

Adsorption and Dimerization of NO Inside Single-Walled Carbon Nanotubes—An Infrared Spectroscopic Study

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The physical adsorption of NO on purified single-walled carbon nanotubes was investigated at low temperatures by means of transmission infrared spectroscopy. Ozone treatment followed by annealing was used as the method of opening the entry ports for adsorption into the interior of the nanotubes. The IR spectra show that the NO that is adsorbed inside nanotubes exists exclusively in its dimer form, with no infrared bands of the monomer visible at a sensitivity level of 5 mol % NO. The internally adsorbed NO dimer species observed is *cis*-(NO)₂, with ν_1 (symmetric) = 1853 cm⁻¹ and ν_5 (asymmetric) = 1754 cm⁻¹. Introduction of Xe into the system leads to selective displacement of the internally bound *cis*-(NO)₂ dimer. A large spectroscopic red shift of the symmetric (-0.80%) and the asymmetric (-1.96%) modes for *cis*-(NO)₂ adsorbed inside nanotubes [relative to gas-phase *cis*-(NO)₂] points to the strong interaction of the dimer with the nanotube interior. The enthalpy of dissociation of the adsorbed dimer molecule is 15.1 ± 0.7 kJ/mol.

Introduction

Single-walled carbon nanotubes exhibit excellent adsorption properties because of their high specific surface area and the enhancement of adsorption energy in their interior.¹ In addition, on the basis of modeling, it is expected that confinement effects will cause the dimerization of NO within the nanotubes under thermodynamic conditions that do not favor dimerization under nonconfined conditions.² Indeed, it is known that the enhancement of dimerization occurs in the micropores of activated carbon particles, where more than 98% of NO is found to be in the dimer form at 298 K.³

NO exists almost entirely in the dimeric form in the condensed phase,⁴ but only about 1% of the molecules in the gas phase are in the dimer form at its boiling point (121 K and 760 Torr).⁵ A number of NO dimers can coexist in the condensed phase, and *cis*-(NO)₂ is the most stable of the dimers.⁶ However, adsorbed NO can exist in its monomer form if there are binding sites where the NO-surface interaction is strong enough to prevent dimerization.⁷

In this work, we report studies of the adsorption of NO in opened single-walled nanotubes using transmission FTIR spectroscopy to discriminate *cis*-(NO)₂ dimers from other dimer forms and to investigate the presence of NO monomers at cryogenic temperatures.

Experimental Section

The SWNTs were obtained from Professor R. Smalley's group, Rice University, Houston, TX. They were produced by means of the pulsed laser vaporization technique and purified by HNO₃/H₂SO₄ treatment.⁸ The tube diameter distribution was centered near that of (10,10) SWNTs with a diameter of 13.6 Å. The length distribution was rather narrow, with a most probable length of 320 nm. This material was identical to that used in our previous studies.^{9–11}

All spectra were recorded at 4 cm⁻¹ resolution, with 1000 scans taken for averaging. CaF₂ pressed into a 7-mm-diameter

spot on a tungsten grid was used as the support material for the nanotubes of ~50-μg mass. An additional spot of CaF₂ was used as a reference to subtract the infrared absorbance of NO adsorbed on the support itself from the spectrum of the nanotube sample and its support. The experimental setup was described elsewhere.¹¹

As NO often contains appreciable amounts of impurities, the NO gas used in the experiments was purified in the following manner:¹² NO from a cylinder (Matheson) was first frozen at liquid nitrogen temperature (77 K) in a glass bulb, and then the liquid nitrogen was replaced with liquid oxygen (90 K). Then the NO was allowed to distill slowly into another evacuated bulb, which was cooled with liquid nitrogen. This permitted the separation of NO from less volatile compounds such as NO₂ and N₂O. Two cycles of purification were carried out, resulting in NO that showed almost no traces of impurities in its infrared spectrum.

The single-walled nanotubes were opened by oxidation with ozone gas at 300 K, followed by annealing in a vacuum at 863 K.¹¹ This procedure produces opened segments of SWNTs, as shown by earlier studies of the ozonation/annealing process.^{9,10,13} Because of the relatively high rate of destruction of ozone in the stainless steel IR cell containing the SWNT sample, four cycles of ozonation were carried out with initially 63% pure ozone at about 19 Torr total pressure. The procedure for preparing and storing high-purity O₃ is given in ref 14.

Results and Discussion

Infrared Spectra of *cis*-(NO)₂ Adsorbed in the Interior of SWNTs. Figure 1 shows two typical pairs of spectra taken under the same conditions through the sample containing adsorbed NO dimers and the bare CaF₂ reference. The spectra shown in Figure 1A were taken at 103 K and a NO pressure of 0.007 Torr. Figure 1B shows the same spectra at 137 K and a NO pressure of 2.85 Torr. It can be noticed that the bands at 1754 and 1853 cm⁻¹ are only observed in the spectra taken of the SWNTs and not in the CaF₂ reference spectra. Furthermore, these bands are weaker in the spectrum taken on nanotubes that

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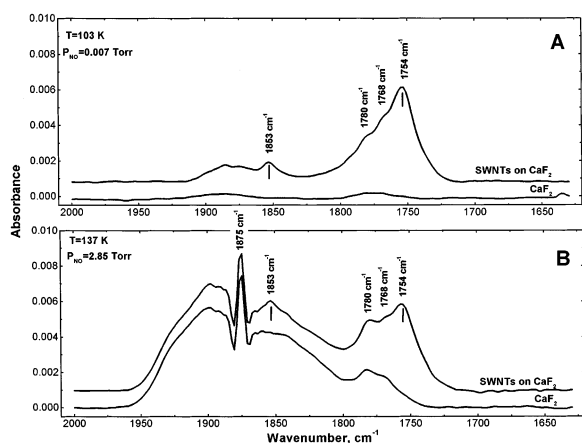


Figure 1. Formation of $(\text{NO})_2$ on SWNTs and CaF_2 support: (A) $T = 103 \text{ K}$ and $P_{\text{NO}} = 0.007 \text{ Torr}$, (B) $T = 137 \text{ K}$ and $P_{\text{NO}} = 2.85 \text{ Torr}$.

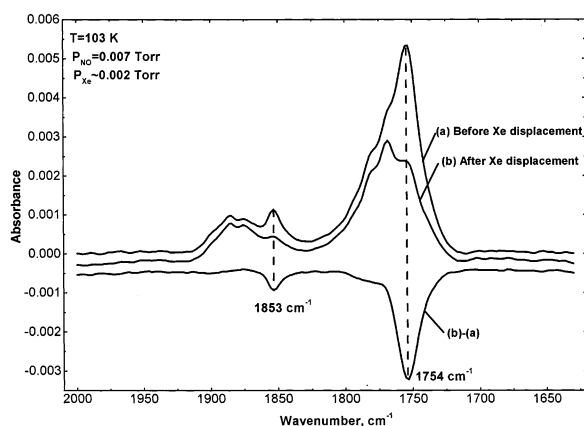


Figure 2. Xe displacement of $\text{cis}-(\text{NO})_2$ adsorbed on SWNTs at $T = 103 \text{ K}$ and $P_{\text{NO}} = 0.007 \text{ Torr}$. $P_{\text{Xe}} \approx 0.002 \text{ Torr}$.

have not been opened by the ozone/annealing treatment (not shown). These bands are assigned to $(\text{NO})_2$ dimer species adsorbed in the nanotube interior, as will be shown below. Bands at 1768 and 1780 cm^{-1} are present in both the spectra of the nanotubes and the CaF_2 reference, but their intensities are higher in the nanotube spectrum. We believe that the 1768 and 1780 cm^{-1} bands originate from $(\text{NO})_2$ species on sites that are not present in the nanotube interior. The spectra in Figure 1B also involve contributions from $\text{NO}(\text{g})$, centered at 1875 cm^{-1} , where the P, Q, and R branches are observed.

Xenon, which adsorbs strongly in the interior of SWNTs,¹⁵ has been shown to preferentially displace other molecules that have been preadsorbed in the nanotube interior.¹¹ We carried out a similar displacement experiment with NO adsorbed on the nanotubes. The results of $(\text{NO})_2$ displacement by Xe are shown in Figures 2 and 3. Figure 2 shows the original spectral data along with a difference spectrum, and Figure 3 shows Fourier self-deconvoluted spectra enhancing the resolution of the spectral features (GRAMS/AI software, Galactic Inc.). Only the two bands at 1754 and 1853 cm^{-1} significantly decrease after the addition of Xe, as can be seen from the difference spectra shown in Figure 2 and in the comparison deconvoluted spectra shown in Figure 3. Taking this fact into account, we assigned these bands respectively as the ν_5 (asymmetric stretch) and ν_1 (symmetric stretch) modes of $\text{cis}-(\text{NO})_2$ adsorbed in the interior of SWNTs.^{5,16} This assignment is supported by the assumption that a molecule adsorbed inside a nanotube should experience a relatively strong interaction with the curved walls. Thus, a comparatively strong spectroscopic red shift can be expected in the IR spectra, which is indeed observed. A

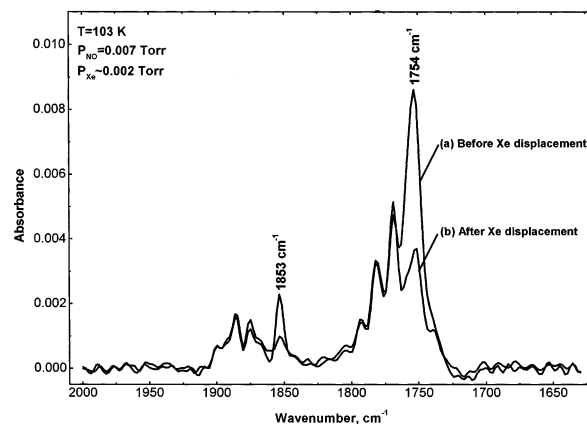


Figure 3. Fourier self-deconvolution of adsorbed $\text{cis}-(\text{NO})_2$ infrared spectra before and after Xe displacement.

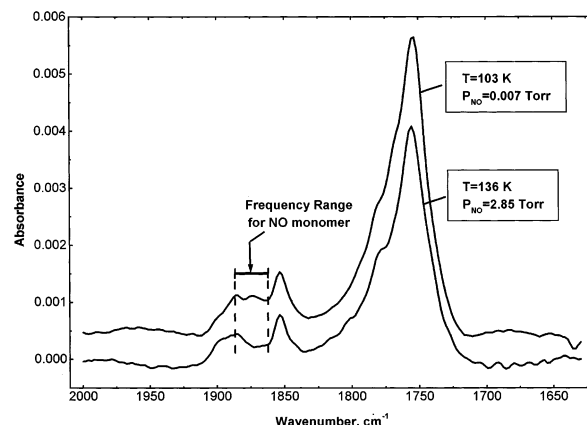


Figure 4. Evidence of absence of NO monomer on SWNTs. Spectra were obtained following NO adsorption by subtraction of the spectrum on CaF_2 from the spectrum on SWNTs and CaF_2 .

TABLE 1: Vibrational Frequencies of $\text{cis}-(\text{NO})_2$ Adsorbed on Various Carbon Surfaces and Gas-Phase $\text{cis}-(\text{NO})_2$

surface	$\nu_1(\text{NO})_2$ (sym) (cm^{-1})	$\nu_5(\text{NO})_2$ (asym) (cm^{-1})	ref
graphite film	1863	1768	17
diamond film	1866	1767	17
C_{60}	1858, 1853	1765, 1755	18
SWNTs (interior)	1853	1754	this work ^a
gas phase	1868	1789	5

^a Comparison with gas-phase $\text{cis}-(\text{NO})_2$ frequencies indicates that the red shift for $\nu_1(\text{sym}, 1853 \text{ cm}^{-1}) = -0.80\%$, and the red shift for $\nu_5(\text{asym}, 1754 \text{ cm}^{-1}) = -1.96\%$.

comparison with the frequencies observed for $\text{cis}-(\text{NO})_2$ adsorbed on exterior carbon surfaces^{17,18} and $\text{cis}-(\text{NO})_2$ in the gas phase is presented in Table 1.

NO Monomer Studies. NO in its monomeric form absorbs at 1875 cm^{-1} in the gas phase.⁵ Figure 4 shows the spectra of NO adsorbed on SWNTs at two different temperatures and NO pressures with the spectra of NO adsorbed on the bare CaF_2 reference subtracted. In the case of the 136 K spectrum, the pressure was adjusted to 2.85 Torr to obtain approximately the same intensity of $\text{cis}-(\text{NO})_2$ as in the spectrum taken at 103 K . It is remarkable that the profiles of the two spectra are very similar. The close similarity between the spectra at two temperatures and two NO pressures in Figure 4 indicates that no detectable monomeric NO is produced by working at higher pressure and temperature in the temperature range $103\text{--}136 \text{ K}$. As for the experiment shown in Figure 2, Xe displacement experiments at 2.85 Torr and 136 K (data not shown) indicate

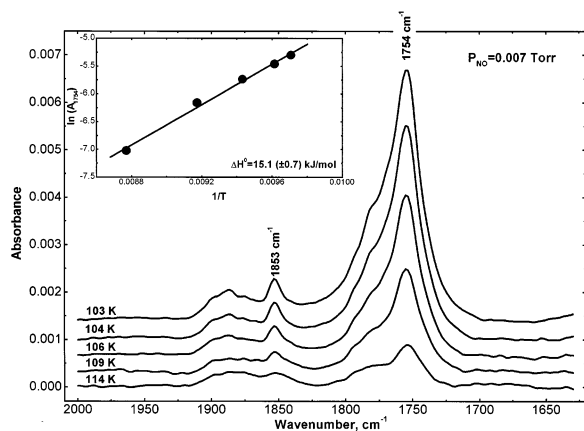


Figure 5. Equilibrium temperature dependence of IR spectra on SWNTs for NO adsorption in the temperature range of 103–114 K at $P_{\text{NO}} = 0.007$ Torr.

that the amount of monomer displaced by Xe is not greater than the level of noise in the 1875 cm^{-1} region. Using the relative IR absorption coefficients for NO and *cis*-(NO)₂ measured elsewhere,^{19,20} we estimate that the maximum amount of adsorbed NO monomer is less than 5 mol % at 2.85 Torr and 136 K.²¹

Thermal Dissociation of Confined *cis*-(NO)₂. We investigated the dependence of the IR spectra of adsorbed *cis*-(NO)₂ on temperature under equilibrium conditions at constant NO pressure as shown in Figure 5. This experiment permits the construction of a van't Hoff plot, which allows for the measurement of ΔH° for the change in state occurring. This method has been successfully employed in other infrared studies of reversibly bound adsorbed species.²² A strong temperature dependence for the 1754 cm^{-1} band is observed, and a similar dependence is also found for the 1853 cm^{-1} band. The van't Hoff plot is shown as an inset in Figure 5, and it yields $\Delta H^\circ = 15.1 \pm 0.7\text{ kJ/mol}$ for the depletion of *cis*-(NO)₂ adsorbed in the nanotube interior. The dissociation energy for the *cis*-(NO)₂ dimer given in the literature ranges from 7.6 to 15 kJ/mol,^{2,4} suggesting that the process being witnessed is the conversion of internally bound *cis*-(NO)₂ to NO(g) by the breaking of the N–N bond in the dimer. During this dissociation process, no absorbance due to the formation of adsorbed NO monomer is observed in the $1875\text{--}1862\text{ cm}^{-1}$ region, consistent with the results of Figure 4. Thus, considering the experiments of both Figure 3 and Figure 4, to within the sensitivity limits of the infrared measurement, adsorbed NO does not exist at significant levels in equilibrium with adsorbed *cis*-(NO)₂ in the interior of the SWNTs over the temperature range 103–136 K.

Comparison with Theoretical Calculations. These results disagree with recent calculations of the NO/(NO)₂ equilibrium ratio for adsorption in the interior of SWNTs.² The calculations show that, although *cis*-(NO)₂ dimers are preferred, there is an equilibrium between dimers and monomers inside nanotubes in the temperature and pressure range studied here. Under the most favorable conditions of our experiment for monomer formation ($T = 136\text{ K}$, $P_{\text{NO}} = 2.85\text{ Torr}$), where adsorbed NO was not detected by infrared spectroscopy at a sensitivity level of 5 mol %, the calculations indicate that the equilibrium mole fraction of NO should be about 70 mol %.

Summary

The following results have been obtained in our study of NO adsorption on opened (10,10) single-walled nanotubes:

(1) NO adsorbed on nanotubes exists predominantly in its *cis*-dimer form, exhibiting two vibrational modes: the ν_1 (symmetric) N=O stretching mode at 1853 cm^{-1} and the ν_5 (asymmetric) N=O stretching mode at 1754 cm^{-1} .

(2) Small absorbances observed at 1780 and 1768 cm^{-1} , which appear as shoulders on the dominant band at 1754 cm^{-1} , might be due to a small fraction of *cis*-(NO)₂ dimers present on other types of sites in the SWNT samples supported on CaF₂.

(3) Xe has been shown to displace *cis*-(NO)₂ in the interior of the SWNTs, in agreement with previous experiments where this displacement effect has also been observed.

(4) NO monomer adsorbed on SWNTs is not observed in equilibrium with *cis*-(NO)₂ dimers in the ranges of temperature (103–136 K) and pressure (0.001–2.85 Torr) employed. The limit of accuracy of the infrared spectroscopic measurements is 5 mol % NO.

(5) The dissociation at equilibrium of internally adsorbed *cis*-(NO)₂ dimers occurs to produce NO(g) in the temperature range 103–136 K with $\Delta H^\circ = 15.1 \pm 0.7\text{ kJ/mol}$, consistent with the known dissociation energy of the dimer.

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