Langmuir **2006,** *22,* 2258−2263

Infrared Spectroscopic Study of O_2 Interaction with Carbon Nanotubes

V. M. Bermudez*

Electronics Science and Technology Division, Naval Research Laboratory, Washington, D.C. 20375-5320

L. M. Ericson†

Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375-5320

Received September 19, 2005. In Final Form: December 21, 2005

Infrared reflection−absorption spectroscopic measurements have been performed on single-wall carbon nanotubes (SWNTs), cleaned by heating to ~500 °C in vacuo, during exposure to pure $^{16}O_2$ or $^{18}O_2$ at room temperature and at pressures of up to ~630 Torr. No vibrational signature of any form of adsorbed O is detected. However, structure is seen which is very similar to that observed for the adsorption of atomic H or D and which indicates changes in the SWNT vibrational spectrum. The close similarity between the spectra for atomic H and D, on one hand, and O_2 on the other is an unexpected result. Changes are also noted in the broad background extending throughout the mid-IR which arises from the Drude contribution to the reflectance. All these effects increase with O_2 exposure and are essentially irreversible upon evacuation of the gas. The results are consistent with other data indicating that O_2 interacts only weakly with, and does not chemisorb on, pristine regions of the SWNT under these conditions. The small and irreversible effects seen upon O_2 exposure are interpreted in terms of enhanced chemisorption, at or near defective regions of the SWNT wall, which saturates at a low O coverage.

1. Introduction

Molecular adsorption on single-wall carbon nanotubes (SWNTs) is an important subject in the development of chemical sensors and electronic devices[1] based on these materials. One example is the reversible decrease in resistivity[2] that occurs when SWNTs are exposed to an atmosphere of O_2, which may be related to a change in the properties of the metal contact[3] rather than to a direct SWNT/O_2 interaction. Questions concerning the role of chemisorption in this O_2 effect make a vibrational-spectroscopic study relevant at this time. Oxygen-containing functional groups on SWNTs, either as-grown or after oxidation by thermal or wet-chemical treatments, have been extensively studied using infrared (IR) spectroscopy.[4−8] However, there has been, to our knowledge, little investigation of either physi- or chemisorption of O_2 using vibrational spectroscopy. Previous adsorption studies have used either X-ray photoemission spectroscopy[9] (XPS) or temperature-programmed desorption[10] (TPD) to investigate the interaction of O_2 with SWNTs at low temperature (≤150 K) under ultrahigh vacuum (UHV) conditions. No evidence is found for species that remain after desorption of physisorbed molecular O_2 above 150 K or for adsorption under low-pressure ($<10^{-6}$ Torr) steady-state conditions at higher temperatures. However, it is difficult to relate such data to processes that might occur at room temperature in an atmosphere of air which is the condition appropriate to the operation of SWNT-based sensors and electronic devices.

The present work "crosses the pressure gap" and investigates the O_2/SWNT interaction at room temperature under steady-state conditions in several hundred Torr of O_2. The experiments make use of polarization-modulated IR reflection−absorption spectroscopy (PM-IRRAS) which has recently[11] been applied to the study of weakly adsorbed species on SWNTs under steady-state conditions during exposure to reagents. This is accomplished by depositing the SWNTs as a thin layer (see below) on a metallic substrate and obtaining reflectance data at a high (~82°) angle of incidence. The experiment is thus governed by the so-called "metal surface selection rule" which mandates that the only observable adsorbate vibrational modes are those having a finite component of the dynamic dipole moment in a direction parallel to the surface normal.[12] These will absorb p-polarized radiation; whereas, s-polarized light will not interact with adsorbates. The PM-IRRAS experiment then measures $\delta(\Delta R/R)$ where $\Delta R/R \equiv (R_s - R_p)/(R_s + R_p)$ and R_s (R_p) is the s- (p-) polarized reflectance. The quantity $\delta(\Delta R/R)$ is the difference between $\Delta R/R$ recorded before and after introduction of the O_2 and represents the effect of gas exposure on the sample.

The PM-IRRAS technique, when employed in the manner used here, is sensitive only to adsorbates and not to unpolarized absorption by isotropic gas-phase molecules. This permits surface species to be observed in the presence of high pressures of IR-

---

* To whom correspondence should be addressed. Phone: +1-202-767-6728. Fax: +1-202-767-1165. E-Mail: victor.bermudez@nrl.navy.mil.

† NRL/NRC Resident Research Associate.

[1] Snow, E. S.; Perkins, F. K.; Houser, E. J.; Badescu, S. C.; Reinecke, T. L. *Science* **2005**, *307*, 1942.

[2] Collins, P. G.; Bradley, K.; Ishigami, M.; Zettl, A. *Science* **2000**, *287*, 1801.

[3] Cui, X.; Freitag, M.; Martel, R.; Brus, L.; Avouris, Ph. *Nano Lett.* **2003**, *3*, 783. Derycke, V.; Martel, R.; Appenzeller, J.; Avouris, Ph. *Appl. Phys. Lett.* **2002**, *80*, 2773.

[4] Feng, X.; Matranga, C.; Vidic, R.; Borguet, E. *J. Phys. Chem. B* **2004**, *108*, 19949.

[5] Kuznetsova, A.; Mawhinney, D. B.; Naumenko, V.; Yates, J. T., Jr.; Liu, J.; Smalley, R. E. *Chem. Phys. Lett.* **2000**, *321*, 292.

[6] Matranga, C.; Chen, L.; Smith, M.; Bittner, E.; Johnson, J. K.; Bockrath, B. *J. Phys. Chem. B* **2003**, *107*, 12930. Matranga, C.; Bockrath, B. *J. Phys. Chem. B* **2004**, *108*, 6170.

[7] Mawhinney, D. B.; Naumenko, V.; Kuznetsova, A.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **2000**, *122*, 2383.

[8] Zhang, J.; Zou, H.; Qing, Q.; Yang, Y.; Li, Q.; Liu, Z.; Guo, X.; Du, Z. *J. Phys. Chem. B* **2003**, *107*, 3712.

[9] Goldoni, A.; Larciprete, R.; Petaccia, L.; Lizzit, S. *J. Am. Chem. Soc.* **2003**, *125*, 11329. Goldoni, A.; Petaccia, L.; Gregoratti, L.; Kaulich, B.; Barinov, A.; Lizzit, S.; Laurita, A.; Sangaletti, L.; Larciprete, R. *Carbon* **2004**, *42*, 2099.

[10] Ulbricht, H.; Moos, G.; Hertel, T. *Phys. Rev. B* **2002**, *66*, 075404.

[11] Bermudez, V. M. *J. Phys. Chem. B* **2005**, *109*, 9970.

[12] Chabal, Y. J. *Surf. Sci. Rep.* **1988**, *8*, 211.

10.1021/la052548v CCC: $33.50

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **DEC 2005**	2. REPORT TYPE	3. DATES COVERED **00-00-2005 to 00-00-2005**

4. TITLE AND SUBTITLE **Infrared Spectroscopic Study of O2 Interaction with Carbon Nanotubes**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Naval Research Laboratory,Electronics Science and Technology DiVision,4555 Overlook Avenue SW,Washington,DC,20375**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S)
	11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**6**	

absorbing gaseous reagents and is a distinct advantage in studies of SWNTs which interact only weakly with many species. While O_2 is of course transparent in the mid-IR, a second advantage of PM-IRRAS is relevant to the present work. Because only the p- and not the s-polarized radiation couples to adsorbate vibrational modes,[11] R_s functions in effect as a reference signal. This makes PM-IRRAS a double-beam experiment, even though there is physically only one beam, and imparts a high degree of baseline stability to the measurement of $\delta(\Delta R/R)$. This stability makes it possible to detect, reliably and reproducibly, small adsorbate-related features and small changes in the broad reflectance background, both of which are important in understanding the O_2/SWNT interaction.

2. Experimental Details

Most of the relevant experimental details, including descriptions of the apparatus, the sample, and the PM-IRRAS technique, have been given previously.[11] Briefly, the SWNT sample was deposited by spraying a suspension in *N*,*N*-dimethylformamide (DMF, ~5 mg/L) from an airbrush onto a polycrystalline Al substrate at about 200 °C. The SWNT stock was single-walled HiPco material obtained from Carbon Nanotechnologies, Inc. (CNI) with a stated purity of about 96% and was used without further processing. The SWNT layer thickness is estimated to be a few hundred Ångstroms, based on numerical simulation of the broad background in $\delta(\Delta R/R)$ observed after adsorption of dimethyl methylphosphonate. Further details are given in ref 11.

The $^{16}O_2$ (Matheson Gas, 99.995% nominal chemical purity) or $^{18}O_2$ (Cambridge Isotopes, 97% nominal isotopic purity) was admitted through a leak valve. The gases were checked for purity using a quadrupole mass spectrometer in the UHV chamber, as well as by the unpolarized IR transmission spectrum through the chamber when filled with the gas. Pressures were measured with cold-cathode ionization, thermocouple, or capacitance gauges as appropriate. No hot-filament gauges were used to avoid electronic excitation[13] of the O_2. Following a high-pressure exposure, the gas was first evacuated using a turbopump then a cryopump. Use of the ion pump during exposure was avoided, again to prevent excitation of the O_2. Theoretical studies[14] have shown that O_2 interaction with SWNTs can be promoted by excitation of the molecule into a singlet electronic state. All O_2 exposures and PM-IRRAS experiments were performed with the sample at room temperature.

The SWNT/Al sample was cleaned by heating in vacuo to ~500 °C. The thin native oxide on the Al substrate inhibits reaction at the interface, and no change in sample characteristics was noted during the course of many annealing treatments. To characterize the sample, Raman spectra were collected (in air) with a Renishaw Microraman 1000 with three excitation wavelengths (energies): an Ar^+ laser at $\lambda_{exc} = 514$ nm (2.41 eV), a He−Ne laser at $\lambda_{exc} = 633$ nm (1.96 eV), and a diode laser at $\lambda_{exc} = 785$ nm (1.58 eV). Figure 1 shows Raman data for the SWNT/Al sample obtained with the three sources following completion of all IR experiments. The *D*-band relative intensity is typical for aggregated SWNTs. Structural defects (such as the Stone−Wales defect[15]), mechanical deformation, and impurities have all been shown[16,17] to increase the intensity of the SWNT *D*-band. It is also known[18] that direct contact with substrates, particularly metals, can further increase the *D*-band intensity for SWNT thin films. In the following, we will use the term "defect" as a generic label for all factors contributing to the *D*-band intensity.

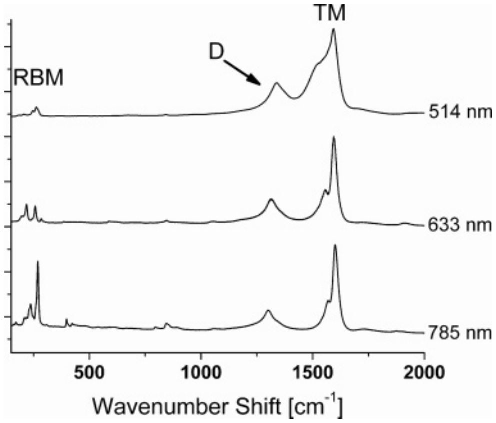

Figure 1. Raman spectra for the SWNT/Al sample at three excitation wavelengths. The three primary Raman bands are labeled—the radial breathing modes (RBM), the disorder band (D), and the tangential modes (TM). The spectra are typical for an aggregated SWNT sample.

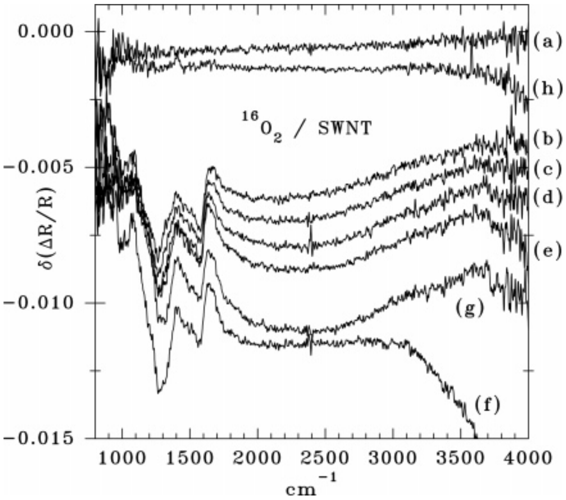

Figure 2. PM-IRRAS data for a SWNT/Al sample in increasing pressures of $^{16}O_2$ and after evacuation. (a) "Baseline", difference between two successive data sets before O_2; (b) 4×10^{-5} Torr; (c) 1 mTorr; (d) 100 mTorr; (e) 40 Torr; (f) 630 Torr; (g) evacuated to ~10^{-7} Torr following (f). Spectra (b)−(g) are referenced to $\Delta R/R$ of the SWNT/Al sample in vacuo before exposure to O_2. Note that spectra (a)−(g) are labeled in the order in which they were recorded. The shift in the background toward higher energy in (f) is an experimental artifact (see text). The structure near 2400 cm^{-1} in some spectra is an artifact of the signal-processing electronics. The relative magnitudes of $\delta(\Delta R/R)$ are quantitative, i.e., the spectra have not been rescaled or repositioned vertically. Trace (h) was recorded for bare Al in 9.4 Torr O_2 and referenced to $\Delta R/R$ in UHV. Prior to admitting O_2, the bare Al was heated in vacuo to 510 °C.

3. Results and Discussion

3.1. Lower O_2 Pressures. Figure 2 shows a series of spectra recorded during exposure to increasing pressures of $^{16}O_2$. Up to ~100 mTorr, the exposure was dynamic, in that the gas flowed continuously through the chamber while being pumped by the throttled cryopump. The leak rate was balanced against the pumping rate so as to maintain a constant pressure. This was done to reduce the influence (if any), at low O_2 pressures, of species desorbed from the internal surfaces of the chamber. Exposures at higher pressures were done by static backfilling. In the $\delta(\Delta R/R)$ difference spectra as defined above, a "positive" (upward-pointing) feature would represent increased absorption

---

[13] Pianetta, P.; Lindau, I.; Garner, C. M.; Spicer, W. E. *Phys. Rev. B* **1978**, *18*, 2792.

[14] Grujicic, M.; Cao, G.; Rao, A. M.; Tritt, T. M.; Nayak, S. *Appl. Surf. Sci.* **2003**, *214*, 289.

[15] Buongiorno Nardelli, M.; Yakobson, B. I.; Bernholc, J. *Phys. Rev. Lett.* **1998**, *81*, 4656.

[16] Furtado, C. A.; Kim, U. J.; Gutierrez, H. R.; Pan, L.; Dickey, E. C.; Eklund, P. C. *J. Am. Chem. Soc.* **2004**, *126*, 6095.

[17] Dillon, A. C.; Yudasaka, M.; Dresselhaus, M. S. *J. Nanosci. Nanotechnol.* **2004**, *4*, 691. Dillon, A. C.; Parilla, P. A.; Alleman, J. L.; Gennett, T.; Jones, K. M.; Heben, M. J. *Chem. Phys. Lett.* **2005**, *401*, 522.

[18] Sangaletti, L.; Pagliara, S.; Parmigiani, F.; Galinetto, P.; Larciprete, R.; Lizzit, S.; Goldoni, A. *Eur. Phys. J. B* **2003**, *31*, 203.

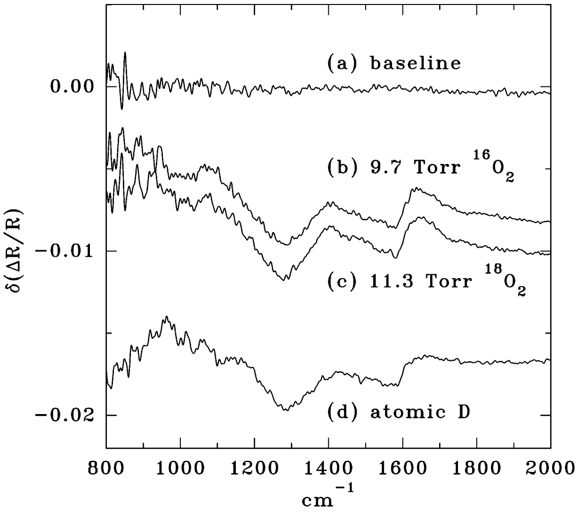

Figure 3. PM-IRRAS data in the structured region of the spectrum. (a) "Baseline", difference between two successive data sets for 9.7 Torr $^{16}O_2$ showing the absence of a significant change *during* data collection at a fixed pressure. (b),(c) Data recorded in O_2 at the indicated pressures. (d) Data obtained after exposure to atomic D (ref 11). Acquisition of each data set (b,c,d) began with a clean SWNT/Al starting surface. The relative magnitudes of $\delta(\Delta R/R)$ are quantitative, i.e., the different spectra have not been rescaled or repositioned vertically.

caused by exposure to O_2 while "negative" (downward-pointing) structure is due to SWNT absorption that is removed by O_2.

At the lowest pressure used here ($\sim 1 \times 10^{-6}$ Torr), two predominantly negative features are seen, near 1600 and 1280 cm^{-1}, which are very similar to structure observed[11] following exposure to atomic H or D. Figure 3 compares the data previously reported for atomic D with results for $^{16}O_2$ and $^{18}O_2$. The three spectra are very similar, and furthermore, there is no measurable O_2 isotope shift. This indicates that the structure is not directly related to a vibrational mode of any form of adsorbed D or O. The structure in the $\delta(\Delta R/R)$ difference spectrum instead arises from a small (see below) adsorbate-induced modification of the SWNT vibrational spectrum. The monotonic shift in the background with increasing exposure will be discussed below.

Recently Kim et al.[19] have analyzed the mid-IR absorption spectrum of SWNTs, including the symmetry assignments for IR-active first- and second-order transitions. For tubes lying essentially flat in the form of a thin film on a metal substrate, only those fundamentals of E_{1u} symmetry are detectable, given the selection rule noted above, since these modes are polarized perpendicular to the SWNT axis.[20] After the sample was annealed in vacuo at 1400 °C to desorb contaminants, the only E_{1u} fundamentals in the 680−1800 cm^{-1} range were found[19] to be a closely spaced pair at 1564 and 1585 cm^{-1} and a mode at 854 cm^{-1}. For a thin film of SWNTs on Cu, the only modes observed[21] in IRRAS occurred at about 1590 and 868 cm^{-1}, which is consistent with the symmetry assignments. Hence, any other absorptions detected in IRRAS under these conditions would have to be extrinsic effects resulting from adsorbed impurities (i.e., functional groups), defects, or a lowering of symmetry caused by disorder. Note that the difference spectra in Figures 2 and 3 show only those modes that are both IR-allowed and affected by exposure to H(D) or to O_2. The 868 cm^{-1} E_{1u} mode is apparently not significantly affected by adsorption since it does not appear in the difference spectra.

Previous results[4−8] for SWNTs subjected to oxidation (as distinct from chemisorption) with ozone or with strong acids, or oxidized during growth, show structure in the ~1550−1750 cm^{-1} range arising from the >C=O stretching mode of various carbonyl species. For such species, depending on the degree of C motion in the normal mode, the expected isotope shift factor is in the range of from $(\mu_{18}/\mu_{16})^{1/2} = 1.025$ (where $1/\mu_x = 1/m_x + 1/m_C$) to $(m_{18}/m_{16})^{1/2} = 1.061$. For a mode at 1600 cm^{-1}, this corresponds to a shift of from 40 to 98 cm^{-1}, which would be easily detectable in the present experiment. Hence, unlike in the case of oxidation,[4−8] carbonyl species are not being observed here under the much milder conditions of a chemisorption experiment, which may be viewed as a "titration" of reactive sites in the SWNT wall.

The negative ~1600 cm^{-1} band corresponds to the removal of sp^2-bonded >C=C< groups in the SWNT wall.[4−8] It is also close to the band previously observed[21] in IRRAS at about 1590 cm^{-1}, due to SWNT fundamentals of E_{1u} symmetry (see above). In the previous study of H and D adsorption,[11] it was shown that only a small fraction (~10%) of the total >C=C< intensity was removed by the adsorption of H or D, beyond which little or no further change in the spectrum was observed. It was suggested, partly on the basis of this saturation at a low coverage, that chemisorption occurs preferentially at or near some form of defect site. The *quantitatively* similar behavior shown in Figures 2 and 3 for two very different reagents, atomic D and molecular O_2, is an unexpected result that indicates a similar chemisorption process for both species.

The derivative-like line shape seen near 1600 cm^{-1} for O_2, and also to a lesser extent for H and D, probably arises from a small (i.e., less than the line width) adsorption-induced shift to higher energy in the >C=C< stretching-mode. Previous work on the oxidation of SWNTs in acids[8] also revealed a small shift to higher energy (~24 cm^{-1}) in the >C=C< stretching mode following reaction, indicating that this mode is perturbed by the presence of O. It is recalled that the $\delta(\Delta R/R)$ spectrum is a difference quantity obtained by subtracting $\Delta R/R$ in vacuo from $\Delta R/R$ in O_2. A band which undergoes a small shift in energy will then appear with a first-derivative shape in the difference spectrum. The presence of a similar (although smaller) effect for H and D (Figure 3) argues against any direct involvement of an adsorbate vibration in the line shape.

The broad structure near 1280 cm^{-1} is close in energy to the *D*-band commonly observed in Raman spectra[16,17,22] of SWNTs (and also in IR data[4−7]) and ascribed to a Raman-inactive mode that is made allowed by the presence of defects. For the present sample, the *D*-band occurs (see Figure 1) at 1296 cm^{-1} for $\lambda_{exc} = 785$ nm. There are no E_{1u} fundamentals near this energy;[19] however, there are A_{2u} modes at 1262 and 1369 cm^{-1} (and also at 1541 cm^{-1}). As noted above, these are dipole-forbidden in the present IRRAS experiment but could become allowed if the symmetry were sufficiently reduced by disorder. These symmetry considerations are consistent with the identification of the structure near 1280 cm^{-1} as a "fingerprint" for defects or disorder. For simplicity, this band will be referred to in the following discussion as "the *D*-band feature", but it might equally well be termed a "disorder-allowed A_{2u} mode".

Figures 2 and 3 again show an adsorption-induced decrease in the intensity of this mode which is independent of O_2 isotope and which is virtually identical to the effect seen for H. It is

---

(19) Kim, U. J.; Liu, X. M.; Furtado, C. A.; Chen, G.; Saito, R.; Jiang, J.; Dresselhaus, M. S.; Eklund, P. C. *Phys. Rev. Lett.* **2005**, *95*, 157402.

(20) Jishi, R. A.; Dresselhaus, M. S.; Dresselhaus, G. *Phys. Rev. B* **1993**, *47*, 16671.

(21) Kuhlmann, U.; Jantoljak, H.; Pfänder, N.; Bernier, P.; Journet, C.; Thomsen, C. *Chem. Phys. Lett.* **1998**, *294*, 237.

(22) Dresselhaus, M. S.; Dresselhaus, G.; Jorio, A.; Souza Filho, A. G.; Saito, R. *Carbon* **2002**, *40*, 2043.

important to note that the intensity of the 1280 cm^{-1} *D*-band feature, relative to that of the 1600 cm^{-1} $>C=C<$ mode discussed above, is essentially independent of O_2 exposure (Figure 2) and of the adsorbed species (Figure 3). *Taken together, these results indicate that the defective regions giving rise to the D-band feature are chemically active and that the small fraction (∼10%) of reactive $>C=C<$ sites are associated with these regions.* These results are consistent with those of a previous study[23] of gas evolution during the reaction between ozone and SWNTs annealed at 1273 K. There it was determined that about 5.5% of the sites are defect-related and are thus reactive with ozone. It was further concluded that a large fraction of these defect sites involve the SWNT wall and not the end caps.

It is recalled that the term “defect” is used here in reference to all factors that contribute to the Raman *D*-band. The present data show that such defects are reactive with H, D, and O_2, all of which affect the SWNT vibrational spectrum similarly; although, it is not possible at present to determine the exact chemical nature of these defects or the specific mode(s) of chemisorption (see below). The defect involved in H and D adsorption was further suggested[11] to be a break in the SWNT wall, based on the similarity of the C−H stretching spectrum to that of an alkane-like $-CH_2CH_3$ species and not to that of the “monohydride dimer” $>C(H)-C(H)<$, which is the theoretically predicted product of H-atom adsorption on an undamaged SWNT (e.g., refs 24 and 25). Formation of a species such as $-CH_2CH_3$ requires the breaking of C−C bonds in the SWNT wall, either before or during chemisorption.

A recent theoretical study[26] has found that SWNTs with a low coverage (0.1 monolayers) of adsorbed H are unstable with respect to opening of the wall, which raises the further possibility of H-induced defects. Experimental results[23,27] show SWNT defects to be reactive with ozone, and theoretical work[28] indicates that such defects are also reactive with O_2. Other theoretical work has suggested that several chemical species [i.e., NO_2 (ref 29), NH_3 (ref 30), and H_2O (ref 31)] react preferentially with SWNT defects. Indirect experimental verification was also obtained in the case of NH_3 and H_2O. Annealing to 1100 K in UHV, which is known to reduce the concentration of defects and impurities, inhibits NH_3 adsorption upon subsequent cooling to 94 K. For H_2O, rapid dissociative chemisorption is observed upon initial exposure, followed by little or no further chemisorption at higher exposures, which is consistent with a defect-activated process. Still other theoretical work[32,33] has indicated that strain in the SWNT wall leads to chemically active sites. However, direct experimental observation of chemisorption at SWNT defects (as seen in the PM-IRRAS difference spectra discussed above) has not to our knowledge been reported previously.

Unlike in the previously studied case[11] of H(D) adsorption, in which clear H(D) vibrational signatures were detected, no vibrational modes due to chemisorbed O are seen here. This is despite the very evident effects of O_2 on both the SWNT vibrational spectrum and the reflectance background (discussed below). As noted above, $>C=O$ carbonyl species are typically observed following oxidation of SWNTs. The $>C=O$ stretching mode has a relatively high oscillator strength in organic molecules and falls in the 1550−1750 cm^{-1} range in which there is no strong interference from SWNT absorption. In the present case of chemisorption at defect sites, it is possible that C−O−C ester groups may be the preferred mode of adsorption. These would be difficult, if not impossible, to detect in the present experiment for three reasons. First, as noted above, only a small fraction of the available sites are affected at saturation. Second, the ν_{as}(C−O−C) asymmetric stretch falls at about 1240 cm^{-1} in normal-incidence transmission IR data[4−8] for oxidized SWNTs. The corresponding ν_s(C−O−C) symmetric stretch lies ∼200 cm^{-1} lower in energy and is weaker than the asymmetric mode for vacuum-annealed SWNTs with adsorbed O. A weak mode at ∼1240 cm^{-1} would be overlapped by the “negative” band at about 1280 cm^{-1} (Figure 3) and would be difficult to detect, particularly if it were broad. Finally, for a C−O−C group in the wall of a SWNT, the dynamic dipole moment of the ν_{as}(C−O−C) mode would lie approximately parallel to the tube axis. This would make the dynamic dipole moment of this mode largely parallel to the metal surface plane (i.e., s-polarized) which would make it undetectable in the present IRRAS experiment (see Introduction).

3.2. Higher O_2 Pressures. Access to the “high-pressure” regime (i.e., several hundred Torr of O_2) enables an investigation of weakly adsorbed species at room temperature. Previously, the vibrational mode of molecular $^{16}O_2$ physisorbed on a C_{60} film at 20 K has been observed,[34] using high-resolution electron energy loss spectroscopy, at 190 meV (1532 cm^{-1}) vs the gas-phase value of 194 meV (1565 cm^{-1}). While it may seem, at first glance, unreasonable to expect to observe an adsorbed homonuclear diatomic in IRRAS, this has in fact been done in several studies. Any effect that removes the equivalence of the two atoms—such as, for example, the end-on adsorption of N_2 on Ni(110)[35] at 80 K—makes the dynamic dipole moment of the stretching mode nonzero. A more subtle effect has been reported[36] for O_2 adsorption on polycrystalline Pt at 80 K. Here the two O atoms remain essentially equivalent, but bonding occurs via charge transfer from the Pt 5d orbitals into the $2\pi^*$ antibonding orbital of the O_2 and produces a large red-shift in the O−O frequency vs the gas phase. The O−O stretching modulates the Pt 5d−O_2 $2\pi^*$ orbital overlap (and thus the charge transfer) which leads to a nonzero dynamic dipole moment along the surface-normal direction and a detectable IRRAS feature. However, neither of these processes appears to be in effect in the present case.

With increasing O_2 pressure, the features discussed above effectively saturate and exhibit only a small further increase in intensity while the broad and nearly structureless background shifts monotonically in the direction of a more negative $\delta(\Delta R/R)$. All these effects are essentially irreversible upon evacuation of the O_2 (cf. Figure 2g). This suggests that they originate in the low coverage of chemisorbed O discussed above, since any effect from physisorbed O_2 would be reversible upon evacuation (see below). As noted above, the effect of chemisorption of H or O_2 on the $>C=C<$ stretching-mode intensity indicates that only a small fraction of the available sites are affected at saturation.

---

[23] Mawhinney, D. B.; Naumenko, V.; Kuznetsova, A.; Yates, J. T., Jr.; Liu, J.; Smalley, R. E. *Chem. Phys. Lett.* **2000**, *324*, 213.

[24] Barone, V.; Heyd, J.; Scuseria, G. E. *J. Chem. Phys.* **2004**, *120*, 7169.

[25] Gülseren, O.; Yildirim, T.; Ciraci, S. *Phys. Rev. B* **2002**, *66*, 121401(R).

[26] Park, K. H.; Seo, K.; Lee, Y. H. *J. Phys. Chem. B* **2005**, *109*, 8967.

[27] Byl, O.; Liu, J.; Yates, J. T., Jr. *Langmuir* **2005**, *21*, 4200.

[28] Grujicic, M.; Cao, G.; Singh, R. *Appl. Surf. Sci.* **2003**, *211*, 166.

[29] Valentini, L.; Mercuri, F.; Armentano, I.; Cantalini, C.; Picozzi, S.; Lozzi, L.; Santucci, S.; Sgamellotti, A.; Kenny, J. M. *Chem. Phys. Lett.* **2004**, *387*, 356.

[30] Feng, X.; Irle, S.; Witek, H.; Morokuma, K.; Vidic, R.; Borguet, E. *J. Am. Chem. Soc.* **2005**, *127*, 10533.

[31] Ellison, M. D.; Good, A. P.; Kinnaman, C. S.; Padgett, N. E. *J. Phys. Chem. B* **2005**, *109*, 10640.

[32] Srivastava, D.; Brenner, D. W.; Schall, J. D.; Ausman, K. D.; Yu, M.; Ruoff, R. S. *J. Phys. Chem. B* **1999**, *103*, 4330.

[33] Astakhova, T. Yu.; Vinogradov, G. A.; Gurin, O. D.; Menon, M. *Izv. Akad. Nauk., Ser. Khim.* **2002**, 704; *Russ. Chem. Bull., Int. Ed.* **2002**, *51*, 764 (English translation).

[34] Niklowitz, P. G.; Li, Z. Y.; Jardine, A. P.; Luo, M. F.; Allison, W. *J. Chem. Phys.* **2004**, *120*, 10225.

[35] Brubaker, M. E.; Trenary, M. *J. Chem. Phys.* **1986**, *85*, 6100.

[36] Canning, N. D. S.; Chesters, M. A. *J. Electron Spectrosc. Relat. Phenom.* **1983**, *29*, 69.

The absence of a detectable coverage of chemisorbed O is consistent with the results of XPS experiments[9] at 150 K which show no detectable O 1s peak after an O_2 exposure of 0.1 Torr s (10^5 Langmuir). Since acquisition of a complete PM-IRRAS scan, under the present conditions, requires $\sim 10^3$ s, this is equivalent to the cumulative O_2 exposure incurred while recording data in an O_2 pressure of ~0.1 mTorr. Although XPS showed adsorption[9] when data were recorded at 150 K in a steady-state ambient of 7.5×10^{-8} Torr, no O 1s signal was observed at higher temperatures (150−300 K) even in 7.5×10^{-7} Torr of O_2. The "bucky-paper" samples used in ref 9 were cleaned by annealing in UHV to temperatures as high as 1800 K and are thus expected[4] to be less defective (and, therefore, less reactive[30] with O_2) than the present samples. In addition, TPD studies[10] show that O_2 condensed at 28 K on SWNTs (cleaned by heating to 1200 K in UHV) desorbs below ~100 K with no evidence of chemisorbed species that survive to higher temperature.

The present results extend these UHV measurements to steady-state conditions in high pressures of O_2 at room temperature and also give evidence of O_2-induced changes in SWNT structure that would not have been detectable in XPS or TPD. The results further suggest that the lack of an observable chemisorption effect at low temperature and low pressure is not simply the result of a small kinetic barrier that can be overcome by increasing temperature and/or pressure to ambient conditions.

At the highest pressures (Figure 2f), a pronounced shift in the background is observed, particularly toward the high-energy end of the spectrum. This is an experimental artifact caused by a minute shift in sample alignment due to the change in the pressure differential between the inside (partial vacuum) and outside (room air) of the bellows in the sample manipulator, which leads to a slight change in $R_s - R_p$. The effect on $\delta(\Delta R/R)$, which is large on the scale of Figure 2, is reversible upon evacuation (Figure 2g) and is also observed for a bare Al sample (with no SWNTs) and when filling with a high pressure of an inert gas (300 Torr of Ne).

The results presented thus far indicate the absence of any vibrational modes directly attributable to either O or O_2 in an O_2 pressure of ≤ 630 Torr at room temperature. It is, however, still possible that weakly adsorbed O_2 is present under steady-state conditions at high pressure but that the O_2 mode is simply too weak to detect in IRRAS (see above). It might then still be possible to detect adsorbed O_2 indirectly through its perturbation of the Drude contribution to the IR dielectric function which is recognizable as a change in the broad and essentially structureless SWNT reflectance background. For the reversible physisorption of dimethyl methylphosphonate (DMMP) on SWNTs under steady-state pressures of a few hundred mTorr, it was previously shown[11] that the background change could be described quantitatively by application of the Drude model. Adsorption affects both the carrier density (n) and the scattering lifetime (τ), and the background in $\delta(\Delta R/R)$ is found to be extremely sensitive to small changes in these quantities. Other groups[37−40] have also noted the sensitivity of the SWNT mid-IR reflectance background to the presence of adsorbates.

The monotonically increasing negative shift in the background seen in Figure 2b−f is accompanied by a gradual small increase in the ~1280 cm^{-1} peak intensity, beyond the initial large increase (Figure 2a,b), which indicates a continued slow uptake of small amounts of O. In contrast, there is little or no difference in the adsorbed O coverage for Figure 2f,g, which presents data obtained before and after evacuation of a high-pressure O_2 ambient. Consistent with this, there is also little or no difference in the background intensity after account is taken of the experimental artifact noted above. With the definition of $\delta(\Delta R/R)$ given above, the negative background shift across the mid-IR corresponds to an adsorption-induced decrease in the Drude contribution to the SWNT reflectance.[11,37−40]

Thus, in this experiment, the adsorption of O_2 is detected not by direct observation of adsorbate resonances but through alteration of the free-carrier (Drude) contribution to the reflectance background which is very sensitive to adsorbates. However, it is clear that the background shift seen in Figure 2 is not due to physisorbed O_2 since it is not reversible upon evacuation. On the other hand, previous results[9,10] indicate that any O_2 physisorption occurring in a high pressure of O_2 would have to be reversible upon evacuation. Hence, the background change is the result of the small coverage of chemisorbed O discussed above. Since chemisorption affects the structure of the SWNTs, as well as the free-carrier properties, quantitative modeling simply in terms of the Drude parameters, as was done[11] for DMMP, is not feasible in this case.

4. Summary

In conclusion, PM-IRRAS has been used to study SWNTs in high (up to ~630 Torr) pressures of O_2 at room temperature. The results are as follows.

(1) The features observed are virtually identical for $^{16}O_2$ and $^{18}O_2$ and are closely similar to those observed for adsorption of atomic H or D. The spectra are thus interpreted in terms of adsorption-induced changes in the SWNT vibrational spectrum.

(2) One of the effects observed is a decrease in the intensity of a mode near 1280 cm^{-1}, which we have ascribed to the presence of "defects", a term used here in reference to the combined effects of structural imperfections and disorder. It is concluded that such defects are chemically reactive with O_2 at room temperature, unlike pristine regions of the SWNT. The enhanced reactivity of defects toward O_2 has been predicted theoretically[28] but not previously observed experimentally. However, it is not possible with the present data to identify the specific mode(s) of O_2 reaction with these defects.

(3) Another result of O_2 exposure is a loss in intensity of the $>C{=}C<$ stretching mode of the SWNT wall, near 1600 cm^{-1}. The magnitude of the effect indicates that only ~10% of such sites are reactive. Upon saturation with H, D, or O_2 (i.e., exposure to a point beyond which little further change in the spectrum is detected), the relative intensities of the 1280 and 1600 cm^{-1} features are very similar for all adsorbates (cf. Figure 3). This indicates a correlation between defects and the reactive $>C{=}C<$ sites and suggests that the latter may be made reactive by the presence of a nearby defect. This result is consistent with previous theoretical and experimental results for other adsorbates.

(4) A shift in the broad mid-IR reflectance background is seen during O_2 exposure which is interpreted qualitatively in terms of an adsorption-induced decrease in the Drude contribution to the SWNT reflectance. In the previously examined case[11] of reversible physisorption of DMMP, the background behavior under steady-state conditions could be modeled quantitatively by varying the Drude parameters describing the free-carrier

---

(37) Bashkin, I. O.; Antonov, V. E.; Bazhenov, A. V.; Bdikin, I. K.; Borisenko, D. N.; Krinichnaya, E. P.; Moravsky, A. P.; Harkunov, A. I.; Shul'ga, Yu. M.; Ossipyan, Yu. A.; Ponyatovsky, E. G. *Pis'ma Zh. Eksp. Teor. Fiz.* **2004**, *79*, 280; *JETP Lett.* **2004**, *79*, 226 (English translation).

(38) Itkis, M. E.; Niyogi, S.; Meng, M. E.; Hamon, M. A.; Hu, H.; Haddon, R. C. *Nano Lett.* **2002**, *2*, 155.

(39) Wu, Z.; Chen, Z.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Hebard, A. F.; Rinzler, A. *Science* **2004**, *305*, 1273.

(40) Skákalová, V.; Kaiser, A. B.; Dettlaff-Weglikowska, U.; Hrnčariková, K.; Roth, S. *J. Phys. Chem. B* **2005**, *109*, 7174.

density and scattering lifetime. In the case of O_2, however, the SWNTs are themselves chemically modified; hence, the background behavior cannot be described quantitatively simply in terms of the changes in the Drude parameters alone.

(5) All the O_2 effects seen here are irreversible in that they are essentially unaffected by evacuation of the O_2 and are thus due to chemi- rather than physisorption. This indicates that they are not directly related to the *reversible* effects of O_2 on SWNT electronic properties that have been seen in other studies.[2,3] The present results support the previously given[3] interpretation of these reversible effects as originating in some process other than direct O_2/SWNT interaction.

Acknowledgment. This work was supported by the Office of Naval Research. This research was performed while L. Ericson held a National Research Council Research Associateship Award at the Naval Research Laboratory.

LA052548V