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**FINAL PROGRESS REPORT**  
**"Thermal and Electronic Excitation of Molecules Inside of**  
**Single Walled Nanotubes"**

41896-CH

~~DAAD19-00-1-0585~~

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**(1) Forward**

The adsorption of gases inside single walled nanotubes (SWNTs) could supply a unique method for the removal of toxic wastes and chemical warfare agents from air streams. We have investigated the sorptive properties of SWNTs using infrared spectroscopy and other surface spectroscopic methods. It is found that the deep adsorption potential well associated with the interior of SWNTs supplies strong adsorption sites which are occupied initially by molecules encountering the sorbent. Four molecules have been studied: CF<sub>4</sub>, CCl<sub>4</sub>, NO and CO<sub>2</sub>.

**(2) Table of Contents - None**

**(3) Appendices - None**

**(4) Statement of the Problem Studied**

Infrared spectroscopy, temperature programmed desorption spectroscopy, and NEXAFS (near edge X-ray absorption spectroscopy) have been employed to observe both the functional groups on the SWNT surface and the adsorbate molecules adsorbed on the inside and the outside of the nanotubes. The IR studies indicate that internally-bound molecules exhibit red shifts in the frequency of their fundamental vibrational modes and this may be used as an analytical tool to discriminate internal from external adsorption sites. The titles and abstracts of the six papers published are given below.

**(5) Summary**

- A. Kuznetsova, I. Popova, J. T. Yates, Jr., M. J. Bronikowski, C. B. Huffman, J. Liu, R. E. Smalley, H. H. Hwu and J. G. Chen, "Oxygen-containing Functional Groups on Single-Wall Carbon Nanotubes – NEXAFS and Vibrational Spectroscopic Studies," J. Am. Chem. Soc. 123, 10699 (2001).

Single-walled nanotubes (SWNTs) produced by plasma laser vaporization (PLV) and containing oxidized surface functional groups have been studied for the first time with NEXAFS. Comparisons are made to SWNTs made by catalytic synthesis over Fe particles in high-pressure CO, called HiPco material. The results indicate that the acid purification and cutting of single-walled nanotubes with either HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> or H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> mixtures produces the oxidized groups

(O/C = 5.5-6.7%), which exhibit both  $\pi^*(\text{CO})$  and  $\sigma^*(\text{CO})$  C K-edge NEXAFS resonances. This indicates that both carbonyl (C=O) and ether C-O-C functionalities are present. Upon heating in a vacuum to 500-600 K, the  $\pi^*(\text{CO})$  resonances are observed to decrease in intensity; on heating to 1073 K, the  $\sigma^*(\text{CO})$  resonances disappear as the C-O-C functional groups are decomposed. Raman spectral measurements indicate that the basic tubular structure of the SWNTs is not perturbed by heating to 1073 K, based on the invariance of the ring breathing modes upon heating. The NEXAFS studies agree well with infrared studies which show that carboxylic acid groups are thermally destroyed first, followed by the more difficult destruction of ether and quinone groups. Single-walled nanotubes produced by the HiPco process, and not treated with oxidizing acids, exhibit an O/C ratio of 1.9% and do not exhibit either  $\pi^*(\text{CO})$  or  $\sigma^*(\text{CO})$  resonances at the detection limit of NEXAFS. It is shown that heating (to 1073 K) of the PLV-SWNTs containing the functional groups produces C K-edge NEXAFS spectra very similar to those seen for the HiPco material. The NEXAFS spectra are calibrated against spectra measured for a number of fused-ring aromatic hydrocarbon molecules containing various types of oxidized functional groups present on the oxidized SWNTs.

- S. Mezheny, D. C. Sorescu, P. Maksymovych and J. T. Yates, Jr. "Dissociation of  $\text{CH}_3\text{I}$  on the Al(111) Surface – An STM and Density Functional Theory Study," J. Am. Chem. Soc. 124, 14202 (2002).

The reaction of methyl iodide with the Al(111) surface was studied by room-temperature scanning tunneling microscopy (STM) and by first principles calculations. It was found that at 300 K methyl iodide decomposes on the Al(111) surface, forming methyl ( $\text{CH}_3$ ), methylidyne (CH), and adsorbed iodine. Methyl groups are observed to occupy atop sites by STM. The occupation of the hollow site by methylidyne was observed in STM measurements. Total energy density functional theory calculations have shown that methyl species occupy atop Al sites ( $E_A = 45.3$  kcal/mol), methylidyne species adsorb on fcc hollow sites ( $E_A = 155.0$  kcal/mol), while individual iodine atoms can bind on both on-top or hollow sites with adsorption energies between 54 and 56 kcal/mol.

- O. Byl, P. Kondratyuk and J. T. Yates, Jr., "Adsorption and Dimerization of NO Inside of Single Walled Carbon Nanotubes – An Infrared Spectroscopic Study," J. Phys. Chem. B. 107, 4277 (2003).

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)<sub>2</sub>, with

$\nu_1$ (symmetric) ) 1853  $\text{cm}^{-1}$  and  $\nu_5$ (asymmetric) = 1754  $\text{cm}^{-1}$ . Introduction of Xe into the system leads to selective displacement of the internally bound *cis*-(NO)<sub>2</sub> dimer. A large spectroscopic red shift of the symmetric (-0.80%) and the asymmetric (-1.96%) modes for *cis*-(NO)<sub>2</sub> adsorbed inside nanotubes [relative to gas-phase *cis*-(NO)<sub>2</sub>] points to the strong interaction of the dimer with the nanotube interior. The enthalpy of dissociation of the adsorbed dimer molecule is  $15.1 \pm 0.7$  kJ/mol.

- O. Byl, P. Kondratyuk, S. Forth, S. FitzGerald, J. T. Yates, Jr., L. Chen and J. K. Johnson "Adsorption of CF<sub>4</sub> on Internal and External Walls of Opened Single Walled Carbon Nanotubes – A Vibrational Spectroscopy Study," J. Am. Chem. Soc. 125, 5889 (2003).

Infrared spectroscopy has been used to make the first experimental discrimination between molecules bound by physisorption on the exterior surface of carbon single-walled nanotubes (SWNTs) and molecules bound in the interior. In addition, the selective displacement of the internally bound molecules has been observed as a second adsorbate is added. SWNTs were opened by oxidative treatment with O<sub>3</sub> at room temperature, followed by heating in a vacuum to 873 K. It was found that, at 133 K and 0.033 Torr, CF<sub>4</sub> adsorbs on closed SWNTs, exhibiting its  $\nu_3$  asymmetric stretching mode at 1267  $\text{cm}^{-1}$  (red shift relative to the gas phase, 15  $\text{cm}^{-1}$ ). Adsorption on the nanotube exterior is accompanied by adsorption in the interior in the case of opened SWNTs. Internally bound CF<sub>4</sub> exhibits its  $\nu_3$  mode at 1247  $\text{cm}^{-1}$  (red shift relative to the gas phase, 35  $\text{cm}^{-1}$ ). It was shown that, at 133 K, Xe preferentially displaces internally bound CF<sub>4</sub> species, and this counterintuitive observation was confirmed by molecular simulations. The confinement of CF<sub>4</sub> inside (10,10) single-walled carbon nanotubes does not result in the production of lattice modes that are observed in large 3D ensembles of CF<sub>4</sub>.

- P. Kondratyuk and J. T. Yates, Jr., "Nanotubes as Molecular Sponges – The Adsorption of CCl<sub>4</sub>," Chem. Phys. Lett. 383, 314 (2004).

A unique adsorptive effect involving carbon nanotubes acting as efficient adsorption sinks for mobile molecules has been quantitatively observed.

- W-L. Yim, O. Byl, J. T. Yates, Jr. and J. K. Johnson, "Vibrational Behavior of Adsorbed CO<sub>2</sub> on Single-Walled Carbon Nanotubes," J. Chem. Phys. 120, 5377 (2004).

We present theoretical and experimental evidence for CO<sub>2</sub> adsorption on different sites of single walled carbon nanotube (SWNT) bundles. We use local density approximation density functional theory (LDA-DFT) calculations to compute the adsorption energies and vibrational frequencies for CO<sub>2</sub> adsorbed on SWNT bundles. The LDA-DFT calculations give a range of shifts for the asymmetric stretching mode from about -6 to -20  $\text{cm}^{-1}$  for internally bound CO<sub>2</sub>, and a range from -4 to -16  $\text{cm}^{-1}$  for externally bound CO<sub>2</sub> at low densities. The magnitude of

the shift is larger for CO<sub>2</sub> adsorbed parallel to the SWNT surface; various perpendicular configurations yield much smaller theoretical shifts. The asymmetric stretching mode for CO<sub>2</sub> adsorbed in groove sites and interstitial sites exhibits calculated shifts of -22.2 and -23.8 cm<sup>-1</sup>, respectively. The calculations show that vibrational mode softening is due to three effects: (1) dynamic image charges in the nanotube; (2) the confining effect of the adsorption potential; (3) dynamic dipole coupling with other adsorbate molecules. Infrared measurements indicate that two families of CO<sub>2</sub> adsorption sites are present. One family, exhibiting a shift of about -20 cm<sup>-1</sup> is assigned to internally bound CO<sub>2</sub> molecules in a parallel configuration. This type of CO<sub>2</sub> is readily displaced by Xe, a test for densely populated adsorbed species, which are expected to be present on the highest adsorption energy sites in the interior of the nanotubes. The second family exhibits a shift of about -7 cm<sup>-1</sup> and the site location and configuration for these species is ambiguous, based on comparison with the theoretical shifts. The population of the internally bound CO<sub>2</sub> may be enhanced by established etching procedures that open the entry ports for adsorption, namely, ozone oxidation followed by annealing in vacuum at 873 K. Xenon displacement experiments indicate that internally bound CO<sub>2</sub> is preferentially displaced relative to the -7 cm<sup>-1</sup> shifted species. The -7 cm<sup>-1</sup> shifted species is assigned to CO<sub>2</sub> adsorbed on the external surface based on results from etching and Xe displacement experiments.

#### (6) Listing

A. Kuznetsova, I. Popova, J. T. Yates, Jr., M. J. Bronikowski, C. B. Huffman, J. Liu, R. E. Smalley, H. H. Hwu and J. G. Chen, "Oxygen-containing Functional Groups on Single-Wall Carbon Nanotubes – NEXAFS and Vibrational Spectroscopic Studies," *J. Am. Chem. Soc.* 123, 10699 (2001).

S. Mezhenny, D. C. Sorescu, P. Maksymovych and J. T. Yates, Jr. "Dissociation of CH<sub>3</sub>I on the Al(111) Surface – An STM and Density Functional Theory Study," *J. Am. Chem. Soc.* 124, 14202 (2002).

O. Byl, P. Kondratyuk and J. T. Yates, Jr., "Adsorption and Dimerization of NO Inside of Single Walled Carbon Nanotubes – An Infrared Spectroscopic Study," *J. Phys. Chem. B.* 107, 4277 (2003).

O. Byl, P. Kondratyuk, S. Forth, S. FitzGerald, J. T. Yates, Jr., L. Chen and J. K. Johnson "Adsorption of CF<sub>4</sub> on Internal and External Walls of Opened Single Walled Carbon Nanotubes – A Vibrational Spectroscopy Study," *J. Am. Chem. Soc.* 125, 5889 (2003).

P. Kondratyuk and J. T. Yates, Jr., "Nanotubes as Molecular Sponges – The Adsorption of CCl<sub>4</sub>," *Chem. Phys. Lett.* 383, 314 (2004).

W-L. Yim, O. Byl, J. T. Yates, Jr. and J. K. Johnson, "Vibrational Behavior of Adsorbed CO<sub>2</sub> on Single-Walled Carbon Nanotubes," *J. Chem. Phys.* 120, 5377 (2004).

**(7) Participating Scientific Personnel Employed by the Project**

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**(8) Report of Inventions - None**

**(9) Bibliography- None**

**(10) Appendices -None**