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Quantum Chemical Study $Ca@C_{60}$ and $Sc^+@C_{60}$ Endo Complexes in the Gas Phase and Pyridine

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Abstract—DFT (U)PBE0/cc-pVDZ calculations were carried out to determine the structural parameters of the endo complexes $Ca@C_{60}$ and $Sc^+@C_{60}$ in the gas phase and in pyridine. The ($^3A_1//C_{3v}$)-$Ca@C_{60}$ and ($^3A_1//C_{3v}$)-$Sc^+@C_{60}$ triplets are higher in energy than the ($^1A_1//C_{2v}$)-$Ca@C_{60}$ and ($^1A_1//C_{2v}$)-$Sc^+@C_{60}$ singlets by 0.21 and 2.61 kcal/mol in the gas and by 0.30 and 2.67 kcal/mol in pyridine. The dipole moments of the zwitter ions ($^1A_1//C_{2v}$)- and ($^3A_1//C_{3v}$)-$Ca@C_{60}$ are 0.86 and 0.99 D (1.44 and 1.77 D in pyridine). The β decay $^{45}Ca \rightarrow {}^{45}Sc^+$ is accompanied by population of the 3*d* orbital of the endo atom and strengthening of its bond with carbon. The $^1A'//C_s$, $^3A_1//C_{2v}$, and $^3A_1//C_{5v}$ electronic states correspond to low (not higher than 0.54 kcal/mol) barrier of calcium migration inside the cavity. The delocalization of the endo atom provides a highly symmetric mixed state of the fluctuating endo complex. The Stone–Wales ($^1A_1//C_{2v}$)-(Ca, Sc^+)$@C_{60}$ rearrangement increases the energy of the endo complex by 9.9 (Ca) and 3.1 kcal/mol (Sc^+).

Keywords: fullerene endo complexes, $Ca@C_{60}$, $Sc^+@C_{60}$, β decay, solvent effects, Stone–Wales rearrangement, DFT method.

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Wang et al. [1] reported an experimental study of the endo complex $Ca@C_{60}$ in the gas phase, carbon sulfide, and pyridine. Chang et al. [2] performed Hartree–Fock calculations for an icosahedral endo complex $Ca@C_{60}$ and obtained a $^3T_{1u}//I_h$ term and transfer of one electron from the calcium atom to the carbon cage. In [3, 4], calculations in the local electron density approximation and in the assumption of the same I_h symmetry predicted transfer of two electrons.

The Hartree–Fock calculations in [1] were performed not only for the highest symmetry nuclear configuration I_h, but for the lower symmetry configurations D_{5d}, D_{3d}, and C_{5v}. The resulting ground state was an $^3A_2//C_{5v}$ triplet with the transfer of two electrons and a 0.7 Å displacement of the calcium nucleus. At the same time, it was noted that the multiplicity of the ground state, predicted by the calculations, is inconsistent with the experimentally established fact of the lack of an EPR signal [1]. The transfer of two electrons was confirmed by the DFT BLYP method in [5].

In the present work, we used the DFT (U)PBE0/cc-pVDZ method to calculate the equilibrium structural parameters and relative energies of the endo complexes $Ca@C_{60}$ and $Sc^+@C_{60}$ (Fig. 1) in the singlet and triplet states and with nuclear configurations of different symmetries (C_1, C_s, C_{2v}, D_{3v}, and C_{5v}), as well as the change in the ground state energy in the Stone–Wales rearrangement of buckminsterfullerene (Figs. 1 and 2) [6, 7] containing an endo atom. Setting any of the above symmetry point groups did not suggest exclusion of higher symmetries (I_h, D_{5d}, D_{3d}).

States with the quantum number $M_S = 1$ were assigned to spin triplets if the calculated mathematical expectation of squared spin $\langle S^2 \rangle$ very little deviated (about 1%) from the integer value 2.

Solvent (pyridine) effects were included using the polarizable continuum model (PCM) [8, 9]. The surface separating the endo complex from the solvent was constructed by fragments of intersecting spheres centered at atomic nuclei. The solvent was isolated

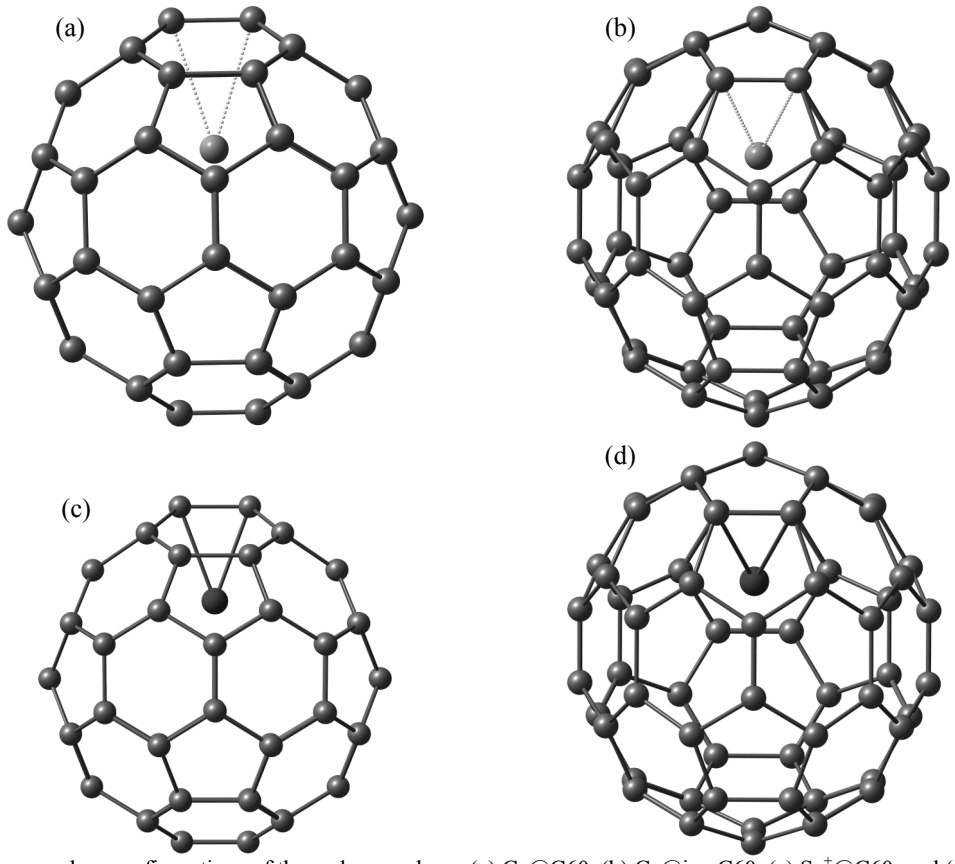

Fig. 1. Equilibrium nuclear configurations of the endo complexes (a) Ca@C60, (b) Ca@iso-C60, (c) Sc^+@C60, and (d) Sc^+@iso-C60, corresponding to the energy minima.

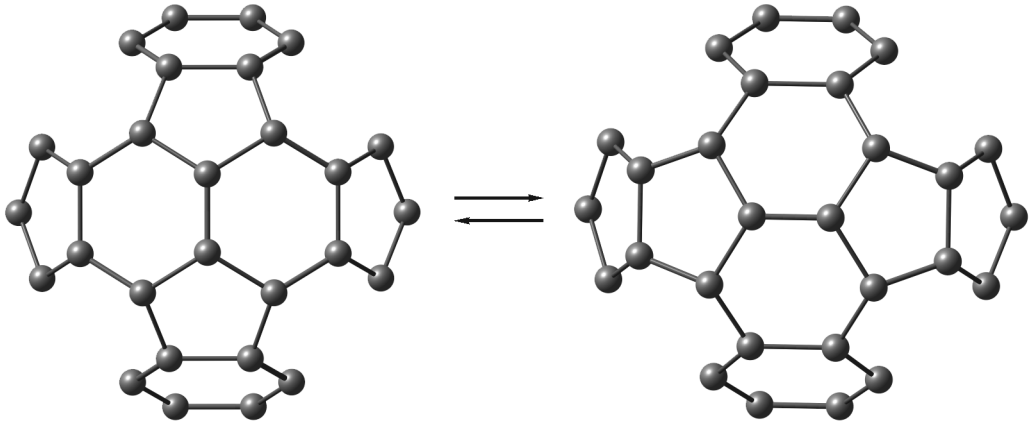

Fig. 2. Stone–Wales rearrangement of buckminsterfullerene.

from the fullerene cage by an additional sphere centered in the vicinity of the fullerene center of inertia [10]. The volume occupied by the endo complex in the solution is invariant with respect to minor changes of the radius of the additional sphere and its centering point [10]. The acceptable variations of these parameters are strictly constrained within the horizontal parts of the curves presented in Fig. 3.

The energy optimization for every equilibrium configuration is completed by the calculations of the vibrational spectrum which allows one to distinguish the minimum of the nuclear motion potential from a saddle point and to include the contribution of zero-point nuclear vibra-tions to the molecular energy. The most interesting calculated structural parameters are listed in the table.

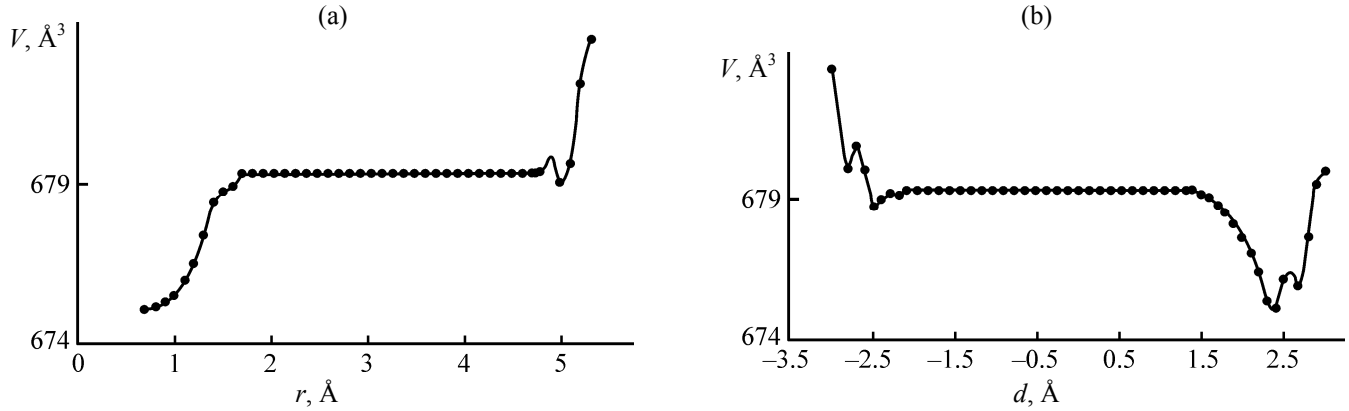

Fig. 3. Dependences of the volume occupied by the endo complex ($^1A_1//C_{2v}$)-Ca@C_{60} in pyridine on the (a) radius of the additional sphere and (b) displacement of its center from the endo complex center of inertia.

The calculations predict a singlet ground state $^1A_1//C_{2v}$ for both endo complexes both in the gas phase and in solution. The endo atom is symmetrically attached to one of the 30 carbon–carbon double bonds. The 4*s* electron pair of Ca in the endo complex is transferred to buckminsterfullerene, and the electron configuration of the scandium cation, obtained by natural population analysis (NPA [11, 12]), is close to $1s^2 2s^2 2p^6 3s^2 3p^6 3d$. The elongation of the equilibrium distance between calcium and its closest carbon nuclei in the endo complex ($^1A_1//C_{2v}$)-Ca@C_{60} to 1.461 Å implies degradation of the C^1=C^2 bond. This value is larger than the bond lengths in a free, empty C_{60} molecule: C=C 1.393 Å and C–C 1.449 Å. The calculations predict additional displacement of the endo atom from the fullerene center of inertia, shortening of the M–$C^{1,2}$ bonds, and elongation of the C^1=C^2 bond to 1.476 Å in the case of the $^{45}Ca \rightarrow {}^{45}Sc^+$ nuclear β decay.

Electronic and structure; characteristics of the endo complexes Ca@C_{60} and Sc^+@C_{60} in the gas phase and pyridine

Term	*E*, kcal/mol	*iv*, cm^{-1}	$<S^2>$, a.u.	Δ, Å	M–C, Å[a]	μ, D
Endo complex Ca@C_{60} in the gas phase						
$^1A_1//C_{2v}$	0	–	0	1.241	2.428 (2)	0.86
$^3A_1//C_{3v}$	0.21	–	2.011	1.224	2.515 (6)	0.99
$^3A_1//C_{2v}$	0.35	–42	2.011	1.221	2.428 (2)	0.99
$^1A'//C_s$	0.46	–114	0	1.231	2.449 (2)	0.96
$^3A_1//C_{5v}$	0.54	–201[b]	2.008	1.193	2.495 (5)	1.02
$^1A'//C_s$, *iso*	9.93	–	0	1.387	2.488 (2)	2.51
Endo complex Sc^+@C_{60} in the gas phase						
$^1A_1//C_{2v}$	0	–	0	1.618	2.131(2)	–
$^3A_1//C_{3v}$	2.61	–	2.025	1.606	2.244 (6)	–
$^1A'//C_s$, *iso*	3.07	–	0	1.755	2.170 (2)	–
Endo complex Ca@C_{60} in pyridine						
$^1A_1//C_{2v}$	0	–	0	1.241	2.428 (2)	1.44
$^3A_1//C_{3v}$	0.30	–	2.011	1.224	2.515 (6)	1.76
$^3A_1//C_{2v}$	0.27	–44	2.011	1.221	2.428 (2)	1.77
Endo complex Sc^+@C_{60} in pyridine						
$^1A_1//C_{2v}$	0	–	0	1.618	2.131 (2)	–
$^3A_1//C_{3v}$	2.67	–	2.025	1.607	2.244 (6)	–

[a] Figures in parentheses show the number of equivalent bonds. [b] Doubly degenerate imaginary wave number.

The Stone–Wales rearrangement of a free, empty buckminsterfullerene converts it into an *iso*-C_{60} isomer with the relative calculated energy of 38.7 kcal/mol.[1]

The presence of an endo atom reduces the energy effect of the ($^1A_1//C_{2v}$)-Ca@C_{60} → ($^1A'//C_s$)-Ca@*iso*-C_{60} rearrangement to 9.93 kcal/mol and that of the ($^1A_1//C_{2v}$)-Sc^+@C_{60} → ($^1A'//C_s$)-Sc^+@*iso*-C_{60} rearrangement to 3.07 kcal/mol. The *iso*-C_{60} polyhedron contains two pairs of five-membered rings sharing a C=C bond. In the course of the rearrangement of the carbon cage the endo atom displaces to the middle point of one of such C=C bonds. An analogous local structure was previously predicted by B3LYP/(C: 6-31G*, Ca: Lanl2DZ) calculations for the endo complex Ca@C_{76} [13].

The endo complex Sc^+@C_{60} can be expected to form in the ionization of Sc@C_{60} by electron detachment and in the β decay of the radioactive isotope ^{45}Ca in the endo complex ^{45}Ca@C_{60}. In this case, the Stone–Wales rearrangement can be initiated by the recoil effect associated with the β decay of the radioactive endo atom.

The $^3A_1//C_{2v}$ state of the endo complex Ca@C_{60} corresponds not to the potential minimum but to the saddle point which is higher than the $^3A_1//C_{3v}$ minimum by 0.59 kcal/mol (by 0.35 kcal/mol in pyridine) and higher than the minimum of the ground state singlet $^1A_1//C_{2v}$ by 0.90 kcal/mol (by 0.63 kcal/mol in pyridine).

In the $^3A_1//C_{3v}$ state corresponding to the potential minimum, the endo atom is symmetrically coordinated to one of the twenty hexagonal faces of fullerene. Its bonds with six carbon atoms are longer than bonds in a singlet endo complex, and the C–C bond lengths in the six-membered ring coordinated to calcium or scandium are alternating in a manner characteristic of fullerenes (C=C 1.402 Å and C–C 1.447 Å). The energy of the triplet state $^3A_1//C_{3v}$ of the calcium endo complex in the gas phase and pyridine are higher respectively by 0.21 and 0.30 kcal/mol than the energy of the ground state $^1A_1//C_{2v}$. In the triplet endo complex, the calcium atom contributes nothing to the spin dispersion DS = $\langle S^2\rangle - \langle S\rangle^2$.

In an electrically charged scandium endo complex, the singlet–triplet splitting is much larger: 2.61 kcal/mol in the gas phase and 2.67 kcal/mol in pyridine. Therewith, the potential minimum corresponding to the $^3A_1//C_{3v}$ state of the endo complex Sc^+@C_{60} is higher than the minimum of the ground state $^1A_1//C_{2v}$ by 2.79 kcal/mol (by 2.99 kcal/mol in pyridine).

The fact that the dipole moment of the endo complex Ca@C_{60} in pyridine is increased by 67% in the singlet state and by 79% in the triplet state at virtually unchanged equilibrium internuclear distances Ca–C^1, Ca–C^2, and C^1=C^2 can be explained in terms of the redistribution of the electron density in the carbon fragment under the action of the solvent reactive field. On transfer of the singlet endo complex ($^1A_1//C_{2v}$)-Sc^+@C_{60} from the gas phase into pyridine the scandium cation, too, remains in the same position with respect to the neighboring carbon atoms and the fullerene centrum of inertia (see table). Apparently, the negatively charged cage of sixty carbon atoms protects the inner cavity from external electric field.

If metal endo complexes of fullerenes in condensed media are calculated by a standard procedure, not including the additional sphere, serious errors may occur. Thus, if the space between the endo atom and the inner surface of the cage is filled with a continuum having dielectric properties of pyridine, the vibrational spectrum of the endo complex ($^1A_1//C_{2v}$)-Ca@C_{60} acquires the imaginary wave number i114 cm^{-1} (a saddle point instead of a minimum), while the energy of the polarization interaction of the endo complex ($^1A_1//C_{2v}$)-Sc^+@C_{60} with the solvent proves to be overestimated by 26 kcal/mol.

The electronic states $^1A'//C_s$ and $^3A_1//C_{5v}$, like $^3A_1//C_{2v}$, correspond to transition structures of the endo complex Ca@C_{60}. In 60 equivalent equilibrium structures with a low symmetry C_s, which result from deformation of more symmetrical structures C_{2v}, calcium is primarily bound to two carbon atoms. In 12 equivalent equilibrium structures with C_{5v} symmetry, whose vibrational spectrum has two imaginary wave numbers, calcium is coordinated with a pentagonal fullerene face.[2]

The metal cations in the endo complex in study coordinate with equal probabilities to any of the thirty

[1] The relative energy of 38.3 kcal/mol was obtained by the B3LYP/6-311G** and B3LYP/6-31G* methods [7].

[2] According to Hartree–Fock calculations, the $^3A_1//C_{5v}$ (UHF/cc-pVDZ) state with an e_1^2 shell is a local potential minimum and Δ = 1.061 Å, bond lengths of five Ca–C bonds 2.588 Å, and dipole moment 0.34 D. The equilibrium point $^1E_1//C_{5v}$ (RCHF/cc-pVDZ) with the same electron configuration is higher by 8.1 kcal/mol of the $^3A_1//C_{5v}$ minimum. The saddle point $^1A_1//C_{2v}$ (RHF/cc-pVDZ) has the Ca–C bond lengths 2.520 Å, Δ = 1.127 Å, and dipole moment 1.00 D and is 1.8 kcal/mol higher than the minimum; with account for zero-point energy, the energy difference is 9.6 kcal/mol.

C=C bonds in the singlet state or to any of the twenty hexagonal faces of the C_{60} polyhedron in the triplet state. The presence of many equivalent equilibrium nuclear configurations separated by low energy barriers makes possible degenerate structural fluctuations and a high (isomorphic to icosahedral) symmetry of the mixed state of the fluctuating endo complex. The increased contribution to the free energy of the negative entropy [14, 15] corresponding to the 30- or 20-fold increase of the symmetry number σ is compensated for by the entropy of mixing of "pure" states, where the metal atom is localized.

In view of the discrepancy in the results of the Hartree–Fock and DFT calculations, we would like to note that the RHF method, unlike DFT B3LYP, proved to be unsuitable for investigations into the prototropic isomerism of porphyrin bases and phthalocyanine bases [16, 17]. It is also known that DFT calculations of metal porphyrins result in an aromatic structure consistent with experiment, whereas RHF calculations give four equivalent polyene structures with alternating bond lengths. This erroneous structure corresponds to the classical structural formula with localized double and single bonds [18]. The chemical and physical properties of molecules with such structure would essentially differ from the experimentally observed properties of metal phthalocyanines.

The calculations were performed using GAUSSIAN-09 [19] at the resource center "Computing Center of St. Petersburg State University (http://cc.spbu.ru)."

REFERENCES

1. Wang, L.S., Alford, J.M., Chai, Y., Diener, M., Zhang, J., McClure, S.M., Guo, T., Scuseria, G.E., and Smalley, R.E., *Chem. Phys. Lett.,* 1993, vol. 207, nos. 4–6, p. 354. DOI: 0.1016/0009-2614(93)89013-8.
2. Chang, A.H.H., Ermler, W.C., and Pitzer, R.M., *J. Chem. Phys*., 1991, vol. 94, no. 7, p. 5004. DOI: 10.1063/1.460535.
3. Saito, S. and Oshiyama, A.*, Solid State Commun*., 1992, vol. 83, no. 2, p. 107. DOI: 10.1016/0038-1098(92)90885-D.
4. Lu, J., Zhang, X., and Zhao, X., *Solid State Commun*., 1999, vol. 110, no. 10, p. 565. DOI: 10.1016/S0038-1098(99)00098-8.
5. Jalbout, A.F., Roy, A.K., Leon, A. de, and Jimenez-Fabian, I.*, J. Mol. Struct. (THEOCHEM),* 2008, vol. 858, nos. 1–3, p. 39. DOI: 10.1016.j.theochem.2008.02.026.
6. Stone, A.J. and Wales, D.J., *Chem. Phys. Lett*., 1986, vol. 128, nos. 5–6, p. 501. DOI: 10.1016/0009-2614(86)80661-3.
7. Bettinger, H.F., Yakobson, B.I., and Scuseria, G.E., *J. Am. Chem. Soc*., 2003, vol. 125, no. 18, p. 5572. DOI: 1021/ja0288744.
8. Tomasi, J. and Persico, M., *Chem. Rev*., 1994, vol. 94, no. 7, p. 2027. DOI: 10.1021/cr00031a013.
9. Tomasi, J., Mennucci, B., and Cammi, R. , *Chem. Rev*., 2005, vol. 105, no. 8, p. 2999. DOI: 10.1021/cr9904009.
10. Semenov, S.G. and Makarova, M.V. , *Opt. Spektrosk*., 2015, vol. 118, no. 1, p. 50; DOI: 10.7868/S0030403415010225.
11. Reed, A.E., Weinstock, R.B., and Weinhold, F., *J. Chem. Phys*., 1985, vol. 83, no. 2, p. 735. DOI: 10.1063/1.449486.
12. Glendening, E.D., Reed, A.E., and Weinhold, F., *NBO*, Ver. 3.1.
13. Yang, T., Zhao, X., Xu, Q., Zheng, H., Wang, W.-W., and Li, S.-T. , *Dalton Trans*., 2012, vol. 41, no. 17, p. 5294. DOI: 10.1039/C2DT12420C.
14. Eliel, E.L., Wilen, S.H., and Doyle, M.P., *Basic Organic Stereochemistry*, New York: Wiley, 2001.
15. Gilson, M.K. and Irikura, K.K. , *J. Phys. Chem. B*, 2010, vol. 114, no. 49, p. 16304. DOI: 10.1021/jp110434s.
16. Ghosh, A. and Almlof, J. , *J. Phys. Chem.,* 1995, vol. 99, no. 4, p. 1073. DOI: 10.1021/j100004a003.
17. Strenalyuk, T., Samdal, S., and Volden, H.V., *J. Phys. Chem. A*, 2008, vol. 112, no. 21, p. 4853. DOI: 10.1021/jp801284c.
18. Semenov, S.G. and Bedrina, M.E.*, Russ. J. Gen. Chem*., 2009, vol. 79, no. 8, p. 1741. DOI: 10.1134/S1070363209080271.
19. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H.P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J.L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J.A., Jr., Peralta, J.E., Ogliaro, F., Bearpark, M., Heyd, J.J., Brothers, E., Kudin, K.N., Staroverov, V.N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Rega, N., Millam, J.M., Klene, M., Knox, J.E., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Martin, R.L., Morokuma, K., Zakrzewski, V.G., Voth, G.A., Salvador, P., Dannenberg, J.J., Dapprich, S., Daniels, A.D., Farkas, O., Foresman, J.B., Ortiz, J.V., Cioslowski, J., and Fox, D.J.*, GAUSSIAN 09*, Rev. C.01. Wallingford, CT: Gaussian, 2010.