

Spin Polarization of Metal (Mn, Fe, Cu, and Mg) and Metal-Free Phthalocyanines on an Fe(100) Substrate

T. Suzuki,* M. Kurahashi, X. Ju, and Y. Yamauchi

National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

Received: June 28, 2002; In Final Form: August 28, 2002

The electronic structure and spin asymmetry of metal phthalocyanines (Pcs) (metal = Mn, Fe, Cu, and Mg) and metal-free Pc thin films of 1-monolayer (ML) thickness on an Fe(100) substrate were investigated using spin-polarized metastable deexcitation spectroscopy (SPMDS). The surface density-of-states (SDOS) of these Pcs observed in MDS was almost identical, and thus, insensitivity of the Pc electronic structure to the variation of the central metal atoms is indicated. On the other hand, the spin asymmetry in the SPMDS measurements exhibited noticeable differences among Pcs. These results are discussed from the viewpoint of the Pcs electronic structure calculated by a discrete variational X α method. The fact that differences are found in the spin asymmetry but not in SDOS among Pcs indicates an important role of the central metal atoms for spin polarization.

1. Introduction

Phthalocyanines (Pcs) are planar organic molecules that have been discussed in thousands of papers. They are one of the most stable organic materials and do not show any noticeable degradation in air up to about 400 °C. This thermal stability, together with their large chemical versatility, has motivated investigations for technological applications using Pcs, such as for pigments, dyes, chemical sensors, catalysis, optoelectronic devices, and solar cells.¹ The structure of a Pc is shown schematically in Figure 1. A metal atom is located at the center of the molecule, creating a perfectly square planar environment, with valence and coordination numbers of two and four, respectively, whereas two hydrogen atoms are substituted for this metal atom in metal-free Pc. The point groups of metal Pcs (MPcs) and metal-free Pc are D_{4h} and D_{2h} , respectively.

Recent emerging research on Pcs involves their magnetic properties in a one-dimensional array or in a thin-film form.^{2–4} Although the research on the magnetism of organic materials in bulk form has a long history, recent investigations of such a low-dimensional system have been motivated by the expectation that the magnetism of those systems may be remarkably different from that in bulk. One of the objectives in the research field called molecular magnetism is to control the magnetic properties at the scale of an individual molecule or single molecule layer. In this context, the magnetic interaction between ultrathin Pc film and the underlying ferromagnetic substrate is quite interesting.

It is difficult to observe the magnetic properties of ultrathin films because an extremely surface-sensitive technique is required to separate adsorbates from underlying substrates. Actually, although many experiments have been conducted to investigate the influence of adsorption on surface magnetism, observations of the magnetism of the adatom itself have been rare.

In our previous study, the spin polarization in the molecular orbitals of the CuPc ultrathin film deposited on a magnetized-

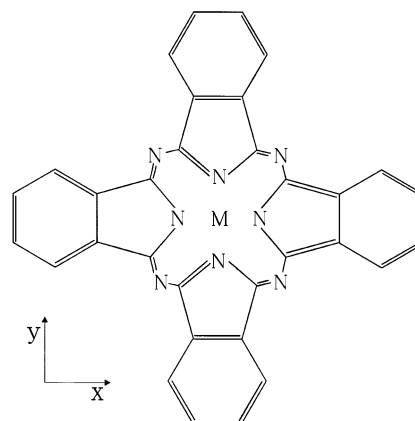


Figure 1. Schematic illustration of the molecular structure of metal phthalocyanine. "M" denotes the central metal atom.

Fe substrate was observed.⁵ This was the first measurement of the spin polarization in the organic molecular adsorption system. In that study, spin-polarized metastable deexcitation spectroscopy (SPMDS) was utilized.⁶ In (SP)MDS, (spin-polarized) metastable He* atoms (2^3S , $1s2s$) with low kinetic energy (~ 0.5 eV) are projected onto the surface, and the number of electrons ejected from the surface as a result of the deexcitation of He* is analyzed as a function of their kinetic energy. The surface sensitivity of SPMDS is extreme, and this provides an advantage in the investigation of magnetic properties of adsorbates or ultrathin films.

In the present paper, a systematic study concerning the adsorption of MPcs ($M = \text{Mn, Fe, Cu, and Mg}$) and metal-free Pc of 1 monolayer (ML) on a magnetized Fe(100) substrate by SPMDS is presented. In the MDS measurements, no remarkable difference in the spectra among Pcs was found, and, thus, the insensitivity of surface density-of-states (SDOS) of a Pc to the presence of a central metal atom is indicated. On the other hand, noticeable differences in spin asymmetry were found among Pcs in SPMDS. These results are discussed in terms of the electronic structure calculated by the discrete variational (DV)-X α method.

* To whom correspondence should be addressed. Fax: +81-298-59-2801. E-mail: suzuki.taku@nims.go.jp.

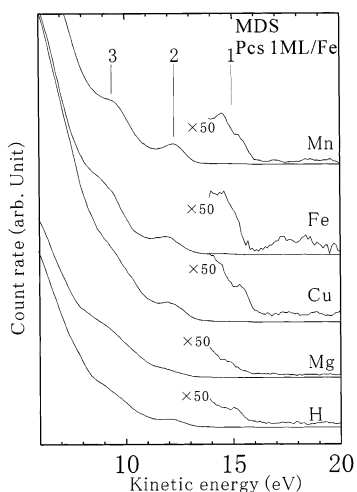


Figure 2. MDS spectra obtained on the Pc films deposited on the Fe(100) substrate, where the thickness of the film was 1 ML.

2. Experiment

The experiments were performed in an ultrahigh vacuum chamber (base pressure $5 \sim 10^{-11}$ Torr), which was equipped with a sample transfer system, a rotatable electrostatic hemispherical sector analyzer (Omicron, SHA50), a beam line for He*, a Stern-Gerlach analyzer, and reflection high-energy electron diffraction (RHEED). In the measurement using (SP)MDS, TOF techniques were employed in combination with a pulsed discharge in the He* source to separate the contributions to the ejected electron spectra from He I photons and He* metastables. The 2^1S atoms were deexcited using a quench lamp, which was positioned between the source and the sample,⁷ and the ratio of the He* 2^3S to He* 2^1S at the sample position measured using a Stern-Gerlach analyzer was 8:1. Circularly polarized 1083 nm radiation from a laser diode (SDL 6702) was utilized to optically pump and, thus, spin-polarize the He* 2^3S beam.⁷ The incidence angle of He* and the emission angle of electrons were 45° and 0° , respectively, with respect to the surface normal. The sample was pulse-magnetized in the plane transverse to the He* beam prior to the SPMDS measurement, that is, along the Fe[100]-easy axis of bcc-Fe, and the spectra were obtained in the remanent state. The MDS spectra were obtained in the constant pass energy mode at 4 eV, whereas SPMDS spectra were obtained in this mode at 10 eV.

Fe(100) films were grown on MgO(100) substrates by vapor deposition of Fe (purity 99.99%) using an electron beam evaporator (Omicron, EFM3T). The epitaxial growth of Fe was confirmed by RHEED. Commercial Pc powder was purified three times by vacuum sublimation prior to vapor deposition. The organic elemental analysis for C, H, and N of the purified CuPc was in agreement with the calculated values in the range of $\pm 0.2\%$, and the same procedure of purification as for CuPc was applied to other Pcs. The deposition of Pcs was performed at room temperature. Using quartz crystals, the deposition rate was monitored to be 0.3 ML/min, where 1 ML corresponds to the molecular plane spacing in the β form of the Pc crystal.⁸

3. Results and Discussion

Figure 2 shows the MDS spectra of Pcs/Fe surfaces, where the coverage of Pcs is 1 ML. The low-kinetic-energy region of the spectra is affected by the intense secondary electrons, and this part of the spectra is omitted. In every spectrum, three peaks originated from the Pc overlayer are observed, which are labeled 1~3 in Figure 2. The energy positions of these peaks are almost

identical among Pcs. On the surface covered with Pcs of 1 ML, He* metastables deexcite via the Auger deexcitation process, and the emitted electron spectrum basically reflects SDOS.⁹ The electronic structure of Pcs derived from Figure 2 agrees with that from a photoemission study reported previously.^{10–12} The similarity in the MDS spectra among Pcs in Figure 2 indicates that the SDOS in the surface-vacuum region detected by MDS is almost identical, and so that the Pc electronic structure is indicated to be insensitive to the central metal atom. The systematic photoemission study concerning the electronic valence band of Pcs by Koch and co-workers indicates that the photoemission spectra are very similar among Pcs.^{11–16} This similarity in the electronic structure derived from a photoemission study is generally interpreted to be a consequence of the low proportion of the central metal atom to Pc electrons and of the small cross-sections of metal d electrons at low photon energy.¹ The similarity in the MDS spectra in Figure 2 is also interpreted to be due to a low ratio of electrons at the central metal atom to the total number of electrons of Pc.

There is a small difference in the peak intensity among Pcs in the MDS spectra in Figure 2. This may be due to the slight deviation in the amount of deposition in our experiment rather than the difference in SDOS. The MDS peak intensity changed remarkably as a function of film thickness in the range below several ML.⁵

In our former study for CuPc/Fe(100), a structural analysis using low-energy ion scattering (LEIS) was performed.⁵ It was revealed that CuPc molecules adsorbed on the Fe(100) surface with their planes parallel to the surface when the film thickness was 1 ML. All Pcs investigated in the present study have an isomorphic structure with CuPc, and it is reasonable to assume that the Pc molecule treated in the present investigation adsorbs with its plane parallel to the Fe(100) surface.

For a better understanding of the Pc electronic structure, we have calculated the molecular orbital energies of Pcs using a DV-X α method. As a first approximation, the calculated electronic structure of a single Pc molecule is compared with the present experiment for Pcs on Fe(100). The details of the calculation have been described by Adachi et al.¹⁷ Briefly, the Hartree–Fock–Slater (HFS) equation for a molecule is solved self-consistently with the use of a localized exchange potential (X α potential). The exchange correlation parameter α is adjustable and is taken to be 0.7.¹⁷ Numerical atomic orbitals, obtained as solutions of the atomic HFS equations, are used as basis sets. The calculation is made using an MPc single molecule with simple basis sets, and the point groups of D_{4h} and D_{2h} are taken into account for the calculation for MPc and metal-free Pc, respectively. The atomic positions indicated in refs 18 and 19 and references therein were used for our calculation.

Figure 3 illustrates the calculated eigenenergy levels of the occupied molecular orbitals of Pcs. NiPc is not treated in the present experiment, but it is included in the calculation to identify a trend in the Pcs electronic structure. The orbitals are labeled in irreducible representation of D_{4h} in Figure 3. Under this point group, a_{1u} , a_{2u} , b_{1u} , b_{2u} , and e_g have an antisymmetric xy mirror plane taking the molecule to lie in the xy plane. Thus, the orbital of these irreducible representations includes π components spreading perpendicularly to the molecular plane. In the MDS measurements, the deexcitation of He* occurs in the surface–vacuum region as a result of the interaction with the surface electrons exuding into the vacuum side. Thus, π orbitals spreading perpendicularly to the molecular plane are effectively attacked by He*. These π orbitals, which are

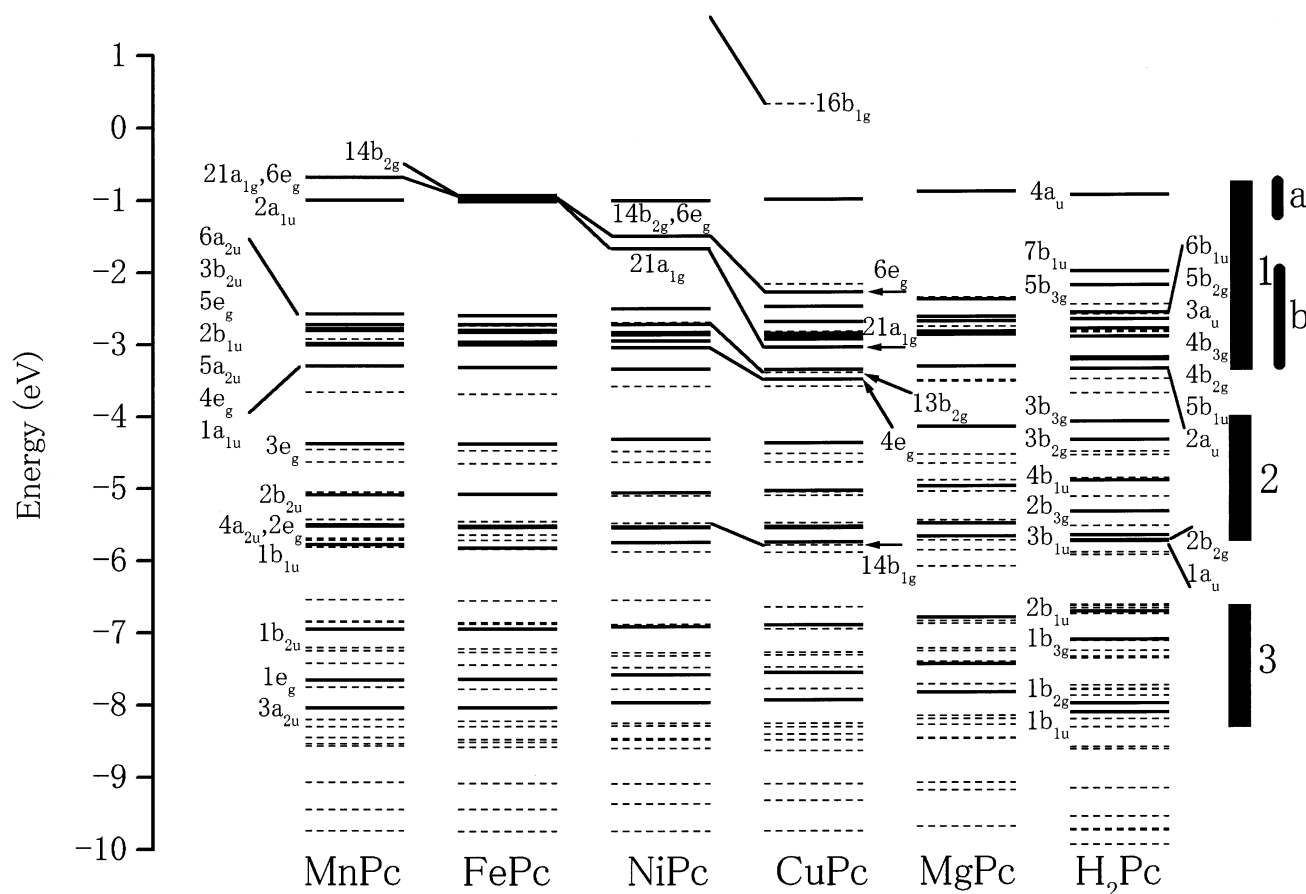


Figure 3. Orbital energy levels in Pcs.

expected to be detected in MDS, are indicated by solid lines, and the other orbitals are indicated by broken lines in Figure 3. Beside the orbitals of Pc macrocycle, metal 3d components are included in the energy level in Figure 3. In the D_{4h} notation, the five metal 3d orbitals are represented as a_{1g} (d_{z^2}), b_{1g} ($d_{x^2-y^2}$), e_g (d_{xz} , d_{yz}), and b_{2g} (d_{xy}). In the spatial distribution of these wave functions, it is expected that a_{1g} and e_g orbitals spread toward the vacuum side, and thus, these levels are indicated as solid lines in Figure 3. To clarify the energy shift of the orbitals originated mainly from the d components among Pcs, such levels are connected by lines in Figure 3, where the orbitals in which the occupation ratio of 3d estimated by Mulliken population analysis is more than 25% are treated as levels mainly from the d components. In the case of H_2Pc (D_{2h} notation), the orbitals of b_{2g} , b_{3g} , a_u , and b_{1u} are indicated as solid lines for the same reason mentioned above.

From the comparison of the calculated electronic structure in Figure 3 with the MDS spectra in Figure 2, the assignments of peaks 1~3 are determined as indicated on the right side of Figure 3. Orti and Bredas calculated the electronic structure of H_2Pc using the nonempirical valence effective Hamiltonian pseudopotential, and they discussed the assignment of the peaks in reported photoemission spectra.¹ Our assignment of MDS of H_2Pc essentially agrees with that by Orti and Bredas.

In the calculated electronic structure in Figure 3, the following two essential features are described. First, the energies of the levels mainly originated from Pc are unaffected by metal substitution. Second, the components of 3d have a lower orbital energy with increasing the numbers of electrons in the 3d orbital. These two features have also been reported in a recent calculation by Liao and Scheiner using a density functional method.¹⁸

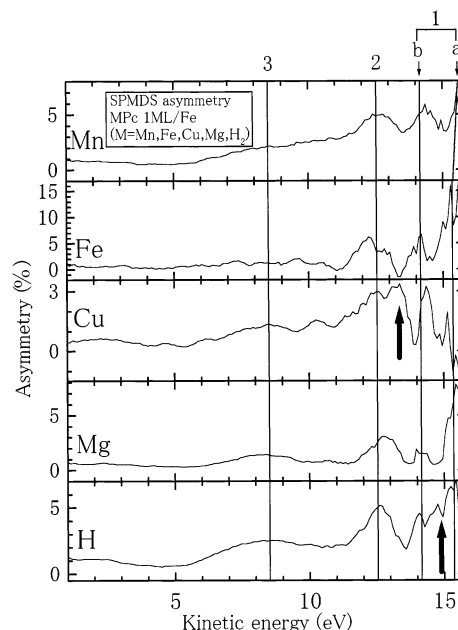


Figure 4. Spin asymmetry observed on the Pc films deposited on the Fe(100) substrate, where the thickness of the film was 1 ML.

Figure 4 shows the spin asymmetry $(I_p - I_a)/(I_p + I_a)$ in SPMDS on Pcs (1 ML)/Fe, where I_p and I_a denote the intensity obtained by He* polarized parallel and antiparallel with respect to the majority spin of the Fe substrate. The spin asymmetry is clearly observed at the molecular orbital positions of 1 and 2. The asymmetry peak is relatively small at the position of peak 3, because the background of the secondary electron decreases the absolute value of the asymmetry in this low-kinetic-energy

region. The sign of the spin asymmetry at the molecular orbitals 1~3 is positive in all Pcs, and this sign of the asymmetry was the same as that of the Fe(100) surface at the Fermi level. It is apparent that there are two maxima of the spin asymmetry at the position of peak 1, indicated as a and b in Figure 4. In a comparison of these asymmetry curves with the electronic structure in Figure 3, the asymmetry at position a is due to a_{1u} for D_{4h} and to a_u for D_{2h} , which are the highest occupied molecular orbitals. On the other hand, the asymmetry at b is attributed to the mixture of several orbitals, as shown on the right in Figure 3.

The fact that the asymmetry curve of CuPc has an additional structure at about 13.4 eV is notable and indicated by an arrow in Figure 4. This additional structure was well reproduced in our experiment. In the calculated electronic structure of CuPc in Figure 3, the orbital of $4e_g$ is situated below the structure of 1b. This may be the origin of this additional structure of CuPc. The same discussion using the calculated electronic structure is applied to the disappearance of the intensity valley between positions 1a and 1b in H_2Pc . The degeneracy is released because of the low symmetry of a H_2Pc molecule, and there appear to be more orbitals than in other Pcs, as shown in Figure 3. Two orbitals, b_{1u} and b_{3g} , are situated above 1b in Figure 3, and this may cause the asymmetry between the positions of 1a and 1b. The slight shift of the asymmetry maximum to the high-kinetic-energy side at 1a in MnPc is also interpreted to be related to the electronic structure in Figure 3. As seen in Figure 3, the orbitals of $21a_{1g}$ and $6e_g$ are located above $2a_{1u}$, and this is interpreted to be the origin for the shift of the asymmetry maximum of MnPc.

The absolute value of the spin asymmetry is easily affected by the crystal quality of the underlying epitaxial Fe film. In this context, the comparison in the magnitude of the asymmetry among Pcs will not be discussed in the present paper, although it was confirmed that the features in the asymmetry curves described in the present paper were well reproduced.

In our previous study on CuPc/Fe, the MDS peak at the position of 1a was assigned to Cu 3d from the comparison of the structural analysis using LEIS and the thickness dependence of this peak intensity.⁵ In that study, the MDS peak at 1a was observed when the thickness was 1 ML, but it disappeared in thicker films. From the spatial distribution of d orbitals of a_{1g} and e_g in the D_{4h} representation, these orbitals are expected to be detected in MDS when the Pc molecule adsorbs with its plane parallel to the surface but not be detected in the disordered adsorption structure because the d wave function is shielded by π and σ orbitals. The present calculation in Figure 3, however, indicates that the $2a_{1u}$ orbital, which is the π component, is attributed to peak 1a. The reason for this contradiction concerning the assignment of the MDS peak at the position of 1a is not clear at this time. One possibility is that this may be due to the fact that $2a_{1u}$ originates mainly from the C 2p of the pyrrole ring, where more than 80% of $2a_{1u}$ comes from the pyrrole carbon according to the Mulliken population analysis. As illustrated in Figure 1, the benzene ring is located outside the pyrrole ring, and the π orbitals from pyrrole may be shielded by π and σ orbitals originating from benzene rings

in the disordered adsorption structure, and thus, the π orbitals from pyrrole may have the same thickness dependence as d of Pcs.

It is noted that the MDS spectra are almost identical among Pcs, indicating nearly the same SDOS, but the differences in the asymmetry curves among Pcs are observed. This indicates that the center atom in Pc molecules plays an important role in the spin polarization and, thus, in the magnetic interaction with the underlying Fe substrate.

4. Conclusion

The data of MDS and SPMDs for MPc ($M = \text{Mn, Fe, Cu, and Mg}$) and metal-free Pc thin films of 1 ML thickness on an Fe(100) substrate are presented. The spin asymmetry was clearly observed at the molecular orbitals of all Pcs, and the sign of the asymmetry was the same as that of the Fe(100) at the Fermi level. No remarkable differences in Pcs were found in the MDS spectra, indicating an almost identical SDOS. On the other hand, some clear differences were found in the SPMDs measurement. These features in (SP)MDS are interpreted in terms of the electronic structure calculated by the DV-X α method. These results are interpreted to be related with the important role of the central metal atom of Pc for spin polarization.

Acknowledgment. The authors are grateful for valuable discussions with Prof. N. Ueno and Dr. S. Kera of Chiba University. The beneficial suggestions of Dr. H. Isago and the help of Dr. H. Kitazawa of National Institute for Materials Science are also greatly appreciated.

References and Notes

- (1) Orti, E.; Bredas, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 2379 and references therein.
- (2) Yamada, H.; Shimada, T.; H.; Koma, A. *J. Chem. Phys.* **1998**, *108*, 10256.
- (3) Ogawa, M. Y.; Hoffman, B. M.; Lee, S.; Yudkowsky, M.; Halperin, W. P. *Phys. Rev. Lett.* **1986**, *57*, 1177.
- (4) Simonyan, M.; Yonehara, Y.; Ding, Y.; Yakushi, K. *Phys. Rev. B* **2001**, *63*, 113103.
- (5) Suzuki, T.; Kurahashi, M.; Yamauchi, Y. *J. Phys. Chem. B* **2002**, *106*, 7643.
- (6) Onellion, M.; Hart, M. W.; Dunning, F. B.; Walters, G. K. *Phys. Rev. Lett.* **1984**, *52*, 380.
- (7) Riddle, T. W.; Onellion, M.; Dunning, F. B.; Walters, G. K. *Rev. Sci. Instrum.* **1981**, *52*, 797.
- (8) Buchholz, J. C.; Somorjai, G. A. *J. Chem. Phys.* **1977**, *66*, 573 and references therein.
- (9) Ozaki, H.; Harada, Y. *J. Chem. Phys.* **1990**, *92*, 3184.
- (10) Berkowitz, J. *J. Chem. Phys.* **1979**, *70*, 2819.
- (11) Iwan, M.; Koch, E. E.; Chiang, T. C.; Eastman, D. E.; Himpsel, F. J. *Solid State Commun.* **1980**, *34*, 57.
- (12) Koch, E. E.; Grobman, W. D. *J. Chem. Phys.* **1977**, *67*, 837.
- (13) Iwan, M.; Eberhardt, W.; Kalkoffen, G.; Koch, E. E.; Kunz, C. *Chem. Phys. Lett.* **1979**, *62*, 344.
- (14) Iwan, M.; Koch, E. E. *Solid State Commun.* **1979**, *31*, 261.
- (15) Tegeler, E.; Iwan, M.; Koch, E. E. *J. Electron Spectrosc. Relat. Phenom.* **1981**, *22*, 297.
- (16) Koch, E. E.; Jugnet, Y.; Himpsel, F. J. *Chem. Phys. Lett.* **1985**, *116*, 7.
- (17) Adachi, H.; Tsukada, M.; Satoko, C. *J. Phys. Soc. Jpn.* **1978**, *45*, 875.
- (18) Liao, M. S.; Scheiner, S. *J. Chem. Phys.* **2001**, *114*, 9780.
- (19) Ghosh, A.; Gassman, P. G.; Almlöf, J. *J. Am. Chem. Soc.* **1994**, *116*, 1932.