PHYSICAL REVIEW B **73**, 205409 (2006)

Aggregation-enhanced luminescence and vibronic coupling of silole molecules from first principles

Shiwei Yin, Qian Peng, and Z. Shuai*
Key Laboratory of Organic Solids, Institute of Chemistry and Beijing National Laboratory for Molecular Sciences (BNLMS), Chinese Academy of Sciences, 100080 Beijing, China

Weihai Fang†
Department of Chemistry, Beijing Normal University, 100875 Beijing, China

Yan-Hua Wang and Yi Luo‡
Theoretical Chemistry, Royal Institute of Technology, AlbaNova, S-106 91 Stockholm, Sweden

(Received 28 February 2006; published 12 May 2006)

Aggregate formation in molecular solids usually quenches the luminescence, a piece of bad news for molecular electronic devices. However, siloles present extremely high luminescent efficiency in solid state as well as in aggregation, but have almost no luminescence in solution. By employing a first-principles calculation to study excited states and vibronic couplings, we find that it is the low-frequency twisting motions of side rings which enhance the nonradiative decay. These motions can be suppressed either by solid-state packing, by aggregation formation in polar solvents, or by increasing the solvent viscosity; thereby, the radiative decay becomes dominant, resulting in peculiar aggregate-induced emission phenomena in siloles.

DOI: 10.1103/PhysRevB.73.205409 PACS number(s): 78.55.Kz, 71.20.Rv, 78.60.Fi

I. INTRODUCTION

Organic and polymeric light-emitting diodes (OLED's and PLED's) have become more and more important in flat display technology since their first discoveries.[1] One strategy in designing OLED materials is to avoid aggregation: usually, aggregation quenches the luminescence because of (i) the intermolecular charge transfer or (ii) the exciton coupling leading to Davydov splitting, and in many cases the dark state stays below the bright state. These are widely accepted concepts in photophysics. However, siloles, a group of five-member silacycles, are exactly in the contrary. Exotic luminescent phenomena have been found. It was demonstrated that the siloles are nonemissive in ethanol solutions, but highly luminescent in aggregate or films[2,3]—i.e., aggregation-enhanced luminescence (AEL). Furthermore, the emission of the siloles in solution can be greatly enhanced by either decreasing temperature or increasing the viscosity of solution.[4]

Recently, more and more molecular systems have been found to exhibit such exotic behaviors.[5–7] In addition to peculiar photophysics, silole-based compounds also exhibit high carrier mobilities,[8,9] highly efficient light emission in OLED devices,[10] and high photovoltaic activity,[11] thus being very promising in organic electronics applications.

In this work, we present our theoretical explanations of the AEL phenomena. The microscopic origin of the peculiar luminescent behaviors is revealed by investigating the radiative and radiationless decays of the excited states in silole molecules. Risko *et al.* have applied time-dependent density functional theory to investigate both the carrier transport behavior and excited-state structures,[12] as well as the molecular structures, for several kinds of siloles molecules. We here adopt the same computational approach to study the electronic structures, and we further explore the excited-state dynamics of two prototypical siloles: 1,1-dimethyl-2,3,4,5-tetraphenylsilole (compound 1) and 3, 4-bis(2′,6′-diisopropyl phenyl)-1,1-dimethyl-2,5-diphenylsilole (compound 2) whose molecular structures are depicted in Fig. 1. The rates of radiation and radiationless transitions from the first excited state to the ground state have been calculated for both systems.

II. METHODOLOGICAL APPROACH AND NUMERICAL RESULTS

The major geometrical difference between the two compounds in Fig. 1(a) is that the two hydrogen atoms on the 2′, 6′ sites of the phenyl groups located at the 3, 4 sites of the silacycle are substituted by two isopropyl groups. These isopropyl groups have a big steric effect, which prevents the phenyl groups from easily rotating. We calculated the rotational energy barriers of the phenyl group at site 2 of the silacycle semicolon; see Fig. 1(b). The phenyl group on this site is strongly associated with the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of both compounds. Its rotation is thus expected to have the largest effect on the optical properties of the compounds. The calculated results, shown in Fig. 1(c), clearly indicate that this phenyl group in compound 1 can rotate much easier than that in compound 2. It is noted that the rotation of the phenyl group at site 3 of the silacycle costs almost the same energy as in the case of site 2 for compound 1, but is completely impossible for compound 2. Compound 1 is a typical AEL-phenomenon system. Recent experiments find that compound 2 is highly luminescent in solution and does not present any AEL phenomena, in sharp contrary to compound 1 (Ref. 13).

The quantum efficiency of photoluminescence can be expressed as $\eta = k_r/(k_r + k_{nr} + k_{ISC})$, where k_r is the radiative de-

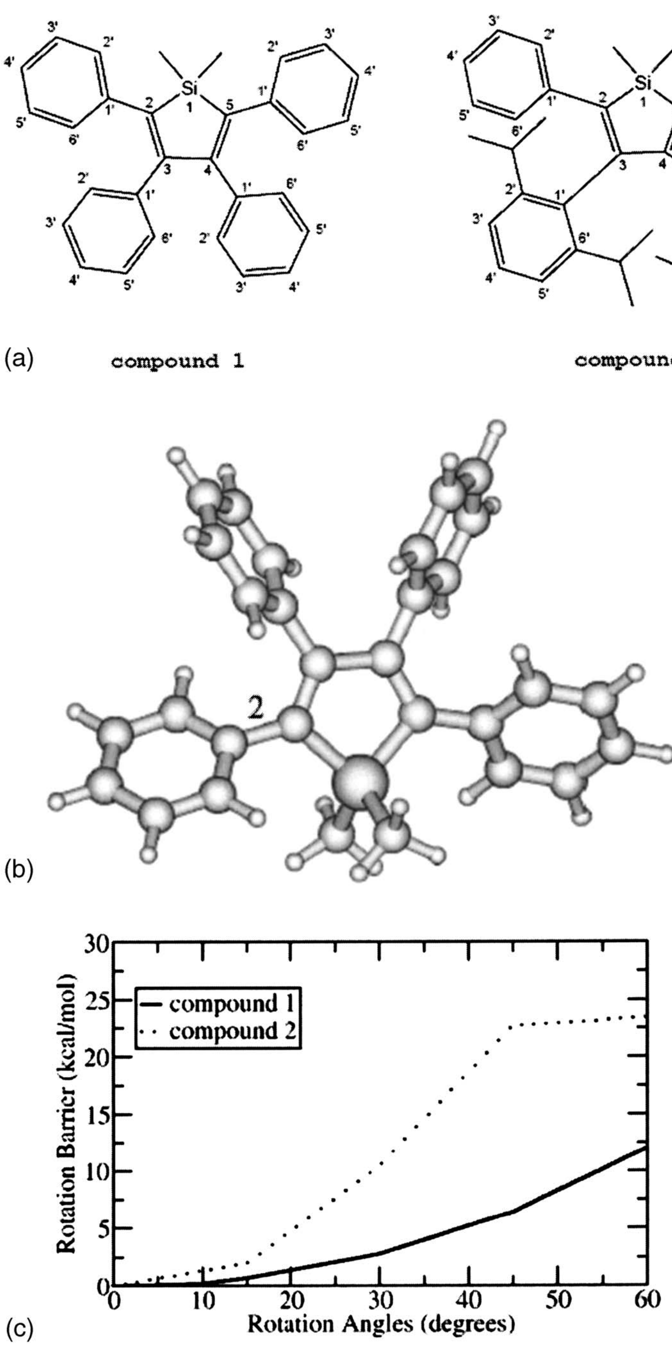

FIG. 1. (A) Molecular structures of 1,1-dimethyl-2,3,4,5-tetraphenylsilole (compound 1) and 3, 4-bis(2′,6′-diisopropylphenyl)-1,1-dimethyl-2,5-diphenylsilole (compound 2). (B) The spatial arrangement of compound 1 and (C) the rotational energy barrier as function of rotational angle of phenyl group at site 2 for both compounds.

cay rate, k_{nr} consists of the nonadiabatic radiationless decay to the ground state, and k_{ISC} is the intersystem cross rate from the singlet to the triplet state. The radiative decay can be evaluated through the Einstein spontaneous emission relationship which can be cast into a simple working formula $k_r = fE_{if}^2/1.499$, where f is the oscillator strength (in electrostatic units) of the excited state, E_{if} is the excited-state energy in cm^{-1}, and k_r is then in unit of s^{-1}. The nonadiabatic process is due to the kinetic energy term of the nuclear motion. We note that in the organic system, the intersystem crossing process (from the singlet to the triplet excited state) is slow when compared with the radiative decay. For siloles, we obtained a value for the electronic coupling (spin-orbit coupling) of 1.6 cm^{-1}, from a correlated electron calculation with the GAMESS package.[14] For the typical radiative or nonradiative process, the electronic coupling is about a few tens to hundreds and even to thousands of cm^{-1}. Thus, we will not address the intersystem crossing contribution for the present study.

We take the molecular geometries for both compounds from the experimental crystal structure data [10(b)] and from quantum chemistry optimization with the hybrid density functional theory (B3LYP) with 6-31g basis as implemented in the GAUSSIAN03 package[15] for the gas-phase structure, which is known to provide reliable results. The radiative decay rates are calculated to be $1.2\times10^8\ \text{s}^{-1}$ for the gas-phase molecular geometry and to be $4.04\times10^8\ \text{s}^{-1}$ for the molecule-in-crystal structure, respectively. When two and

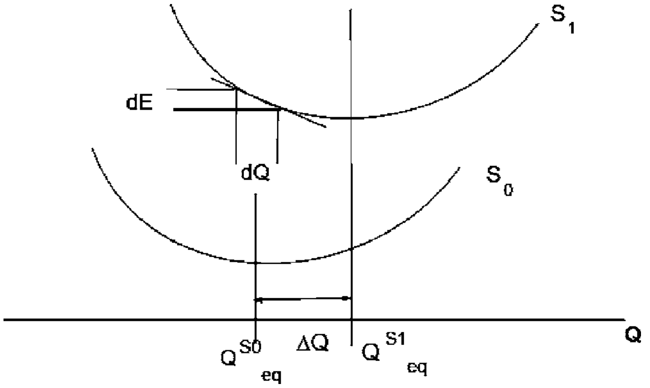

FIG. 2. Scheme of displaced harmonic model for the nonradiative decay process.

four siloles molecule clusters as cut from the bulk crystal structure are considered, the radiative decay rate are calculated to be $3.2\times 10^8\ \mathrm{s}^{-1}$ and $3.0\times 10^8\ \mathrm{s}^{-1}$, respectively. These data show (i) a slight enhancement in radiative decay rates from the gas-phase molecular structure to the molecule-in-crystal structure (from $1.2\times 10^8\ \mathrm{s}^{-1}$ to $4.04\times 10^8\ \mathrm{s}^{-1}$), but certainly not enough to explain the huge enhancement (more than 800 times) of luminescence for compound 1; (ii) the crystal packing only very slightly decreases the radiative decay rate (from $4.04\times 10^8\ \mathrm{s}^{-1}$ to $3.0\times 10^8\ \mathrm{s}^{-1}$); namely, such a crystal packing does not quench the radiative decay process.

We then look at the nonradiative decay processes. Under the first-order time-dependent perturbation and Condon approximations, the rate constant of a radiationless transition through vibronic coupling is expressed as the Fermi golden rule:[16]

$$W_{i\text{-}f}^{S_1\text{-}S_0} = \frac{2\pi}{\hbar^2}\sum_l |R_l(fi)|^2 \sum_v \sum_{v'} P_{iv} \left| \left\langle \Theta_{fv'} \middle| \frac{\partial \Theta_{iv}}{\partial Q_l} \right\rangle \right|^2 \times \delta(E_{fv'} - E_{iv}), \qquad (1)$$

where initial state i means the lowest singlet state S_1: according to Kasha's rule, it is S_1 that is responsible for radiative decay; final state f means the ground state S_0; $R_l(fi) = -\hbar^2 \langle \Phi_f | \frac{\partial}{\partial Q_l} | \Phi_i \rangle$; P_{iv} denotes the Boltzmann distribution for the initial vibrational states; Θ and Φ are vibrational and electronic wave functions, respectively; Q is the normal-mode coordinate. Under the displaced harmonic approximation, the shape of the potential energy surface, for the excited state is assumed to be the same as that for the ground state, except for a rigid displacement in their normal-mode coordinates; see Fig. 2. Therefore, the equation can be recast into the following simpler form:[17]

$$W_{i\text{-}f}^{S_1\text{-}s_0} = \sum_l \frac{1}{\hbar^2}\left(\frac{\omega_l}{2\hbar} |R_l(fi)|^2 \right) N_{\mathrm{FC}}, \qquad (2)$$

$$N_{\mathrm{FC}} = \sqrt{\frac{2\pi}{\sum_j' S_j \omega_j^2 (2\bar{n}_j + 1)}} \exp\left[-\frac{(\omega_{fi} + \omega_l + \sum_j' S_j \omega_j)^2}{2\sum_j' S_j \omega_j^2 (2\bar{n}_j + 1)} \right], \qquad (3)$$

where N_{FC} refers to the density weighted Franck-Condon (FC) factor, ω_{fi} is the energy gap between the final state and initial state, S_j is the Huang-Rhys (HR) factor for the jth mode, $\Sigma_j' S_j \omega_j$ is the sum of the relaxation energies for all modes except the promoting mode l, and $\bar{n}_j$ is the Boltzmann averaged number of phonon for the jth mode. According to the linear coupling model,[18] the HR factor is obtained through the normal-mode displacement ΔQ_j (evaluated from the excited-state energy gradient; see Fig. 2):

$$\Delta Q_j = \frac{1}{\omega_j^2} \frac{\partial E^{exc}}{\partial Q_j}, \qquad (4)$$

$$S_j = (\omega_j \Delta Q_j^2)/2\hbar . \qquad (5)$$

The HR factor characterizes the averaged number of phonons emitted (absorbed) by electron into (from) nuclears in the relaxation process. From Eqs. (2) and (3), it is readily seen that if both the electronic coupling prefactor and N_{FC}, factor are large, the radiationless decay will be fast. In fact, both factors have vibrational origin: the electronic coupling is a derivative of the wave function with respect to the promoting vibrational mode l, while N_{FC} is exponentially proportional to the HR factors of a sum of all the modes except the promoting mode: the most important contribution comes from the denominator in the exponential function. In the case of conjugated polymers, many studies have indicated that the double-bond stretching and single-bond stretching modes contribute the most to the vibronic coupling, which presents the two most prominent features in the resonant Raman spectroscopy,[19] a common phenomenon for conjugated systems. Previous studies indicated that the double-bond stretching contributes the most to the nonradiative decay coupling. For several conjugated molecules, the coupling strength [Eq. (1)] has been calculated to be around $R_l = 1800\ \mathrm{cm}^{-1}$ (Ref. 20). But the linear-structured conjugated systems do not necessarily possess a large nonradiative decay rate. In fact, for many conjugated polymers, the light-emitting efficiency is generally high, because when excluding the double-bond stretching mode, other vibrational modes do not show any appreciable HR factors, resulting in a very small FC factor. However, the structure of silole (see compound 1 in Fig. 1) is remarkably different from the usual conjugated molecules in the sense that in addition to the conjugation backbone, from site 2 to site 5 of the silacycle, two more phenyl rings are attached to sites 3 and 4 of the silacycle. These two rings are not fully in the conjugation backbone and can twist more readily than the conjugated parts. Our quantum chemistry calculations show that these ring-twisting motions contribute largely to the Franck-Condon factor.

The excited-state energy gradient [Eq. (4)] with respect to a normal mode is calculated numerically by slightly displacing the atom position according to this normal mode, the

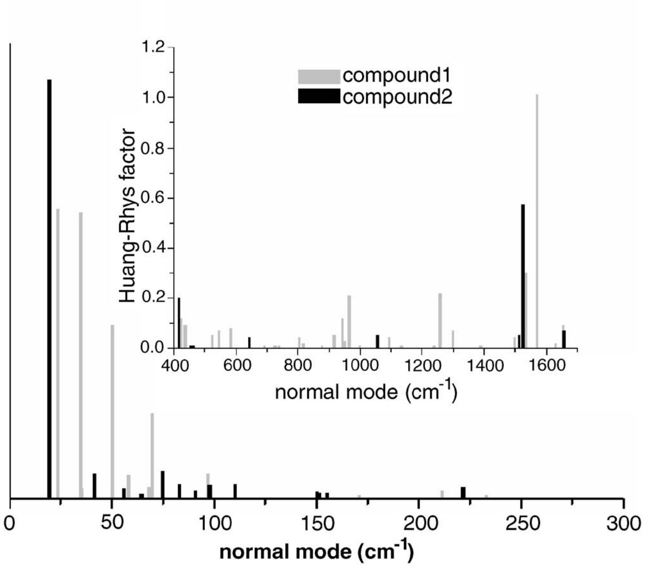

FIG. 3. First-principles linear-coupling-model-calculated Huang-Rhys factors versus the normal-mode wave numbers for silole compound 1 (grey bar) and compound 2 (black bar). The four remarkable HR factors for compound 1 are 31.8, 31.5, 19.1, and 9.4.

norm of the Euclidean displacement being 0.01 Å. This displacement is small enough to guarantee convergence of the numerical derivative. The energy of the excited state is calculated with time-dependent density function theory both for the equilibrium geometry and for the displaced geometry. The HR factors of the lowest singlet excited state (S_1) for both compounds are calculated according to Eq. (5) and are presented in Fig. 3. It is clearly seen that (i) the double-bond stretching modes 1573 cm^{-1} and 1522 cm^{-1} possess HR factors 1.01 and 0.57 for compounds 1 and 2, respectively, and (ii) there appear four modes with huge HR factors (>9) in the low-frequency sides ($<100\ \mathrm{cm}^{-1}$) for compound 1, while only one such mode for compound 2.

We then evaluate the FC factor Eq. (3) for the two compounds. In both cases, we assume that there is only one pro moting mode; namely, the double-bond stretching contributes to the electronic coupling part R_l. We have found that for compound 1 the FC factor is about 10^{32} times larger than that for compound 2. This means that the nonradiative decay process is completely suppressed for compound 2, due to the steric hindrance by the isopropyl groups. The nonadiabatic radiationless decay rate for compound 1 is calculated to be $1.8\times 10^{11}\ \mathrm{s}^{-1}$ at room temperature, two to three orders of magnitude larger than the radiative decay rate.

III. CONCLUSION AND DISCUSSION

It can be concluded that for compound 1 the proper combination of the double-bond stretching (electronic coupling) and the twisting motions of phenyl rings at sites 3 and 4 of the silacycle dissipates the excited-state energy nonradiatively. We have shown that the steric hindrances from the isopropyl substitutions can completely suppress this energy dissipation channel and make compound 2 to be highly luminescent in solution. The AEL phenomena in siloles have exactly the same origin: the aggregation, solid-state structure, sticky solvent, or cluster formation can form steric hindrances which restrict the twisting motions of the side-phenyl rings and enhance the radiative decay.

Our results would imply that conjugated molecules with phenyl groups, which are not in a fully conjugated position and are ready to rotate, are promising systems to exhibit AEL phenomena. From our theoretical perspective, the conjugation backbone stretching motion can provide the first prefactor in Eq. (2) and the rotating phenyl groups provide the second factor N_{FC}. Indeed, so far the AEL molecules do possess this common feature.[2–12] More comprehensive and detailed investigations are in active progress. And finally, the prerequisite for AEL to occur is that the usual aggregation quenching is not detrimental to the radiative decay, as indicated by our computation for the molecular clusters of 2 and 4 siloles.

ACKNOWLEDGMENTS

We thank Ben Zhong Tang and Yunqi Liu for numerous discussions on the experimental findings. The authors are indebted to Chad Risko and Tommy Ohyun Kwon for discussing the quantum chemical computations for the excited state. The work in Beijing is supported by the Ministry of Science and Technology in China (973 program, Grant No. 2002CB613406) and National Science Foundation of China (Grant Nos. 2043070, 10425420, 90301001, and 20420150034). It is also supported by the CNIC Supercomputing Center of the Chinese Academy of Sciences. Y.L. acknowledges support from the Swedish Research Council (VR) and the Carl Trygger Foundation (CTS).

---

*Electronic address: zgshuai@iccas.ac.cn
†Electronic address: fangwh@bnu.edu.cn
‡Electronic address: luo@kth.se

[1] C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987); J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, Nature (London) **347**, 539 (1990); G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, *ibid.* **357**, 477 (1992).

[2] J. D. Luo, Z. L. Xie, J. W. Y. Lam, L. Cheng, B. Z. Tang, H. Chen, C. F. Qiu, H. S. Kwok, X. W. Zhan, Y. Q. Liu, and D. B. Zhu, Chem. Commun. (Cambridge) **2001**, 1740.

[3] B. Z. Tang, X. W. Zhan, G. Yu, P. P. S. Lee, Y. Q. Liu, and D. B. Zhu, J. Mater. Chem. **11**, 2974 (2001).

[4] J. W. Chen, C. C. W. Law, J. W. Y. Lam, Y. Dong, S. M. F. Lo, I. D. Williams, D. B. Zhu, and B. Z. Tang, Chem. Mater. **15**, 1535

(2003); J. W. Chen, Z. Xie, J. W. Y. Lam, C. C. W. Law, and B. Z. Tang, Macromolecules **36**, 1108 (2003); J. W. Chen, H. Peng, C. C. W. Law, Y. Dong, J. W. Y. Lam, I. D. Williams, and B. Z. Tang, *ibid.* **36**, 4319 (2003); J. W. Chen, B. Xu, X. Y. Ouyang, B. Z. Tang, and Y. Cao, J. Phys. Chem. A **108**, 7522 (2004).

[5] B. K. An, S. K. Kwon, S. D. Jung, and S. Y. Park, J. Am. Chem. Soc. **124**, 14410 (2002).

[6] J. W. Chen, B. Xu, X. Ouyang, B. Z. Tang, and Y. Cao, J. Phys. Chem. A **108**, 7522 (2004).

[7] Z. Xie, B. Yang, G. Cheng, L. Liu, F. He, F. Shen, Y. Ma, and S. Liu, Chem. Mater. **17**, 1287 (2005).

[8] K. Tamao, M. Uchida, T. Izumizama, K. Furukawa, and S. Yamaguchi, J. Am. Chem. Soc. **118**, 11974 (1996).

[9] C. Chuit, R. J. P. Corriu, C. Reye, and J. C. Young, Chem. Rev. (Washington, D.C.) **93**, 1371 (1993).

[10] H. Y. Chen, W. Y. Lam, J. D. Luo, Y. L. Ho, B. Z. Tang, D. B. Zhu, M. Wong, and H. S. Kwok, Appl. Phys. Lett. **81**, 574 (2002); G. Yu, S. W. Yin, Y. Q. Liu, J. Chen, X. Xu, X. Sun, D. Ma, X. Zhan, Q. Peng, Z. G. Shuai, B. Z. Tang, D. B. Zhu, W. H. Fang, and Y. Luo, J. Am. Chem. Soc. **127**, 6335 (2005).

[11] B. X. Mi, Y. Q. Dong, Z. Li, J. W. Y. Lam, M. Häußler, H. H. Y. Sung, H. S. Kwok, Y. P. Dong, I. D. Williams, Y. Q. Liu, Y. Luo, Z. G. Shuai, D. B. Zhu, and B. Z. Tang, Chem. Commun. (Cambridge) **2005**, 3583.

[12] C. Risko, G. P. Kushto, Z. H. Kafafi, and J. L. Brédas, J. Chem. Phys. **121**, 9031 (2004).

[13] Z. Li, Y. Dong, B. Mi, Y. Tang, M. Haussler, H. Tong, Y. Dong, J. W. Y. Lam, Y. Ren, H. H. Y. Sung, K. S. Wong, P. Gao, I. D. Williams, H. S. Kwok, and B. Z. Tang, J. Phys. Chem. B **109**, 10061 (2005).

[14] The computation is carried out with complete active space self-consistent-field method, which is reliable in calculating the spin-orbit coupling constant. The GAMESS package can be freely downloaded from http://www.msg.ameslab.gov/GAMESS/GAMESS.html

[15] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, computer code GAUSSIAN 03, revision A.I, Gaussian Inc., Pittsburgh, PA, 2003. The hybrid DFT functional is chosen to be B3LYP—namely, Becke's three-parameter exchange functional plus Lee-Yang-Parr correlation functional.

[16] S. H. Lin, J. Chem. Phys. **44**, 3759 (1966).

[17] S. H. Lin, C. H. Chang, K. K. Liang, R. Chang, J. M. Zhang, T.-S. Yang, M. Hayashi, Y. J. Shiu, and F. C. Hsu, Adv. Chem. Phys. **121**, 1 (2002).

[18] T. E. Sharp and M. J. Rosenstock, J. Chem. Phys. **41**, 3453 (1964); E. V. Doktorov, I. A. Malkin, and V. I. Manko, J. Mol. Spectrosc. **23**, 1(1975).

[19] G. Zerbi, H. W. Siesler, I. Noda, M. Tasumi, and S. Krimm, *Modern Polymer Spectroscopy* (Wiley, New York, 1999).

[20] G. Orlandi, F. Zerbetto, and M. Z. Zgierski, Chem. Rev. (Washington, D.C.) **91**, 867 (1991); A. Troisi and G. Orlandi, J. Chem. Phys. **118**, 5356 (2003).