NO dimer absorption.



Fig. 6. Infrared spectra of the $2v_1$ and $2v_2$ regions of ²A' NTiO at 10 K in solid argon. For all samples, Ti/NO/Ar = 0.5/1/100. The stronger absorption near 1789 cm⁻¹ corresponds to unreacted ¹⁵N ¹⁸O.

Nevertheless, two bands at 1100 and 1531 cm⁻¹ increasing on annealing and disappearing with photolysis could be assigned to $Ti(NO)_2$ complexes. They exhibit triplets with NO isotopic mixtures ($^{14}N \, ^{16}O / ^{15}N \, ^{16}O$ or $^{14}N \, ^{16}O / ^{14}N \, ^{18}O$), which denotes a vibration of a species involving two equivalent NO bonds.

4. Discussion and vibrational analysis

The products of cocondensation of nitric oxide with Ti, as described previously, showed that the insertion reaction of Ti into the NO bond takes place without any energy activation, to give the NTiO species. A similar situation has been observed and discussed in the reaction of Ti atom with CO_2 molecules [9].

The results of the most recent theoretical studies [10], which have calculated the three harmonic frequencies for NTiO on the ground ²A' state, are given in Table 2. The agreement with the observed frequencies is reasonable, but if the isotopic shifts (¹⁴N ¹⁸O and ¹⁵N ¹⁶O) are very well reproduced for v_2 and v_3 modes, for the v_1 mode the error on the calculated isotopic shifts exceeds 40% (Table 2). The computed IR intensities for each mode are in qualitative agreement with the experimental relative intensities. The TiN and TiO stretching modes have comparable infrared intensities, but the low frequency bending mode is twice as intense as predicted.

Since the anharmonicity corrections are indeed very small for this molecule, semi-empirical harmonic force-field calculations were performed to test the information about the predicted bonding properties and molecular shape of NTiO. First, based on the equilibrium geometry calculated with DFT BP86 method in Ref. [10] ($r_{\text{TiO}} = 1.661$ Å, $r_{\text{TiN}} = 1.715$ Å and \angle NTiO = 105.8°), we searched the set of force constants which yielded an acceptable agreement with the experimental results, better than the ab initio force field. Next, to test the geometry, we varied the NTiO bond angle stepwise between 180° and 80° (the bond lengths are thus kept constant). For each given angle, the

Table 1

	v ₃ (bending)		v ₂ (Ti–N stretch)		v ₁ (Ti–O stretch)	
	Observed	Calculated ^a	Observed	Calculated	Observed	Calculated
¹⁴ N ⁴⁸ Ti ¹⁶ O	248.2	246.5	718.3	761.1	900.7	936.3
¹⁵ N ⁴⁸ Ti ¹⁶ O	244.8	243.1	701.3	744.4	898.2	932.2
Isotopic shifts	3.4	3.4	17.0	16.7	2.5	4.1

Table 2 Observed and calculated^a frequencies (cm⁻¹) of the various isotopic species of NTiO^b (²A')

^a DFT calculation BP86 [10].

^b The geometric parameters of the NTiO are $r_{\text{TiO}} = 1.661$ Å, $r_{\text{TiN}} = 1.715$ Å and $\angle \text{NTiO} = 105.8^{\circ}$.

best set of potential constants is searched for, giving the best overall agreement with the experimental isotopic shifts (14N 16O/15N 16O and ${}^{14}N{}^{16}O/{}^{14}N{}^{18}O)$ on all three v_1 , v_2 and v_3 modes. Fig. 7 shows the standard deviations between the experimental and calculated isotopic shifts (normalized to 100 cm^{-1}), as a function of the bond angle value. It is clear that the best results are obtained for a bond angle in the vicinity of that calculated by quantum chemical method $(\angle NTiO = 110^\circ \pm 5^\circ)$ (Table 3). The TiN, TiO and NTiO force constants are of the order of 3.56, 5.61 mdyn Å⁻¹ and 0.6 mdyn Å rad⁻², respectively. Calculations of the potential energy distribution



Fig. 7. Standard deviations on the difference between experimental and calculated isotopic shifts on the v_1 , v_2 and v_3 modes, normalized to 100 cm⁻¹. The error bars represent the experimental uncertainties on the isotope effects.

show that the TiN and TiO coordinates are only slightly coupled in the v_1 and v_2 modes (roughly a 90% TiO–10% TiN coordinate combination for the v_1 mode and a reverse combination for the v_2 mode) while the v_3 mode involves an almost pure bending motion. Our results also confirm that the titanium isotopic structure is well within the bandwidth for the v_3 mode.

Interestingly, the TiN bond force constant is found to be notably (\approx -40%) weaker than that of the TiO bond, thus, providing a clue for the preferred O-atom abstraction channel in the gas phase as deduced in the studies of Ritter [5], Campbell [7] and Naulin [4]:

$$\operatorname{Ti} + \operatorname{NO}_{\stackrel{\longrightarrow}{1}} \operatorname{NTiO}_{\stackrel{\longrightarrow}{2}} \operatorname{TiO} + \operatorname{N}, \quad E_{\operatorname{a}} = \Delta H_1 + E_2.$$

As discussed in Refs. [4,7], the total activation energy E_a in the gas phase is small and positive (\approx 3.6 kJ/mol), while the enthalpy change ΔH_1 is negative (the first step is exothermic) and E_2 not much larger in absolute value. In the condensed phase at low temperature, the reaction is quenched at the first step, most likely the internal energy of the NTiO insertion product is too small to overcome the second step activation energy, E_2 which is thus notably higher than E_a , and reach the abstraction channel. These results cast a serious doubt on the likelihood of a harpooning, or electron-jump mechanism as previously discussed for the gas phase reaction.

5. Conclusions

Reaction of ground state Ti atoms, produced by thermal effusion, and NO molecules at a low temperature in solid argon shows that the

NTiO	<i>v</i> ₃		v ₂		<i>v</i> ₁	
	Observed	Calculated	Observed	Calculated	Observed	Calculated
¹⁴ N ⁴⁸ Ti ¹⁶ O	248.2	248.1	718.3	718.5	900.7	900.6
¹⁴ N ⁴⁶ Ti ¹⁶ O	_c	249.3	722.2	722.4	904.9	904.7
¹⁴ N ⁴⁷ Ti ¹⁶ O	c	248.7	720.2	720.4	902.7	902.6
¹⁴ N ⁴⁹ Ti ¹⁶ O	c	247.6	716.5	716.6	898.7	898.6
¹⁴ N ⁵⁰ Ti ¹⁶ O	_c	247.0	714.7	714.8	896.9	896.9
¹⁵ N ⁴⁸ Ti ¹⁶ O	244.8	244.5	701.4	701.4	898.2	898.1
¹⁵ N ⁴⁶ Ti ¹⁶ O	c	245.7	705.4	705.4	902.4	902.3
¹⁵ N ⁴⁷ Ti ¹⁶ O	c	245.1	703.3	703.4	900.4	900.2
¹⁵ N ⁴⁹ Ti ¹⁶ O	c	244.0	699.5	699.5	896.3	896.1
¹⁵ N ⁵⁰ Ti ¹⁶ O	_c	243.4	697.7	697.7	894.3	894.2
¹⁴ N ⁴⁸ Ti ¹⁸ O	243.0	243.1	716.1	715.9	865.8	865.4
¹⁴ N ⁴⁶ Ti ¹⁸ O	_c	244.3	720.1	720.0	870.1	869.6
¹⁴ N ⁴⁷ Ti ¹⁸ O	_c	243.7	718.3	717.9	867.9	867.3
¹⁴ N ⁴⁹ Ti ¹⁸ O	_c	242.6	714.1	714.0	863.8	863.3
¹⁴ N ⁵⁰ Ti ¹⁸ O		242.1	712.4	712.1	861.8	861.4

Table 3 Observed and calculated^a frequencies (cm⁻¹) of the various isotopic species of NTiO^b

^a The force constants are $F_{\text{TIN}} = 3.56 \text{ mdyn } \text{Å}^{-1}$, $F_{\text{TIO}} = 5.61 \text{ mdyn } \text{Å}^{-1}$, $F_{\text{NTIO}} = 0.60 \text{ mdyn } \text{Å} \text{ rad}^{-2}$, $F_{\text{TIN,TIO}} = 0.95 \text{ mdyn } \text{Å}^{-1}$, $F_{\text{TIO,NTIO}} = 0.0 \text{ mdyn } \text{Å} \text{ rad}^{-1}$, $F_{\text{TIN,NTIO}} = 0.15 \text{ mdyn } \text{Å} \text{ rad}^{-1}$.

^b The geometric parameters of the NTiO are $r_{\text{TiO}} = 1.661$ Å, $r_{\text{TiN}} = 1.715$ Å and $\angle \text{NTiO} = 110^\circ$.

^cTi isotopic effects are unresolved.

 $Ti + NO \rightarrow NTiO$ takes place with no or very little activation energy. No metastable titanium mononitrosyl species could be detected under these conditions in contrast with late row transition metal atoms such as Ni. In this study, the detection of the third, bending fundamental and two overtone levels have completed our knowledge of the IR spectrum of the NTiO species. A normal coordinate analysis based on complete vibrational data for several isotopic species (¹⁴N Ti ¹⁶O, ¹⁵N Ti ¹⁶O and ¹⁴N Ti ¹⁸O, with the ⁴⁶Ti/⁴⁷Ti/⁴⁸Ti/ ⁴⁹Ti/⁵⁰Ti naturally occurring isotopes) confirms the result previous ab initio predictions of the molecular shape and spectral properties.

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