Stable dispersion of single wall carbon nanotubes in polyimide: the role of noncovalent interactions

Kristopher E. Wise [a,*], Cheol Park [a], Emilie J. Siochi [b], Joycelyn S. Harrison [b]

[a] *National Institute of Aerospace, Hampton, VA, USA*
[b] *Advanced Materials and Processing Branch, NASA Langley Research Center, MS226, Hampton, VA, USA*

Abstract

Single wall carbon nanotubes (SWNTs) have been dispersed in a nitrile functionalized polyimide matrix and the resulting composite shows excellent stability with respect to reaggregation of the nanotubes. This contrasts with the behaviour of structurally similar polyimides in which the dispersion is only stable for short periods of time. Shifts in certain characteristic FTIR and Raman peaks which indicate a charge transfer interaction between the nanotubes and polymer matrix are observed. A simple model for charge transfer stabilization is presented and shown to be consistent with the experimental observations.
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1. Introduction

New avenues in the design of future aerospace vehicles can be enabled by taking advantage of multifunctionality in structures. State-of-the art lightweight aerospace structures are built from graphite fiber composites. It is envisioned that with its impressive suite of properties, carbon nanotube (CNT) nanocomposites have the potential to surpass the performance of conventional graphite fiber composites by providing both sensing and load bearing functionalities in vehicle structures. However, this will not be possible until some problems associated with the use of CNTs can be resolved. In particular, the issue of CNT dispersion in polymer matrices typically used in composite fabrication will be addressed here. As has frequently been noted in the literature, achieving a high degree of dispersion of single wall carbon nanotubes (SWNTs) in a polymer matrix is quite difficult, due primarily to CNTs' high affinity for one another (i.e. their tendency to aggregate in bundles and agglomerates) and their rather weak interaction with common polymers. Early efforts, using a combination of mechanical mixing, sonication, and in situ polymerization techniques, yielded composite solutions which were kinetically stable but which tended to phase separate over a period of days or weeks, indicating thermodynamic instability [1]. In an attempt to produce solutions having long term stability, a number of polyimide compositions were screened for compatibility with SWNTs. This Letter describes the preparation and characterization of a composite which exhibits good long term stability and a number of desirable materials properties. A qualitative rationale for the success of this particular polymer in stabilizing the SWNT dispersion is proposed.

2. Experimental

The experiments described below were performed using purified laser ablated (LA) and high pressure carbon monoxide (CO) decomposition (HiPco) single wall carbon nanotubes. The LA and HiPco SWNTs were purchased from Rice University and Carbon Nanotechnologies, Inc., respectively. The LA and HiPco SWNTs were about 1.2–1.6 nm and 0.8 nm in diameter, respectively. The concentration of the catalysts in both the purified LA (Ni and Co) and HiPco (Fe) SWNTs was less than 3 wt% based on elemental analysis (Desert

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Analytics, ICP-MS). The polymer chosen for this work was (ß-CN)APB/ODPA polyimide, the structure of which is shown in Fig. 1. Through energy-filtered transmission electron microscopy (EELS), (ß-CN)APB/ODPA polyimide has been shown to wet SWNTs very well [2]. This particular polyimide was selected because of the presence of nitrile functionalized aromatic moiety. Nitrile bearing aromatic compounds are generally good electron acceptors due to their ability to accommodate excess charge in low lying unoccupied orbitals. Of particular relevance is a recent report describing the adsorption of 9, 10-anthracenedicarbonitrile on SWNT [3]. These authors found that of a series of substituted anthracenes, the dicarbonitrile derivative exhibited the highest adsorption coverage. This result was attributed to a higher SWNT binding affinity promoted by stronger charge transfer interactions.

For the purposes of forming a composite with well dispersed SWNT reinforcement, it was necessary to prepare the mixture in a particular sequence. The complete synthetic procedure is described in detail elsewhere [1], but will be briefly recounted here and is schematically depicted in Fig. 1. A dilute SWNT suspension, typically around 0.05 wt%, in *N,N*-dimethylacetamide (DMAc), was prepared by homogenizing for 10 min (750 rpm with a 6 mm diameter rotor homogenizer) and sonicating for 1 h at 47 kHz. The sonicated SWNT suspension was used as a solvent for the poly(amic acid) synthesis with the diamine, 2,6-bis(3-aminophenoxy) benzonitrile ((ß-CN)APB), and the dianhydride, 4,4-oxydiphthalic anhydride (ODPA) (Fig. 1). The entire reaction was carried out with stirring in a nitrogen-purged flask immersed in a 40 kHz ultrasonic bath until the solution viscosity increased and stabilized. Sonication was stopped and stirring continued for several hours to form a SWNT-poly(amic acid) solution. The unimidized SWNT poly(amic acid) solutions exhibited
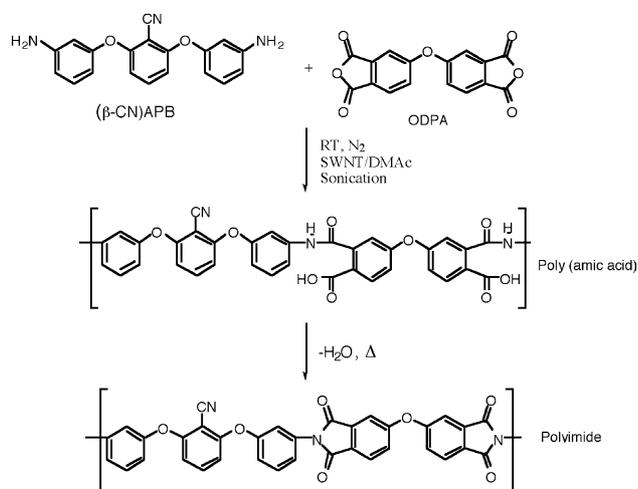
excellent stability, remaining in solution for over two years in sealed bottles under refrigeration.

A series of SWNT-polyimide nanocomposite films with SWNT concentrations of 0, 0.02, 0.1, 0.2 and 0.5 wt% were prepared in the following manner. The SWNT-poly(amic acid) solution was cast onto a glass plate and dried in a dry air-flowing chamber. Subsequently, the dried tack-free film was thermally imidized in a nitrogen-circulating oven to obtain a solvent-free SWNT-polyimide film. The transparent films containing SWNTs were deep green in color while pristine films were pale yellow. This color change was not observed in other polyimides used in previous work [1].

3. Results and discussion

One mechanism consistent with both long term dispersion stability and the observed color change is the formation of an electron donor–acceptor (EDA) complex between the nanotube filler and the polymer matrix. EDA complexes, formed between a molecule of high electron affinity and another of low ionization potential, are not covalently bound, but can nevertheless be quite stable. Previous reports have shown that SWNTs behave amphoterically (in a Lewis acid/base sense), interacting strongly with both electron donors and electron acceptors. Many of these studies have focused on alkali metals as donors and halogens as acceptors [4–9], due to their low ionization potentials and high electron affinities, respectively. Other work has employed various small molecules as electron donors (NH_3, H_2) and electron acceptors (NO_2, O_2) [10–13]. Finally, reports describing doping by larger organic molecules (various aromatic acceptors [3,14] and organic amine donors [15,16]), as well as by polymers functionalized with donor or acceptor groups [17] have appeared. The cited literature suggests that the direction of any charge transfer found in the present situation can be controlled by the electron donating/electron accepting nature of the polymer matrix.

SWNT composites prepared using related polyimides synthesized from ODPA monomers and other diamines showed no noticeable color change. Based on these negative results, ODPA was provisionally eliminated as the active participant in the proposed EDA complex with the SWNT. To test for the involvement of the (ß-CN)APB diamine monomer, a solution of the monomer in DMAc was prepared and observed to be pale yellow in color. Upon addition of SWNTs the solution immediately turned green, as observed in the composite described above. These qualitative observations support the idea of EDA complex formation between SWNTs and the polymer matrix, evidently via the (ß-CN)APB monomers.

Fig. 1. Synthetic route to (ß-CN)APB/ODPA.

To further examine the role of EDA interactions in stabilizing the SWNT/(ß-CN)APB/ODPA composite, Raman spectroscopy was employed to probe the impact of the EDA interaction on the electronic structure of the SWNT. Raman scattering spectra were taken using an Almega[TM] dispersive Raman spectrometer (Thermo Nicolet). A 532 nm incident laser light excitation was employed and the laser beam was focused on the sample with the aid of an optical microscope. Low excitation laser power (15 mW) was used to minimize heating of samples, which often caused downshifting of the observed peaks. The spectrum of a reference sample of pure SWNT was monitored through the entire experiment and Raman shift of the G band caused by heating was less than 1 cm^{-1}.

Previous experimental and theoretical work have shown that doping SWNTs with either electron donors or acceptors [4,8,18,19] or electrochemically [20] resulted in noticeable shifts in certain characteristic vibrational modes. Specifically, removing charge from a SWNT (i.e. p-doping or oxidizing) resulted in an upshift in the G band peak around 1592 cm^{-1}, while adding charge (i.e. n-doping or reducing) to a SWNT resulted in a downshift. The downshift observed upon n-doping is easily understood: as the additional electron density is placed in the antibonding conduction bands of the SWNT, the average C–C bond strength is weakened, resulting in a downshift or softening of the vibrational frequency. The reason for the upshift that occurs upon p-doping is less obvious. One would intuitively expect that removing electron density from the fully occupied, bonding valence band of a SWNT would weaken the C–C bonding, resulting in a downshift in the G band frequency. This was not, in fact, what was observed. One possible explanation for this behaviour is that the addition of some sp^3 character to the sp^2 hybridized orbitals, which results from the curvature of the graphitic structure required to form a tube, results in Coulomb repulsion, particularly in small diameter tubes [21]. Removing electron density from these orbitals reduces the repulsion, resulting in stronger net bonding and a higher G band frequency.

Based on these considerations, if the SWNTs were to lose charge to the polymer matrix, one would expect an upshift in the G band and, conversely, a downshift is expected if charge is gained from the matrix. Fig. 2a shows the measured Raman spectra of the laser ablated tubes before and after dispersion in the (ß-CN)APB/ODPA matrix at a concentration of 0.5%. An upshift of 4 cm^{-1} is observed in the G band. Similar results are found for a 0.2% composite using HiPco tubes (4 cm^{-1} upshift), as shown in Fig. 2b. While the magnitude of this peak shift is relatively small, it is virtually constant across a range of concentrations and is very reproducible. In contrast to the disorder induced dispersive D band and its related second-order harmonic G′ band,
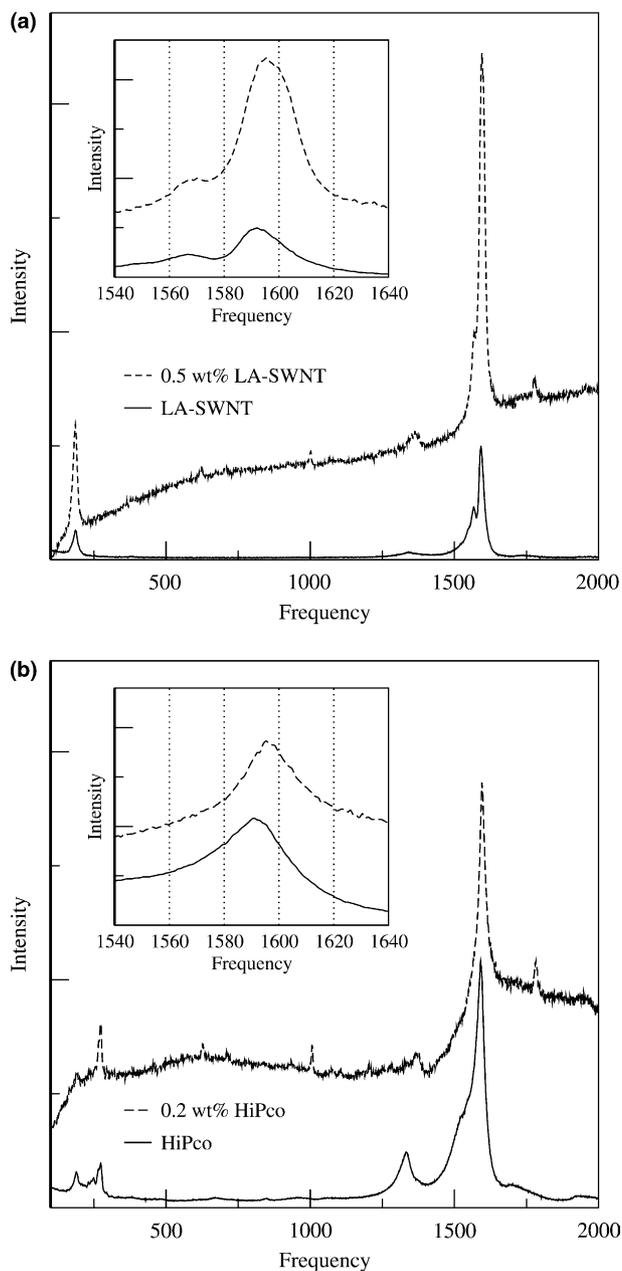

Fig. 2. (a) Raman spectra of LA SWNTs in isolation and in 0.5 wt% composite. (b) Raman spectra of HiPco SWNTs in isolation and in 0.2 wt% composite. All intensities in arbitrary units.

the G band is not highly sensitive to hydrostatic pressure or strain. The upshift of the G band was not observed with other polymers such as polystyrene, poly(methyl methacrylate), or the structurally similar CP2 polyimide, none of which have a strong electron withdrawing group [1]. This indicates that hydrostatic pressure or strain, caused by thermal expansion mismatch between SWNT and the matrix, does not significantly influence the position of the G band peak.

To evaluate the participation of the polymer matrix as an acceptor in the proposed EDA complex, an FTIR

spectrometer was used to collect nitrile stretching mode shift in an ATR mode with a Nicolet Continu μm IR microscope. Fig. 3 shows the spectral region containing the CN stretching mode for a pristine (ß-CN)APB/ODPA film and for a 0.5% laser ablated SWNT/polyimide composite. If the nitrile group in the (ß-CN)APB monomer were acting as a Lewis acid and withdrawing charge density from the SWNT, one would expect to observe a downshift in the CN stretching mode due to partial occupation of the low lying antibonding acceptor orbital. A downshift of approximately 2 cm^{-1} was in fact observed in this case. Interestingly, spectra taken on samples with higher SWNT loadings showed no increase in the magnitude of the shift. This invariance indicates that SWNT/matrix coordination is saturated, even at the lowest loading level (0.02 wt%), although it is unclear why this should be the case. The downshift observed, while small, is reproducible and consistent with the EDA model of the interaction.

A computational study of this system initiated to augment understanding of the nature of the SWNT-matrix interaction in this composite will be briefly described here. While it is not currently possible to perform quantum chemical calculations for systems of this size, qualitative insight may be gained by performing calculations on small analogs of the polymers (monomers, dimers, etc) and extrapolating the results to larger systems. One way of assessing the likelihood of electron transfer from the SWNT to the polymer matrix is to consider the relative electronic chemical potentials (μ) of the two components. When two systems of differing electronic chemical potential are brought into contact, the composite system will

reach an intermediate potential, i.e. equalize, through a process of charge transfer [22–24]. For periodic materials with band type electronic structure, the chemical potential is simply the negative of the Fermi level which, for metallic or small band gap semiconducting tubes, is essentially the negative of the work function (neglecting the dipole potential) [7,25]

$$\mu_{\mathrm{NT}} = -E_{\mathrm{F}} \cong -\mathrm{WF}_{\mathrm{NT}},$$

$$\mathrm{WF}_{\mathrm{NT}} \cong 4.8 - 5.0 \ \mathrm{eV}.$$

The situation is similar for molecular materials with localized electronic structure, except that the chemical potential is defined as the negative of the electronegativity [26,27]. The molecular electronegativity, within the finite difference approximation, is calculated as the negative of the average of the ionization potential and the electron affinity

$$\mu_{\mathrm{P}} = -\chi_{\mathrm{P}},$$

$$\chi_{\mathrm{P}} \cong (\mathrm{IP} + \mathrm{EA})/2.$$

The geometry of a (ß-CN)APB/ODPA monomer was optimized using the B3LYP density functional method with a 6-31G* basis set. The geometries of the radical cation and anion were optimized starting from the neutral geometry. Finally, single point energy calculations were performed at these geometries using the larger 6-31+G* basis set. This basis set adds diffuse functions to the heavy atoms which are known to be particularly important in anions. While the per monomer charge transfer in the real polymer composite is much less than a full electron, this calculation provides a limiting value. All calculations were done using either GAMESS [28] or NWChem4 [29].

Using the B3LYP/6-31+G* calculated energies of the neutral, radical cation, and radical anionic forms of the (ß-CN)APB/ODPA monomer, the ionization potential and electron affinity were found to be 8.64 and 1.58 eV, respectively. The average of these numbers is the Mulliken electronegativity of the monomer, 5.11 eV. Rather than calculating the chemical potential of a SWNT, the experimentally derived value of 4.8–5.0 eV was adopted [7,25]. This approach is more sound because the experimental value reflects the statistical distribution of radii and chiral indices found in real SWNT samples while a calculated value would be biased by the selection of a particular type of tube. Comparing the electronic chemical potentials of the polymer model compound (μ$_{\mathrm{P}}$ = −5.1) with the range determined for SWNT (μ$_{\mathrm{NT}}$ = −4.8 to −5.0), it is apparent that chemical potential equalization will drive partial charge transfer from the SWNT to the polymer. This result agrees with the conclusions drawn from the experimental work described above and supports the idea that charge is transferred from the SWNT to the polymer matrix at equilibrium.

Finally, it is noted that other factors that have necessarily been excluded from these calculations would
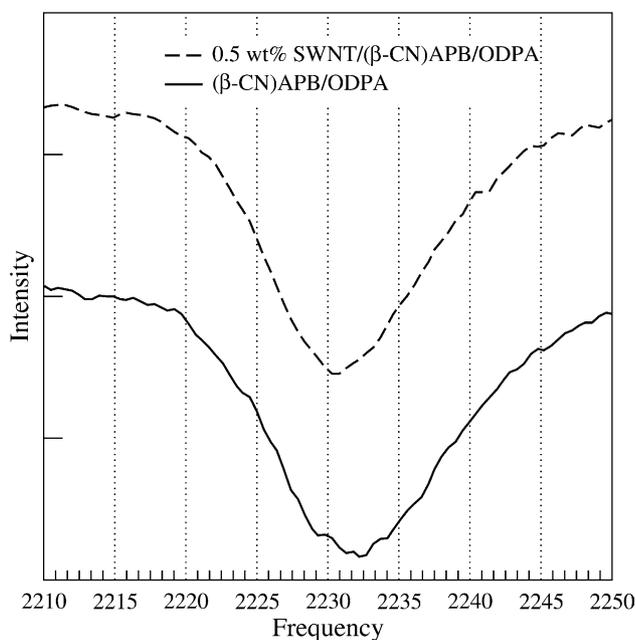

Fig. 3. FTIR spectra of pure (ß-CN)APB/ODPA and 0.5 wt% LA SWNT composite in nitrile stretching region. The peak is downshifted by about 2 cm^{-1} in the composite. Intensity in arbitrary units.

tend to further stabilize charge transfer interactions in this system. First, it is well known that a polar, polarizable environment, such as the bulk polymer in the present case, can significantly stabilize EDA complex formation. This is known to occur in both liquid and solid 'solutions', where reorganization of the surrounding media lowers the energy of the EDA complex relative to its unsolvated value, usually significantly. A second mechanism for stabilizing the EDA complex is geometric distortion of one or both components to a structure which, while unfavorable in isolation, is actually lower in energy when in conjunction with the other component of the complex. An example of this is the narrowing of the HOMO/LUMO gap which occurs upon deformation of aromatic π systems. An interesting example of this was recently described by Morin and coworkers [30] in a study of benzene adsorption on a platinum surface. It was found that distorting the planar aromatic core of the benzene molecule raised the HOMO energy and lowered the LUMO energy, which allowed for an improved match with the metal Fermi energy, and therefore, a more stable interaction.

4. Conclusions

In summary, a new SWNT – polymer composite that exhibits excellent dispersion and long term stability has been produced. The polymer, (ß-CN)APB/ODPA, is believed to stabilize the dispersion of SWNTs by way of a donor acceptor interaction between the tubes and the (ß-CN)APB subunit of the polymer. This mechanism is supported by both Raman spectra of the SWNTs and FTIR spectra of the CN stretching band of the polymer, as well as by ab initio calculations on the (ß-CN)APB monomer. Work is underway to develop analogous polyimides with high electron affinity substituent groups for further improvement in SWNT dispersion and the resultant physical properties of the composites.

Acknowledgements

References

[1] C. Park, Z. Ounaies, K. Watson, R.E. Crooks, J. Connell, S.E. Lowther, E.J. Siochi, J.S. Harrison, T.L.St. Clair, Chem. Phys. Lett. 364 (2002) 303.

[2] C. Park, R.E. Crooks, E.J. Siochi, J.S. Harrison, N. Evans, E. Kenik, Nanotechnology 14 (2003) L1.

[3] J. Zhang, J.-K. Lee, Y. Wu, R.W. Murray, Nano Lett. 3 (2003) 403.

[4] A.M. Rao, P.C. Eklund, S. Bandow, A. Thess, R.E. Smalley, Nature 388 (1997) 257.

[5] P. Petit, C. Mathis, C. Journet, P. Bernier, Chem. Phys. Lett. 305 (1999) 370.

[6] S. Kazaoui, N. Minami, R. Jacquemin, H. Kataura, Y. Achiba, Phys. Rev. B 60 (1999) 13339.

[7] S. Suzuki, C. Bower, Y. Watanabe, O. Zhou, Appl. Phys. Lett. 76 (2000) 4007.

[8] A. Claye, S. Rahman, J.E. Fischer, A. Sirenko, G.U. Sumanasekera, P.C. Eklund, Chem. Phys. Lett. 333 (2001) 16.

[9] N. Bendiab, L. Spina, A. Zahab, P. Poncharal, C. Marliere, J.-L. Bantignies, E. Anglaret, J.L. Sauvajol, Phys. Rev. B 63 (2001) 153407.

[10] J. Kong, N.R. Franklin, C. Zhou, M.C. Chapline, S. Peng, K. Cho, H. Dai, Science 287 (2000) 622.

[11] P.G. Collins, K. Bradley, M. Ishigami, A. Zettl, Science 287 (2000) 1801.

[12] C.K.W. Adu, U. Sumanasekera, B.K. Pradhan, H.E. Romero, P.C. Eklund, Chem. Phys. Lett. 337 (2001) 31.

[13] J. Zhou, A. Buldum, J. Han, J.P. Lu, Mat. Res. Soc. Symp. Proc. 633 (2001) A13.48.

[14] E. Jouguelet, C. Mathis, P. Petit, Chem. Phys. Lett. 318 (2000) 561.

[15] K.D. Ausman, R. Piner, O. Lourie, R.S. Ruoff, M. Korobov, J. Phys. Chem. B 104 (2000) 8911.

[16] J. Kong, H. Dai, J. Phys. Chem. B 105 (2001) 2890.

[17] M. Shim, A. Javey, N.W.S. Kam, H. Dai, J. Am. Chem. Soc. 123 (2001) 11512.

[18] N. Bendiab, E. Anglaret, J.-L. Bantignies, A. Zahab, J.L. Sauvajol, P. Petit, C. Mathis, S. Lefrant, Phys. Rev. B 64 (2001) 245424.

[19] N. Bendiab, E. Anglaret, J.-L. Bantignies, J.L. Sauvajol, P. Petit, C. Mathis, Physica B 323 (2002) 259.

[20] P. Corio, P.S. Santos, V.W. Brar, Ge.G. Samsonidze, S.G. Chou, M.S. Dresselhaus, Chem. Phys. Lett. 370 (2003) 675.

[21] T. Dumitrica, C.M. Landis, B.I. Yakobson, Chem. Phys. Lett. 360 (2002) 182.

[22] R.F. Nalewajski, J. Am. Chem. Soc. 106 (1984) 944.

[23] W.J. Mortier, S.K. Ghosh, S. Shankar, J. Am. Chem. Soc. 108 (1986) 4315.

[24] P. Geerlings, F. De Proft, W. Langenaeker, Chem. Rev. 103 (2003) 1793.

[25] S. Kazaoui, N. Minami, N. Matsuda, H. Kataura, Y. Achiba, Appl. Phys. Lett. 78 (2001) 3433.

[26] R.G. Parr, R.A. Donnelly, M. Levy, W.E. Palke, J. Chem. Phys. 68 (1978) 3801.

[27] C.-G. Zhan, J.A. Nichols, D.A. Dixon, J. Phys. Chem. A 107 (2003) 4184.

[28] GAMESS Version 25 June 2001 M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347.

[29] High Performance Computational Chemistry Group, NWChem, A Computational Chemistry Package for Parallel Computers, Version 4.0.1 (2001), Pacific Northwest National Laboratory, Richland, WA.

[30] C. Morin, D. Simon, R. Sautet, J. Phys. Chem. B 107 (2003) 2995.