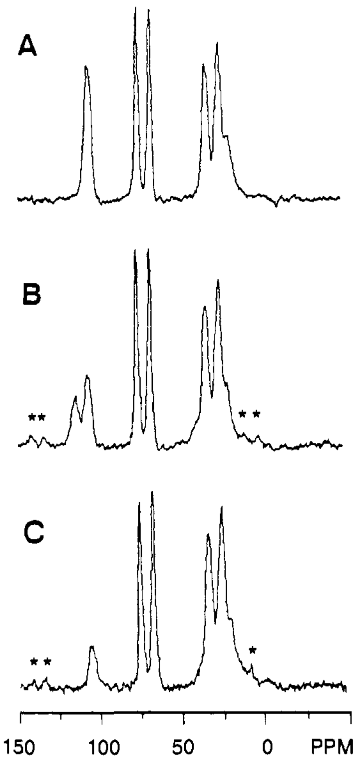

Figure 1. (A) Solid-state CP MAS ^{13}C NMR spectrum of 98% isotopically enriched ketone **2b** in MTHF at 77 K. The four lines between 0 and 80 ppm are MTHF resonances. The line at 105 ppm is the signal of the labeled exocyclic methylene groups of **2b**. (B) Spectrum obtained after irradiation of the above sample at 310 nm at 77 K. The purple color of **1b** is visible. (C) Spectrum obtained by annealing sample of B to 120 K and then recooling to 77 K. Sample C is colorless. Spinning sidebands in each trace are marked with asterisks.

intensity of the **2b** resonance is matched quantitatively (≥95%) by the increase in intensity of the 113 ppm resonance, and the extent of photoconversion (~40% in this experiment) is in good agreement with the growth in the UV–vis optical density expected from a species having the extinction coefficient reported[6] for TMB biradical **1a**. Experiments in toluene glass[8] confirm the observation in MTHF that only one new NMR resonance appears. This 113 ppm resonance is that of a transient species, since it disappears (Figure 1C) when the sample is annealed at 120 K. The data indicate that only one photoproduct is formed and that its symmetry cannot be lower than that of the precursor **2b**.

The simplest interpretation of the facts is that the carriers of the UV–vis signal (λ_{max} 490 nm, $\epsilon \sim 4200$) and the NMR signal are the same species, a kinetically stable singlet state of TMB. The values of λ_{max} and ϵ so derived are in good agreement with those ($\lambda_{max} > 417$ nm, $\epsilon \sim 3600$) calculated[5b] for the $^1A_g \rightarrow {}^1B_{3u}$ transition of singlet TMB. An alternative but less satisfactory hypothesis would assign the NMR signal to 2,3,5,6-tetramethylenebicyclo[2.2.0]hexane (**4**) and the UV–vis spectrum to a small amount (≤5%) of the biradical TMB. In this hypothesis, the UV–vis extinction coefficients of the biradical would have to be ≥20 times as strong as previously[6] reported. The strong absorption at 490 nm then would have $\epsilon \geq 84\,000$, corresponding to $f \sim 1.7$, which lies beyond the Kuhn–Thomas[10] approximate theoretical limit of oscillator strength. Even if that is disregarded, the "weak" long-wavelength bands now would have $\epsilon \sim 8000$–$12\,000$, so that the previous assignment[6] to the forbidden triplet transition would become inappropriate.[11]

We note that the major photoproduct, the TMB singlet species **1a** or **1b** (monitored by UV–vis and CP MAS ^{13}C NMR spectroscopy), persists at 77 K for >17 days, behavior expected of the theoretically predicted singlet ground state.[12]

Acknowledgment. We thank the National Science Foundation (Grants 8820073 and 9018455) and the Swiss National Science Foundation for support of this work.

Supplementary Material Available: Details of the synthesis of **2b**, description of photochemical equipment, and CP MAS NMR spectra in toluene glasses (10 pages). Ordering information is given on any current masthead page.

---

(10) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley, New York, NY, 1966; p 172.

(11) The third formal hypothesis, that **4** is the only photoproduct, necessarily would imply that TMB has not been generated under the present or previous[6] conditions. In that case, the proposed[6] conflict with theory would vanish also.

(12) Since we can provide no direct assurance that an equilibrium distribution of spin states exists in these experiments, we prefer to call our major photoproduct a "kinetically stable singlet". None of our results so far permit an assignment of our ESR signals to triplet species. In the absence of further evidence, it is conceivable that the carrier of the previously reported[6] triplet ESR signal may be a small amount of triplet TMB which is not in rapid equilibrium with the singlet species observed here.

Electrochemical Intercalation of Lithium into Solid C$_{60}$

Yves Chabre,[*,†] David Djurado,[†,‡] Michel Armand,[§]
William R. Romanow,[‖] Nicole Coustel,[‖,⊥]
John P. McCauley, Jr.,[‖,#] John E. Fischer,[‖,⊥] and
Amos B. Smith, III[‖,#]

Laboratoire de Spectrométrie Physique
Université Joseph Fourier
Grenoble I BP 87
F-38042 St. Martin d'Hères, France
Laboratoire d'Ionique et d'Electrochimie du
Solide de Grenoble
ENSEEG, INPG, BP 75
F-38042 St. Martin d'Hères, France
Laboratory for Research on the Structure of Matter
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6272
Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323
Department of Materials Science
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6272

Received August 16, 1991
Revised Manuscript Received November 19, 1991

We have succeeded in intercalating fullerite electrodes with lithium using all-solid-state electrochemical cells and polymer electrolytes. This method offers several advantages over previous studies of fullerenes in solution[1-3] and fullerite films in liquid electrolytes.[4] First, polymer electrolytes generally exhibit larger electrochemical stability windows than liquid electrolytes, especially at negative potential, while avoiding dissolution of the working electrode, the possibility of solvent co-intercalation, and problems associated with limited solubility of neutral, ionized, or

---

[†] Université Joseph Fourier.

[‡] Permanent address: Laboratoire de Chimie des Solides, Université Blaise Pascal, F-63177, Aubiere, France.

[§] ENSEEG.

[‖] Laboratory for Research on the Structure of Matter, University of Pennsylvania.

[⊥] Department of Materials Science, University of Pennsylvania.

[#] Department of Chemistry, University of Pennsylvania.

(1) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Cuifollini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 9634.

(2) Allemand, P. M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050.

(3) (a) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364. (b) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773.

(4) Jehoulet, C.; Bard, A. J.; Wudl, R. *J. Am. Chem. Soc.* **1991**, *113*, 5446.

0002-7863/92/1514-764$03.00/0 © 1992 American Chemical Society

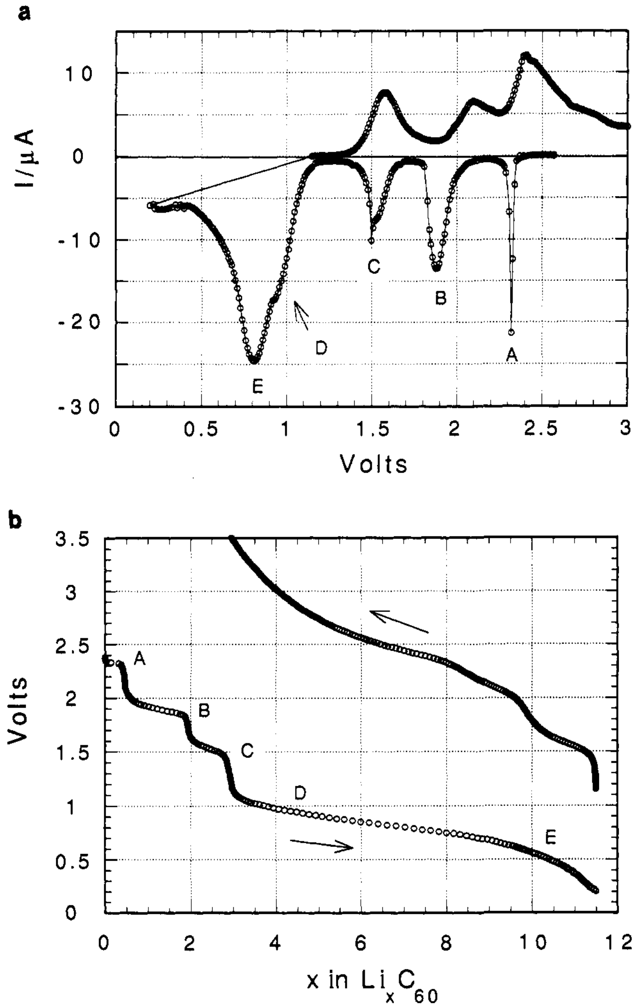

Figure 1. (a) Voltammogram of the first reduction/oxidation cycle of pure C_{60} (3.16 mg). Dots are the current averaged over the 1-h duration of each 10-mV step. The open-circuit voltage relaxed to 1.2 V after reducing to 0.2 V. (b) Voltage vs composition obtained by integration of voltammogram a. The error in x is ±5%, mainly from the C_{60} mass.

complexed fullerenes. Second, electrochemical intercalation may provide another synthetic route to alkali-metal-intercalated fullerites M_xC_{60} (M = K, Rb, or Cs) in addition to previously described chemical methods,[5,6] in particular for the superconducting compounds with $x = 3$.[7] Electrochemical intercalation would most likely be problematic using acetonitrile[4] or similar solvent-based liquid electrolytes because, while C_{60} and C_{70} may be negligibly soluble, the stronger dipolar interactions in $M^{n+}C_{60}{}^{n-}$ might lead to appreciable solubility of the compound.

Powder samples of >99.5% pure C_{60} (crystallite size > 1500 Å) were prepared and purified using the now-standard protocol.[8,9] Solvent residues were removed by vacuum-drying at 200 °C for several hours. Coin-type cells were constructed with metallic Li negative electrode, $P(EO)_8LiClO_4$ polymer electrolyte film, and a composite positive electrode containing ca. 60% active material

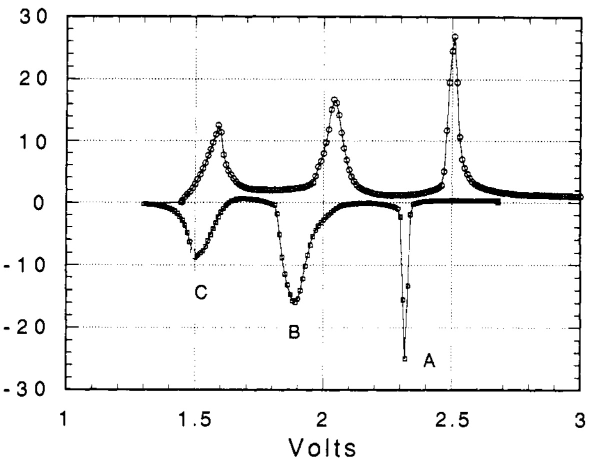

Figure 2. Voltammogram of the first reduction/oxidation cycle of a second cell (3.67 mg), in which the potential steps were confined to the range 1.3–3.0 V. V_{oc} relaxed to only 1.4 V after reducing to 1.3 V.

and 40% electrolyte by volume, cast from acetonitrile suspension onto a stainless steel current collector. The cells were operated at 80 °C to maintain the electrolyte in the high ionic conductivity amorphous phase.[10] Experiments were carried out using a microprocessor-controlled system we specifically designed for studying intercalation processes in solids.[11] The step potential electrochemical spectroscopy[12] performed with this system is a combination of the potentiostatic intermittent titration technique developed by Wen et al.[13] and the electrochemical potential spectroscopy used by Thompson for studying the Li_xTiS_2 system.[14]

The first redox cycle for pure C_{60} is shown in Figure 1a as a linear sweep voltammogram (3.0 → 0.2 → 3.0 V). Three well-defined reduction peaks A, B, and C are apparent at 2.3, 1.9, and 1.5 V respectively vs Li. A fourth peak D is observable as a shoulder at 1.0 V on the very large fifth wave (E) at 0.8 V. By integrating the current vs time, the same sequence of redox events is expressed in Figure 1b as cell voltage vs x in Li_xC_{60}. The domain limits for the successive electron plus ion injection processes appear at $x = 0.5$, 2, 3, 4, and 12. Of these, only $x = 3$ and 4 (C and D) correspond to known structural phases of the intercalation compounds with K or Rb;[9] nothing is known about intercalation phases of Li in C_{60}.

At each potential within the C peak we observed a slow relaxation of the current, as in Li_xTiS_2,[14] indicating a low diffusion coefficient characteristic of a solid state intercalation process. The absence of trailing current after the A, B, and C peaks proves that all the available sites have been occupied in the C_{60} solid at each of these reduction steps.[10,14] Furthermore, the noninteger values of δx in waves A and B are also strong indications of truly solid state processes, in contrast to the integer electron steps associated with electroactivity of isolated molecules. The fifth wave at 0.8 V leads to $x = 12$. It is similar to a peak at about 0.6 V which we observe when performing lithium intercalation into graphite in such cells. Note that the Li:C ratio is about the same for $Li_{12}C_{60}$ and LiC_6, the saturated value for the Li intercalated graphite compound which can be obtained in this way with the same polymer electrolyte.[15]

Reduction beyond the fourth wave implies extensive reorganization of the C_{60} solid, as corroborated by the markedly different shape of the first oxidation following the deep reduction to 0.2 V (see Figure 1a). Only three oxidation waves are observed, even on extending the sweep to 3.5 V, and no peaks are observed on the second reducing potential sweep. Limiting the first reduction

---

(5) Wang, H. H.; Kini, A. M.; Savall, B. M.; Carlson, K. D.; Williams, J. M.; Lykke, K. R.; Wurz, P.; Parker, D. H.; Pellin, M. J.; Gruen, D. M.; Welp, U.; Kwok, W.-K.; Fleshler, S.; Crabtree, G. W. *Inorg. Chem.* **1991**, *30*, 2838.

(6) McCauley, J. P., Jr.; Zhu, Q.; Coustel, N.; Zhou, O.; Vaughan, G.; Idziak, S. H. J.; Fischer, J. E.; Tozer, S. W.; Bykovetz, N.; Liu, C. L.; McGhie, A. R.; Allen, B. H.; Ramanow, W. J.; Denenstein, A. M.; Smith, A. B., III. *J. Am. Chem. Soc.* **1991**, *113*, 8537.

(7) Holczer, K.; Klein, O.; Huang, S.-M.; Kaner, R. B.; Fu, K.-J.; Whetten, R. L.; Diederich, F. *Science* **1991**, *252*, 1154.

(8) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(9) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Kratschmer, W.; Rubin, Y.; Shriver, K. E.; Sensharma, D.; Whetton, R. L. *J. Phys. Chem.* **1990**, *94*, 8630.

(10) Armand, M. B. *Polymer Electrolyte Reviews*; Mac Callum, J. R., Vincent, C. A., Eds.; Elsevier Applied Science: London, 1987; Vol. 1, p 1.

(11) BIO-LOGIC, Ave. de l'Europe, F-38640 Claix, France.

(12) Chabre, Y. *J. Electrochem. Soc.* **1991**, *138*, 329.

(13) Wen, C. J.; Boukamp, B. A.; Huggins, R. A.; Weppner, W. *J. Electrochem. Soc.* **1979**, *126*, 2258.

(14) Thomson, A. H. *J. Electrochem. Soc.* **1979**, *126*, 608.

(15) Yazami, R.; Touzain, Ph. J. *J. Power Sources* **1983**, *9*, 365.

to 1.3 V in another cell produced the results shown in Figure 2. Under these conditions reoxidation is quantitative, and the three peaks have the same potential separation for both negative and positive sweeps.

It is interesting to note that the roughly constant 0.5-V separation between waves A and B, B and C, and C and D corresponds approximately to the electron-by-electron reduction in solution (up to C_{60}^{4-}).[3] This could be interpreted as evidence for weakly perturbed molecular orbitals in the solid state which continue to dominate the electroactivity. On the other hand, the succession of waves leading to $x = 3$ could be assigned to full occupancy of octahedral (O) and tetrahedral (T) sites in the fcc lattice, as in the superconducting compounds with K and Rb.[16] Similarly, $x = 4$ could be assigned to the recently-discovered body-centered tetragonal phase,[17] which can be viewed as a shear-distorted fcc structure with the correct symmetry to eventually transform to the (saturated) body-centered cubic phase at $x = 16$.[18] This latter interpretation would provide a natural explanation for the lack of reversibility upon reducing to $x = 4$ which exceeds the fcc isostructural range. However, preliminary X-ray studies on positive composite electrode materials reduced at 2.2 and 1.3 V (i.e., $x = 0.5$ and $x = 3$, respectively) give new diffraction patterns which do not correspond to those of the K and Rb compound structures.[6,16] In situ X-ray diffraction experiments, with all-solid-state electrochemical cells built in the same way as the coin ones used in this study, are currently in progress. The phase diagram of this system turns out to be far more complex than originally envisioned.

Acknowledgment. Research at Penn was supported by the National Science Foundation through the Materials Research Laboratory Program, Grant No. DMR-88-19885, and by Grant No. DMR-89-01219.

---

(16) Stephens, P. W.; Mihaly, L.; Lee, P. L.; Whetten, R. L.; Huang, S.-M.; Kaner, R. B.; Diederich, F.; Holczer, K. *Nature* **1991**, *351*, 632.

(17) Fleming, R. M.; Rosseinsky, M. J.; Ramirez, A. P.; Murphy, D. W.; Tully, J. C.; Haddon, R. C.; Siegrist, T.; Tycko, R.; Glarum, S. H.; Marsh, P.; Dabbagh, G.; Zahurak, S. M.; Makhija, A. V.; Hampton, C. *Nature* **1991**, *352*, 701.

(18) Zhou, O.; Fischer, J. E.; Coustel, N.; Kycia, S.; Zhu, Q.; McGhie, A. R.; Romanow, W. J.; McCauley, J. P., Jr.; Smith, A. B., III. *Nature* **1991**, *351*, 462.

Estimation of Dynamic Effects on Product Ratios by Vectorial Decomposition of a Reaction Coordinate. Application to Thermal Nitrogen Loss from Bicyclic Azo Compounds

Thomas H. Peterson and Barry K. Carpenter*

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853-1301

Received October 21, 1991

Application of the traditional models of kinetics to the calculation of product ratios in thermal reactions is possible only when there are potential energy barriers to the competing processes. In reactions where branching to products occurs *after* the rate-determining transition state, the traditional models can therefore not be applied.[1] In this communication we propose a model for estimating the product ratios in such reactions by approximating the reaction dynamics, without resort to trajectory calculations. The model is illustrated for thermal reactions of bicyclic azo compounds but could have application to other systems.

The thermal extrusion of nitrogen from 2,3-diazabicyclo-[2.2.1]hept-2-ene-*exo,exo*-5,6-d_2 (**1**, see Figure 1) is believed[2] to occur via the diazenyl biradical **2** and has been known for some time[3] to yield the inverted structure bicyclo[2.1.0]pentane-*exo,exo*-2,3-d_2 (**4x**) as the major product. We have recently[4] interpreted this result with the help of classical trajectory calculations on a model three-dimensional projection of the potential energy surface for conversion of **2** to **3**, **4x**, and **4n**. The alternative analysis presented here is complementary to the previous work in the sense that it treats the problem in its full dimensionality but does not involve calculation of explicit trajectories.

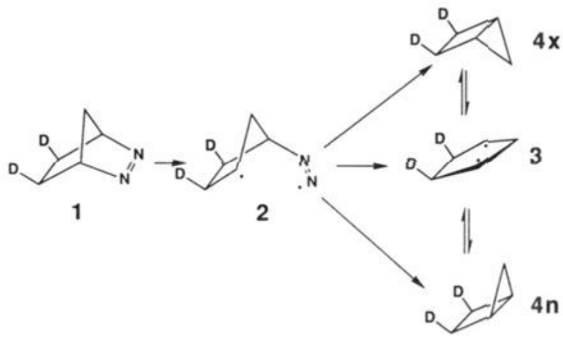

Figure 1.

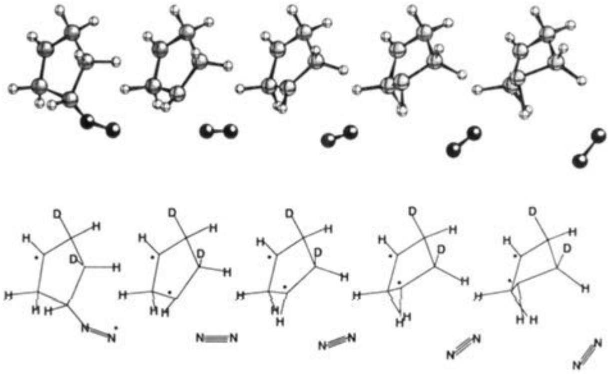

Figure 2. Pictorial representation of the reaction coordinate for N_2 loss from the diazenyl biradical **2**. Based on an AM1 CI frequency calculation on the transition state.

Molecular orbital calculations[5] were carried out on the transition state for nitrogen loss from **2**. The vibrational analyses that were part of these computations revealed, as required, a single imaginary frequency for **2**. The normal vector associated with this imaginary frequency could be translated into a pictorial representation of the reaction coordinate by adding multiples of the elements of the vector to the Cartesian coordinates of the transition structure. This is illustrated in Figure 2 for an AM1 CI calculation on the singlet state of **2**. UHF/6-31G* calculations on the triplet yielded a picture that looks virtually identical.

A striking feature of Figure 2 is the conformational change occurring in the hydrocarbon fragment as the nitrogen departs. *This is a purely dynamic phenomenon*; according to the calculations, the reaction coordinate for nitrogen expulsion "imprints"

---

(1) (a) Carpenter, B. K. *J. Am. Chem. Soc.* **1985**, *107*, 5730. (b) Newman-Evans, R. H.; Simon, R. J.; Carpenter, B. K. *J. Org. Chem.* **1990**, *55*, 695.

(2) Simpson, C. J. S. M.; Wilson, G. J.; Adam, W. *J. Am. Chem. Soc.* **1991**, *113*, 4728.

(3) (a) Roth, W. R.; Martin, M. *Justus Liebigs Ann. Chem.* **1967**, *702*, 1. (b) Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 4695. For related studies, see: (c) Allred, E. L.; Smith, R. L. *J. Am. Chem. Soc.* **1967**, *89*, 7133. (d) Allred, E. L.; Smith, R. L. *J. Am. Chem. Soc.* **1969**, *91*, 6766.

(4) Lyons, B. A.; Pfeifer, J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1991**, *113*, 9006.

(5) Semiempirical calculations were carried out using the AM1 Hamiltonian (Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902) with the minimal CI necessary for a proper description of a singlet biradical. Ab initio calculations used the Gaussian 88 package (Gaussian 88, M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA).

0002-7863/92/1514-766$03.00/0