PHYSICAL REVIEW B **72**, 094413 (2005)

Theory of photoinduced high-spin states in organic molecules

Ping Huai,* Yukihiro Shimoi, and Shuji Abe
Nanotechnology Research Institute (NRI) and Synthetic Nano-Function Materials Project (SYNAF),
National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

(Received 20 May 2005; published 13 September 2005)

We present a theoretical study on optically controlled spin alignment in purely organic molecules. A quantum electron-spin model is applied to simulate molecular systems, in which localized spin densities on radical groups are coupled with a π-conjugated moiety through exchange interactions. We numerically solve the model up to highly excited states including all the correlation effects. It is demonstrated in the anthracene-based molecules that the lowest triplet of π moiety plays the role of ferromagnetic coupler for the localized spins. A metastable high-spin state can be generated by photoexcitation and subsequent relaxation processes. It is further clarified in the biphenyl-based molecules that such spin alignment depends sensitively on the molecular geometry and the strength of the exchange interactions. Our study offers a theoretical basis for understanding photoinduced high-spin states observed in π-conjugated molecular systems.

DOI: 10.1103/PhysRevB.72.094413 PACS number(s): 75.50.Xx, 71.10.Fd, 75.20.Hr

I. INTRODUCTION

Great advances have been achieved in the molecule-based magnetism after decades of extensive studies.[1–6] However, most studies of organic molecular magnets are limited to the neutral ground state, in which spin polarization governs spin alignment. In recent years, new strategies have been applied to molecular magnets by utilizing novel properties of excited and doped states. In these molecular magnets, their intramolecular spin alignment is controllable by external stimuli, e.g., charge doping[7–9] or photoexcitation.[10–14]

A typical example of such molecular magnets is shown in Fig. 1. Each molecule is made of three components: two stable radicals carrying unpaired electrons, and a π-conjugated moiety with delocalized spin density. It is well known that molecular magnetism can arise from spins of unpaired electrons on delocalized molecular orbitals. Since the radical spins are coupled by the π moiety, it is feasible to control their alignment by changing the role of the π-conjugated moiety from an antiferromagnetic coupler to a ferromagnetic one.

This type of controllable spin alignment has been demonstrated by Teki *et al.* in the molecule *a*.[10,11] The ground state of the molecule is a spin singlet ($S=0$) with a weak antiferromagnetic correlation between the radical spins. After the molecule is excited by short pulses of a laser, a metastable spin quintet ($S=2$) species has been detected in several microseconds, indicating ferromagnetic couplings among the two stable radicals and a photogenerated π triplet.

It has been confirmed that spin alignment of excited states depends sensitively on the molecular structure, but in a way different from that of the ground state. A topological isomer *b* has a similar singlet spin alignment in the ground state. However, no high-spin signal was detected in the relaxation processes following photoexcitation, indicating that the metastable state is a spin singlet ($S=0$).

In addition to the photoinduced high-spin states, an unusual dependence on the molecular structure has also been observed in some thianthrene derivatives upon charge doping.[7] It was found that one-electron oxidation leads to similar quartet states in two topological isomers despite different spin alignment in their neutral states. These experiments indicate that the mechanism of spin alignment in the doped and excited states is different from that in the neutral ground state.

Many efforts have been made to improve the understanding of spin alignment in molecular magnets.[15–31] The topological rule based on the dynamical spin polarization effect has been proved to be effective to explain spin alignment in the ground state.[32–35] The topological rule here implies that spin correlation between arbitrary two sites is positive or negative depending on whether the number of bonds along any one of the links between them is even or odd. However, the topological rule cannot be applied to doped or excited molecules, and only a few special cases, such as the strong-correlation limit,[36] can be analytically solved. Most discussions on spin alignment in the excited or doped state have been given on the basis of a valence-bond study,[16–20] mean-field approaches,[23–28] *ab initio* calculations,[30,31] or molecular

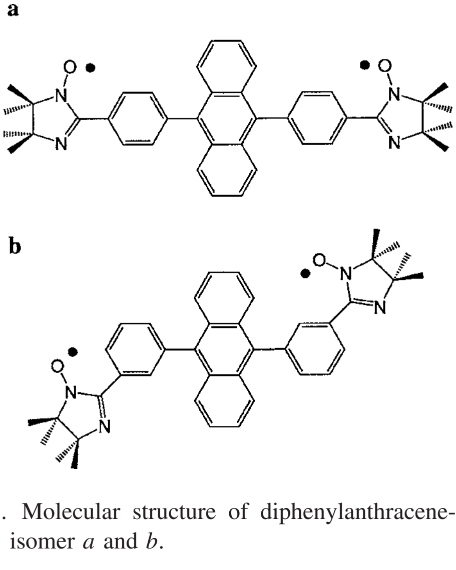

FIG. 1. Molecular structure of diphenylanthracene-bis(iminonitroxide): isomer *a* and *b*.

orbitals treatment.[37–43] Clarifying spin alignment in a molecular magnet from a general point of view has become an important theoretical subject.

We have theoretically investigated doping-controlled spin alignment by modeling π-conjugated molecules in terms of a quantum electron-spin system with electron-lattice couplings.[44] It has been demonstrated that high-spin states can be induced by hole-doping in the polyene-based molecules,[45] depending sensitively on the molecular structure and the system parameters.[46] More recently, we have conducted studies on the spin-alignment alteration upon hole-doping in more realistic molecules.[47] However, besides all these efforts, few theoretical investigations have been oriented to spin alignment in excited states related to photoinduced high spin.

The aim of this study is then to clarify the mechanism of optically controlled spin alignment in organic molecules based on π-conjugated hydrocarbon rings. Unlike linear chain systems such as polyene, these ring systems have small dimensions and rigid structures so that the long-range Coulomb interactions are likely to give more influence on intramolecular spin alignment than the electron-lattice coupling. Thus, a theoretical model has been designed to take into account intersite Coulomb interactions in the π-conjugated moiety and successfully applied to the thianthrene-based molecules for doping-induced high spin.[47] Instead of doped states, in this paper, we numerically study optically excited states to elucidate the mechanism of photoinduced high-spin states.

The rest of the paper is organized as follows. In Sec. II, a theoretical model is introduced to describe organic molecules composed of radical groups and a π-conjugated moiety. We numerically solve the model by exact diagonalization based on the Lanczos algorithm. Section III presents the numerical results and the discussions on spin alignment in the excited molecules based on two types of π moiety: anthracene and biphenyl. The anthracene-based molecules are discussed in Sec. III A for a metastable high-spin state and the dependence on molecular structure. In Sec. III B, we focus on the dependence of spin alignment on the molecular geometry, i.e., the dihedral angle between the two benzene rings of biphenyl. We further examine the dependence on the exchange coupling in the metastable state of the biphenyl-based molecules. These results are summarized in Sec. IV.

II. KONDO-PARISER-PARR-POPLE MODEL AND TREATMENT

We consider molecular systems, in which two localized radical spins are coupled to delocalized π electrons through exchange interactions, as is schematically shown in Fig. 2. The π-conjugated moiety is treated by the Pariser-Parr-Pople (PPP) model,[48,49] which is a semiempirical treatment for the long-range Coulomb interactions. The PPP model describes the π-electron system by including one π orbital per atom and assuming zero differential overlap between these orbitals. The localized spins correspond to the unpaired electrons of the stable radical groups attached to the π moiety. Thus, the present model is given in the Hamiltonian,

$$H = H_\pi + H_{\text{ex}}, \tag{1}$$

in which H_π indicates the π electron system and H_{ex} is the exchange interaction between the localized spins and the π electrons. They are given, respectively, by

$$H_\pi = -\sum_{i,j,s} t_{i,j}(C_{i,s}^\dagger C_{j,s} + \text{H.c.}) + \sum_{i,s}(-I_i)n_{i,s} + \sum_i U_{i,i}n_{i,\uparrow}n_{i,\downarrow} + \frac{1}{2}\sum_{i\neq j} U_{i,j}(n_i - Z_i)(n_j - Z_j), \tag{2}$$

$$H_{\text{ex}} = -J(\mathbf{S}_{i1}\cdot\mathbf{S}_{R1} + \mathbf{S}_{i2}\cdot\mathbf{S}_{R2}), \tag{3}$$

$$\mathbf{S}_i = \frac{1}{2}C_i^\dagger \sigma C_i. \tag{4}$$

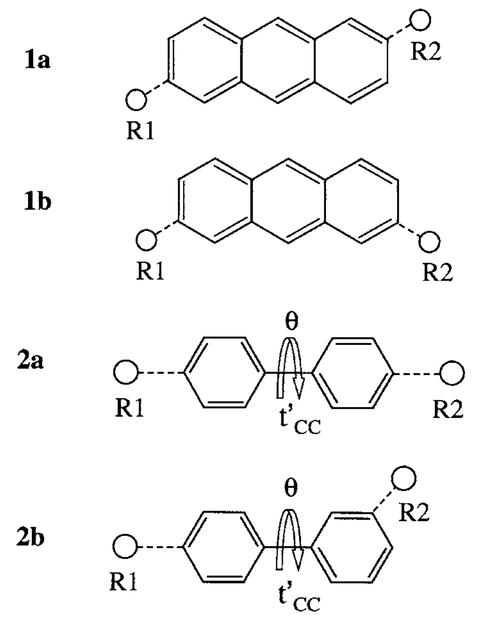

FIG. 2. Schematic picture of organic molecules based on the π moiety of anthracene: 1*a* and 1*b*; biphenyl: 2*a* and 2*b*. The transfer integral between two benzene rings is defined as t'_{CC}, which depends on the dihedral angle θ.

In Eq. (2), $C_{i,s}^\dagger$ and $C_{i,s}$ are the creation and the destruction operators for an electron with a spin $s(=\uparrow \text{ or } \downarrow)$ on the ith site, and $t_{i,j}$ is the one-electron matrix element between the neighboring sites i and j. The electron-number operator is defined as $n_{i,s}=C_{i,s}^\dagger C_{i,s}$, and $n_i=\Sigma_s n_{i,s}$. The effective ionization potential is I_i. The Coulomb energies denoted by $U_{i,j}$ are assumed in the form of the Ohno potential,

$$U_{i,j} = e^2\left\{ r_{i,j}^2 + \left[\frac{2e^2}{U_{i,i}+U_{j,j}}\right]^2\right\}^{-1/2}, \tag{5}$$

where $r_{i,j}=|\mathbf{r_i}-\mathbf{r_j}|$ is the distance between the ith and the jth sites, and $U_{i,i}$ is the on-site Coulomb repulsion at the ith site. Z_i is the net charge of the ion core at the ith site. In this study, we use the PPP parameters for carbon as follows: $U_{\text{CC}}=11.26$ eV, $t_{\text{CC}}=2.318$ eV, $I_{\text{C}}=11.42$ eV, and $Z_{\text{C}}=1$.[50]

The long-range Coulomb interactions are determined for a fixed molecular geometry so that the formation of a polaron or soliton is forbidden, although π-conjugated molecules are believed to be more planar in excited states than in the ground state. The structural relaxation of such excited molecules is an interesting and important theoretical subject, but will be left for future studies. We choose anthracene and biphenyl as the π moiety in the target molecules shown in Fig. 2. We consider each of these two topological isomers with different positions of one localized spin. For the anthracene-based molecules, the atomic coordinates are obtained from the crystal structures[51] from the Cambridge Structural Database.[52] On the other hand, the biphenyl-based molecules are chosen to investigate the dependence on molecular geometry, in particular, the dihedral angle θ between the benzene rings. An idealized structure is assumed in the biphenyl-based molecules: all the bonds are 1.397 Å and all the bond angles are 120°, while the transfer integral between the two benzene rings $t'(\theta)$ dependents on θ as $t'(\theta) = t_{CC}\cos(\theta)$.

As shown in Eq. (3), the radical spins are simplified to two localized $\frac{1}{2}$ spins $\mathbf{S}_{R1}$ and $\mathbf{S}_{R2}$ in our model. They are coupled to the π spins on the sites $i1$ and $i2$ with the coupling constant J. $C_i^\dagger$ is defined as $(C_{i,\uparrow}^\dagger, C_{i,\downarrow}^\dagger)$ and $\sigma \equiv (\sigma_x, \sigma_y, \sigma_z)$ are the Pauli matrices. The exchange interaction strength J cannot be directly measured in experiment. Although the *ab initio* calculation is capable of predicting the J value of a certain system with good accuracy, the purpose of this study is to yield physical insight into the mechanism of photoinduced high-spin state, rather than interpret the experimental result of a specific molecule. Thus, we choose a reasonable J to satisfy the condition that the calculated spin gap is in the same order of magnitude as that measured in experiment. Under this consideration, the exchange coupling constant is set to $J = 0.75$ eV. We are also interested in the J-dependence on spin alignment and give a brief discussion in Sec. III B.

We exactly diagonalize the Hamiltonian in Eq. (1) by the Lanczos algorithm taking into account of all the correlation effects. To calculate highly excited states up to mth ($m \gg 1$) level with good precision, we employ a step-by-step diagonalization as follows:

(1) Diagonalize H to calculate the ground state, and save the energy (E_1) and the wave function ($|\psi_1\rangle$) for the next step; set $k=1$.

(2) Increase the value of k by one; prepare the effective Hamiltonian H^k by shifting the lth ($l<k$) level as,

$$\begin{aligned} H^k &= H + \sum_{l=1}^{k-1} \Delta E|\psi_l\rangle\langle\psi_l| \\ &= \sum_{l=1}^{k-1} (E_l + \Delta E)|\psi_l\rangle\langle\psi_l| + \sum_{l=k}^{m} E_l|\psi_l\rangle\langle\psi_l| + \sum_{l>m} E_l|\psi_l\rangle\langle\psi_l|, \end{aligned} \tag{6}$$

where E_l ($E_1 < E_2 < \cdots < E_m$) is the energy of the lth state, while ΔE is an artificial energy shift satisfying the condition $E_1 + \Delta E > E_k$. All states $|\psi_l\rangle$ of $l<k$ are now above $|\psi_k\rangle$. Thus, $|\psi_k\rangle$ becomes the ground state of H^k and can be readily calculated by the Lanczos method.

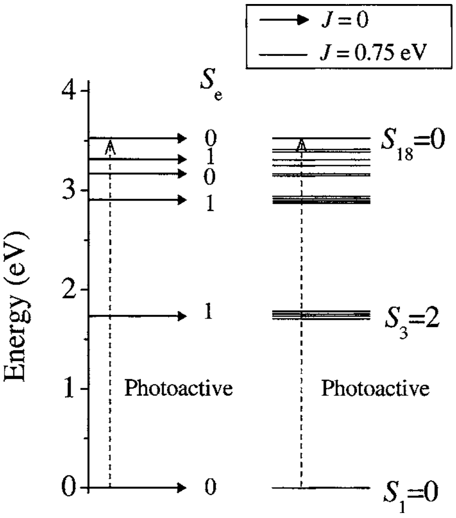

FIG. 3. Energy diagram of anthracene ($J=0$) and the molecule 1a ($J=0.75$ eV).

(3) Diagonalize H^k to calculate the ground state, and save the energy (E_k) and the wave function ($|\psi_k\rangle$) for the next step.

(4) Go to step (2) if $k<m$, otherwise end the iteration.

It should be noted that the choice of ΔE does not affect the final results despite round-off error, as long as the condition $E_1 + \Delta E > E_k$ is maintained. Because only one (the lowest) state is calculated for each iteration step, the excited states obtained by the iterative calculation are more precise than those calculated by a single step of the Lanczos diagonalization, but at the cost of extra memory to save all the wave functions.

In the exact diagonalization calculation, the symmetry between the up and the down spins is preserved. If a system has equal numbers of electrons with spins ↑ and ↓, the calculated spin density is zero. To figure out spin alignment, we calculate spin-correlation functions with respect to one localized spin, e.g., $\mathbf{S}_{R1}$ in the ground and excited states.

III. RESULTS AND DISCUSSION

A. Spin alignment in excited anthracene-based molecules

We begin with an anthracene-based molecule 1a shown in Fig. 2. For each state $|\psi_k\rangle$, the spin (S) of the whole molecule is calculated as well as the spin of the π moiety (S_e) defined by

$$S_e(S_e+1) = \langle\psi_k|\mathbf{S}_e \cdot \mathbf{S}_e|\psi_k\rangle, \tag{7}$$

in which $\mathbf{S}_e$ ($=\Sigma_i \mathbf{S}_i$) is the operator of the total π-spin. We also compute the norm of the transition dipole moments between the ground state $|\psi_1\rangle$ and the exited state $|\psi_k\rangle$ as,

$$\mu_k = |\langle\psi_1|\mu|\psi_k\rangle|, \tag{8}$$

in which $\mu = \Sigma_i n_i \mathbf{r}_i$ is the dipole moment operator.

First we examine the energy diagram of 1a without the exchange interaction, i.e., $J=0$. As shown in Fig. 3, the ground state is a singlet ($S_e=0$), and the lowest excited state

TABLE I. Results of the anthracene-based molecule 1*a* with $J=0.75$ eV.

k	Energy (eV)	S	$\mathbf{S}_\mathrm{e}$	$\langle \mathbf{S}_{R1} \cdot \mathbf{S}_{R2} \rangle$	μ_k (a.u.)
1	0	0	0.015	−0.742	0
2	0.001 84	1	0.013	0.247	0
3	1.709 87	2	1.004	0.248	0
4	1.736 32	1	1.002	−0.742	0
5	1.757 58	1	1.000	0.246	0
6	1.784 39	0	0.997	0.245	0
18	3.532 27	0	0.012	−0.744	0.726

($E_2=1.734$ eV) is a triplet ($S_\mathrm{e}=1$). By calculating the transition dipole moments, we confirm that the fifth excited state ($E_6=3.525$ eV) is the first dipole-allowed singlet state. These results are in a good agreement with the calculation based on the configuration interaction (CI).[53]

We move on to the case of a finite-exchange coupling $J=0.75$ eV. As the exchange interactions are added to the Hamiltonian, energy levels start to split. Each singlet state has two branches, while each triplet state has four branches. To analyze properties of excited states, we list the energy, S, S_e, and the spin correlation $\langle \mathbf{S}_{R1} \cdot \mathbf{S}_{R2} \rangle$ as well as the transition dipole moments μ_k, for $|\psi_1\rangle \cdots |\psi_6\rangle$ and $|\psi_{18}\rangle$ in Table I. In the ground state, the localized spins are coupled to each other antiferromagnetically, resulting in a spin singlet $S=0$ with $S_\mathrm{e} \approx 0$. The spin of the π moiety S_e is fractional because it not a good quantum number in the coupled system.

The spin-correlation pattern $\langle \mathbf{S}_{R1} \cdot \mathbf{S}_i \rangle$ demonstrates a weak correlation between the π moiety and the localized spin $\mathbf{S}_{R1}$, as shown in Fig. 4(a). The meshed circle indicates R1 as a reference site. The open and filled circles denote negative and positive correlations, respectively. The area of each circle is proportional to the magnitude of the spin-correlation function. These definitions will also be applied in the following figures as well.

The ground state is nearly degenerate with a spin triplet, in which the π moiety is barely excited. As shown in Fig. 4(b), the ferromagnetic correlation between the two localized spins leads to this spin triplet. The ground and the first-excited states are the splitting branches of the singlet ground state of anthracene. The calculated spin gap (1.84 meV) is comparable with the effective coupling strength (5.8 K) measured in the diphenylanthracene-based molecules.[11]

The excited states $|\psi_3\rangle \cdots |\psi_6\rangle$ are the branches of the first-excited state of anthracene. Their spins are arranged in the following order: a quintet, two triplets, and a singlet, as shown in Table I. The remarkable feature of this system is that the lowest π-excited state $|\psi_3\rangle$ is a high-spin state ($S=2$). The excited π moiety plays the role of ferromagnetic coupler for the localized spin and gives rise to the high-spin alignment, as shown in Fig. 4(c). The energy splitting between the quintet and the triplet are an order of magnitude larger than the spin gap of the ground state, indicating a strong coupling between the localized spin and the excited π triplet.

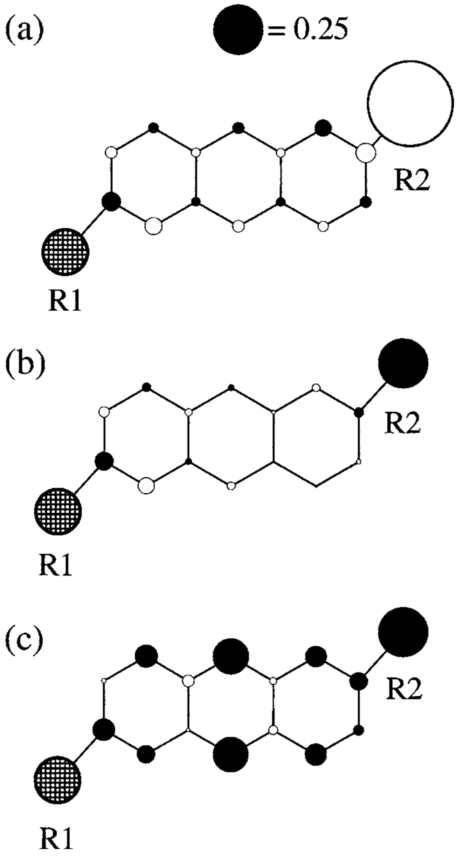

FIG. 4. Spin correlation $\langle \mathbf{S}_{R1} \cdot \mathbf{S}_i \rangle$ of the anthracene-based molecule 1*a*: (a) the ground state, (b) the first excited state, (c) the lowest π-excited state. The open (filled) circles denote negative (positive) correlations. The area of each circle is proportional to the magnitude of the spin-correlation function.

However, the quintet state cannot be optically excited from the singlet ground state. The results of the transition dipole moments indicate that the lowest photoactive state is $|\psi_{18}\rangle$ with $S_\mathrm{e} \approx 0$, as shown in Table I. This state belongs to the branches of the fifth excited state of anthracene. Thus, it is possible to generate the metastable state $|\psi_3\rangle$ via optical pumping and subsequent relaxations in the following scenario. First the molecule is optically excited from the singlet ground state to an excited singlet state like $|\psi_{18}\rangle$. As optically excited states have a very short lifetime, the excited molecule transfers back to the ground state by emitting a photon, or goes down slowly via the nonradiative relaxation processes. By intersystem crossing, these relaxation processes lead to the lowest-excited quintet state $|\psi_3\rangle$. Such a high-spin state can have a relatively long lifetime, because there is no other near-lying state below the quintet state, and $|\psi_1\rangle$ and $|\psi_2\rangle$ are forbidden for optical transition. The existence of high spin in the lowest π-excited state has been confirmed by the experiment.[10,11] In the time-resolved electron spin resonance (ESR) observation of diphenylanthracene-bis(iminonitroxide), the high-spin signals are detected 1 μs after the laser irradiation and lasts for almost 10 μs.

Next we investigate the other topological isomer 1*b*, in which the localized spin $R2$ is moved to a nearest-neighboring site. Table II shows that the ground state is a triplet $S=1$ corresponding to parallel alignment between the localized spins. This dependence on the radical position can

TABLE II. Results of the anthracene-based molecule 1*b* with $J=0.75$ eV.

k	Energy (eV)	S	$\mathbf{S}_e$	$\langle \mathbf{S}_{R1}\cdot\mathbf{S}_{R2}\rangle$	μ_k (a.u.)
1	0	1	0.014	0.248	0
2	0.001 49	0	0.012	−0.744	0
3	1.709 81	2	1.005	0.249	0
4	1.731 45	1	1.002	−0.741	0
5	1.759 27	1	0.999	0.243	0
6	1.782 07	0	0.997	0.245	0
18	3.527 98	1	0.016	0.160	0.695

be understood based on the topological rule. As shown in Fig. 5(a), the spin alignment in the π moiety is governed by the spin polarization. The localized spin $R2$ is coupled to a site that is in a ferromagnetic correlation with $R1$. On the other hand, the first-excited state becomes a singlet $S=0$ with an antiferromagnetic correlation between $R1$ and $R2$. The π electrons are only weakly excited in either of the states, and the spin gap is 1.49 meV.

We are more interested in the topological effects on spin alignment in excited states and, in particular, that of the lowest π-excited state. As shown in Table II, the lowest π-excited state $|\psi_3\rangle$ is a quintet, same as that of the isomer 1*a*. By comparing the spin alignment shown in Fig. 4(c) and Fig. 5(c), we find that the sites coupled with $R2$ are always in the ferromagnetic correlation with $R1$ despite the position of $R2$. As pointed out by Teki,[11] the spin delocalization mechanism is much more dominant in such an excited state than in the ground state. A strong ferromagnetic coupling is induced to the localized spins by the excited π moiety. Thus, the quintet is a metastable state, which can be generated during the nonradiative relaxation from a highly excited triplet state such as $|\psi_{18}\rangle$.

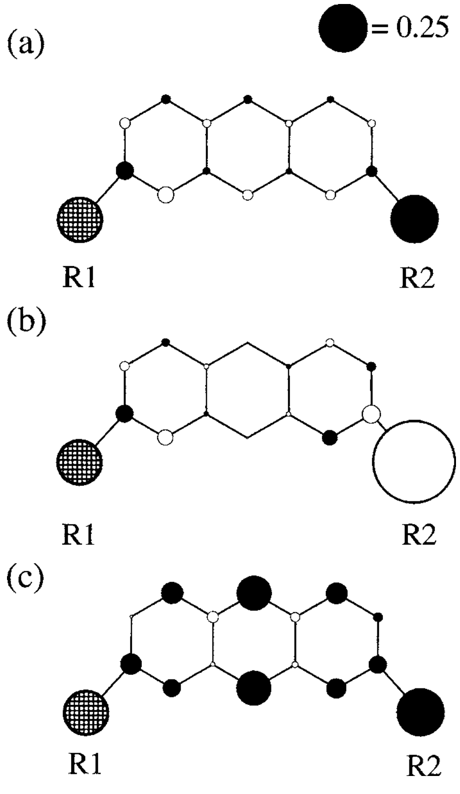

FIG. 5. Spin correlation $\langle \mathbf{S}_{R1}\cdot\mathbf{S}_i\rangle$ of the anthracene-based molecule 1*b*: (a) the ground state, (b) the first excited state, (c) the lowest π-excited state. The notational conventions are same as in Fig. 4.

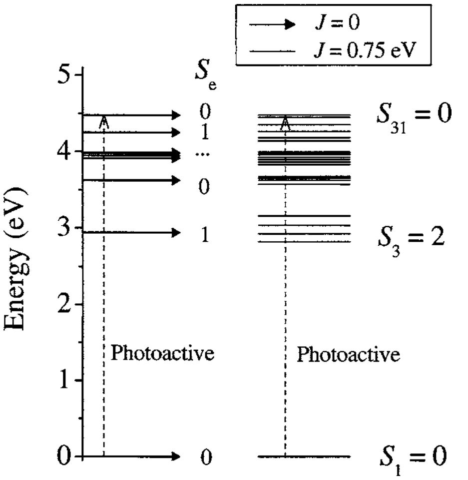

FIG. 6. Energy diagram of biphenyl ($J=0$) and the molecule 2*a* ($J=0.75$ eV).

B. Spin alignment in excited biphenyl-based molecules

The π moiety presented in Sec. III A shares many important characters of molecular structure as the aforementioned diphenylanthracene in spite of its small dimension. However some structural features are not reflected in the anthracene, e.g., single bonds connecting benzene rings. In order to further investigate such a type of structure, we introduce biphenyl as the π moiety of a molecule with two isomers 2*a* and 2*b*. It is well known that the dihedral angle (θ) between the two benzene rings in biphenyl depends on its thermal phase. Biphenyl in the vapor and the solution phases has a larger dihedral angle than that in the crystalline phase. Even in the crystalline phase, biphenyl undergoes a structural change accompanied by alteration of the dihedral angle as shown by an experiment of neutron scattering.[54] As was already mentioned in Sec. II, to focus on the main purpose, we assume an idealized structure for biphenyl taking into account the dihedral angle as the only changeable geometry factor.

First we investigate the isomer 2*a* with $\theta=0$. The energy diagram of biphenyl ($J=0$) is shown in Fig. 6. The lowest-triplet state is 2.938 eV above the singlet ground state. The first dipole-transition-allowed state is a singlet state $|\psi_{10}\rangle$ over a 4.479 eV gap above the ground state. These results are in a good agreement with those by CI calculation.[55]

In the case of a finite-exchange coupling $J=0.75$ eV, all levels split into branches as shown on the right side of Fig. 6. In Table III, the details of the lowest six states are listed together with that of the lowest photoactive singlet state $|\psi_{31}\rangle$. The ground state is a spin singlet with an antiferromagnetic correlation between the localized spins. Figure 7(a)

TABLE III. Results of the biphenyl-based molecule 2*a* with $J=0.75$ eV.

k	Energy (eV)	S	$\mathbf{S}_{\mathrm{e}}$	$\langle \mathbf{S}_{R1} \cdot \mathbf{S}_{R2} \rangle$	μ_k (a.u.)
1	0	0	0.012	−0.744	0
2	0.001 43	1	0.011	0.248	0
3	2.821 80	2	1.002	0.249	0
4	2.925 39	1	0.999	−0.726	0
5	3.037 61	1	0.999	0.222	0
6	3.158 47	0	0.992	0.238	0
31	4.480 65	0	0.013	−0.743	0.923

TABLE IV. Results of the biphenyl-based molecule 2*b* with $J=0.75$ eV.

k	Energy (eV)	S	$\mathbf{S}_{\mathrm{e}}$	$\langle \mathbf{S}_{R1} \cdot \mathbf{S}_{R2} \rangle$	μ_k (a.u.)
1	0	1	0.011	0.248	0
2	0.000 72	0	0.010	−0.745	0
3	2.873 61	1	1.001	−0.429	0
4	2.875 50	2	1.005	0.249	0
5	3.035 33	1	0.999	−0.082	0
6	3.050 04	0	0.998	0.246	0
31	4.481 43	1	0.012	0.248	0.923

shows that π spins are weakly correlated with the localized spin $R1$. A low-lying spin triplet is nearly degenerate with the ground state. The spin gap is 1.43 meV, which is less than the gaps of the anthracene-based molecules. It is caused by a weakened correlation between the benzene rings due to the single bond in biphenyl. The spin-correlation pattern in Fig. 7(b) illustrates that this spin triplet is induced by the ferromagnetic coupling of the localized spins.

The third excited state is the lowest π-excited one and also demonstrates high-spin alignment with $S=2$. The excited π moiety creates a ferromagnetic correlation between the two localized spins, as shown in Fig. 7(c). The energy splitting (0.1 eV) between $|\psi_3\rangle$ and $|\psi_4\rangle$ is quite large because of the strong coupling between the localized spin and the π triplet. Since the quintet state is the lowest π-excited one, it has a longer lifetime than the other excited states and can be detected during the relaxation processes from a highly excited-singlet state such as $|\psi_{31}\rangle$.

As already demonstrated by experiment, photoinduced metastable states are different in the isomers of the diphenylanthracene-based molecules, whose ground states are both spin singlets.[10,11] On the other hand, in Sec. III A, we have shown similar metastable quintet states in the topological isomers of the anthracene-based molecules that bear different spin alignments in the ground state. The question now becomes whether the excited π triplet always plays the role of ferromagnetic coupler for the localized spin in spite of its position. Motivated by such a question, we search for a different type of spin alignment in excited molecules.

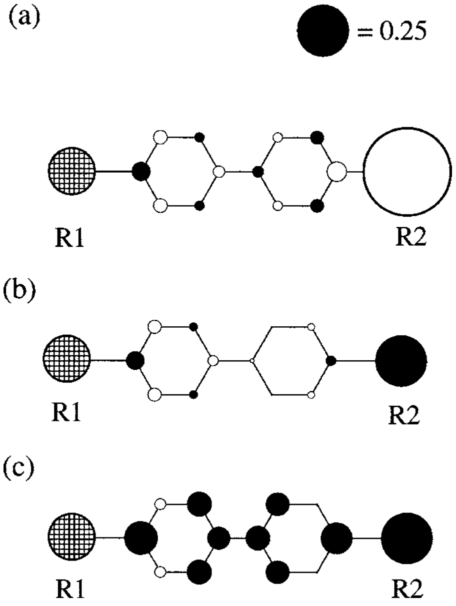

FIG. 7. Spin correlation $\langle \mathbf{S}_{R1} \cdot \mathbf{S}_i \rangle$ of the biphenyl-based molecule 2*a*: (a) the ground state, (b) the first excited state, (c) the lowest π-excited state. The notational conventions are same as in Fig. 4.

Thus, a topological isomer 2*b* is studied with $\theta=0$, and its results are summarized in Table IV. As $R2$ is the only localized spin moved to the neighboring site, the ground state is a spin triplet with a ferromagnetic correlation between the localized spins. The first excited state is a singlet and is separated from the ground state by a spin gap of 0.72 meV that is merely half that of the isomer 2*a*. The metaconnection between $R2$ and the π moiety is responsible for such a small gap. Figures 8(a) and 8(b) show that the localized spins are weakly correlated to the barely excited π moiety in both states. The spin alignment of $R1$ and $R2$ determines the spin of the whole molecule.

It is very interesting that the spin alignment in $|\psi_3\rangle$ exhibits clear dependence on the topology. As shown in Table IV, the lowest π-excited state is a spin triplet. Figure 8(c) shows that $R1$ has an antiferromagnetic correlation with the site connected with $R2$. It should be noted that the mechanism of the excited triplet states is different from that of the ground state. As shown in Fig. 8(c), the localized spin $R1$ is in ferromagnetic correlation with most of the other sites in the excited π moiety. If $R2$ is moved to any of these sites, the lowest π-excited state becomes a quintet. On the other hand, the correlation between $R1$ and the π moiety maintains the alternating pattern of spin polarization in the ground state as shown in Fig. 8(a). If we imagine molecules in which $R2$ is coupled to one of these sites, half of them would yield singlet ground states, and the other half would yield triplet ones. Here the excited π moiety plays the role of an antiferromagnetic coupler for the localized spins, in contrast to the ferromagnetic one shown in the case of 2*a*. As a result, the lowest π-excited triplet can be generated by relaxation processes from a highly excited triplet such as $|\psi_{31}\rangle$. However, since the ground state is also a spin triplet, the lowest π-excited triplet state may relax more quickly than the quintet state of the isomer 2*a*.

As is mentioned occasionally, a finite-exchange coupling J causes the splitting of a triplet state of the π moiety to four

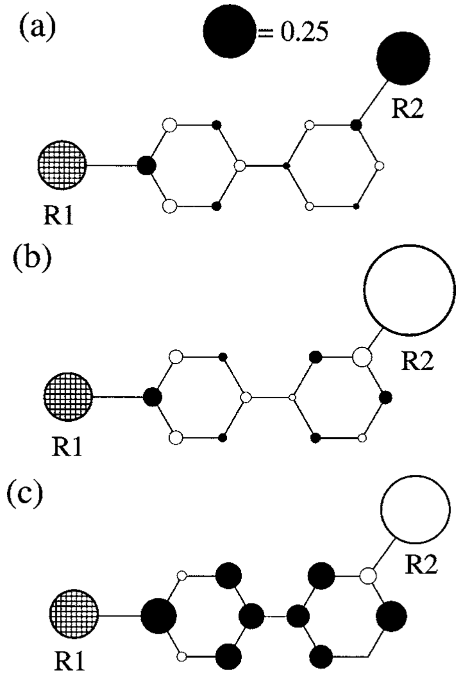

FIG. 8. Spin correlation $\langle \mathbf{S}_{R1} \cdot \mathbf{S}_i \rangle$ of the biphenyl-based molecule 2*b*: (a) the ground state, (b) the first excited state, (c) the lowest π-excited state. The notational conventions are same as in Fig. 4.

branches, which include two triplets, a quartet, and a singlet. As shown in Table IV, $|\psi_4\rangle$ is a quintet state nearly degenerate with a triplet. The energy splitting between these two levels is merely 1.9 meV, which is less than 2% of that of the corresponding levels in the isomer 2*a*. Thus, the quintet state is a metastable one with a tiny gap. Mixed signals of quintets and triplets can be observed in such a molecule during relaxation.

Existence of a quintet in the pseudodegenerate state $|\psi_4\rangle$ raises a question of whether the lowest π-excited state can be a quintet if the geometry of the molecule is changed. In the study of the biphenyl-based molecules, the only conformational change allowed in this model is the dihedral angle (θ) between the two benzene rings. A small dihedral angle has been confirmed to exist in the biphenyl molecule, depending on the phase and the temperature.[54]

To answer this question, we investigate the energies of the lowest π-excited quintet ($E_{S=2}$) and triplet ($E_{S=1}$) by varying the dihedral angle within the range 0–40°. The exchange interaction J maintains 0.75 eV. The energy difference $\Delta E(=E_{S=2}-E_{S=1})$ is plotted as a function of θ in Fig. 9. Although ΔE is positive at the zero dihedral angle, it decreases as θ increases and crosses zero at $\theta \approx 14°$. It indicates that if the dihedral angle exceeds the critical value (14°), the lowest π-excited state can also be a spin quintet even in the isomer 2*b*. As the angle becomes even larger, the quintet is quickly stabilized as a metastable state. Since the dihedral angle increases with temperature,[54] it might be possible to observe the temperature dependence of spin alignment.

We find that the θ-dependence is a unique feature of the excited states of the isomer 2*b*. In the case of the ground and the first-excited states, there is no evidence of any crossover behavior. Furthermore, we cannot find any dependence on the dihedral angle in the ground or excited states of the isomer 2*a*. This difference can be understood on the basis of the spin-correlation pattern. In the lowest π-excited state of the molecule 2*b*, *R*1 has an antiferromagnetic correlation with the site coupled with *R*2, as shown in Fig. 8(c), but this correlation is weak and unstable. An increase in θ causes a decrease of the transfer integral of the single bond that connects the benzene rings. Since each benzene ring becomes more isolated, the strong ferromagnetic correlation overcomes the weak antiferromagnetic spin polarization and takes control of the whole ring. On the other hand, in the molecule 2*a*, *R*1 has a ferromagnetic correlation with the site coupled to *R*2. This correlation is enhanced by a finite dihedral angle. Thus, spin alignment in the lowest π-excited state is not affected by changing the dihedral angle.

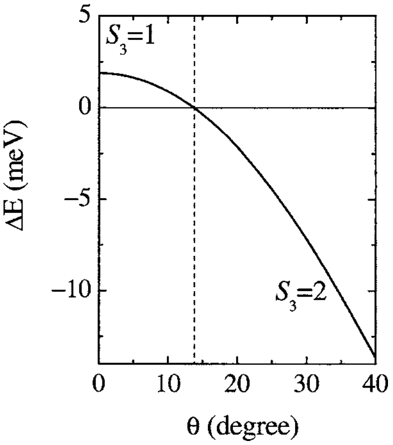

FIG. 9. Energy gap $\Delta E = E_{S=2} - E_{S=1}$ of the molecule 2*b* as a function of the dihedral angle θ (J=0.75 eV).

The J dependence of spin alignment is also an interesting aspect. As was already shown in the molecule 2*b*, the spin alignment of the lowest π-excited state is sensitive to the dihedral angle between the benzene rings. Strong exchange interactions can stabilize spin correlation by competing with the spin-delocalization mechanism and, thus, affect the spin alignment in the excited states. In order to shed light on the J dependence, we examine energies of the lowest π-excited quintet ($E_{S=2}$) and triplet ($E_{S=1}$) in the molecule 2*b* within $0 < J < 2$ eV. Here we assume a zero dihedral angle.

The energy difference $\Delta E(=E_{S=2}-E_{S=1})$ is plotted as a function of J in Fig. 10. If the exchange interactions are omitted, i.e., $J=0$, the quintet state is perfectly degenerate with the triplet, and ΔE becomes zero. On the other hand, a small exchange interaction gives rise to a negative value, implying that the quintet is the lowest π-excited state in the case of weak coupling ($J < 0.5$ eV). The quintet is most stable at $J \approx 0.25$ eV. As $J > 0.5$ eV, ΔE passes through the zero line and increases quickly. Therefore, the strong exchange interactions enhance the triplet as the lowest π-excited state.

Like θ dependence, the dependence on the exchange interactions only appears in the excited states. We also have investigated J dependence in the ground state of the molecule 2*b*, but there is no indication of a singlet ground state.

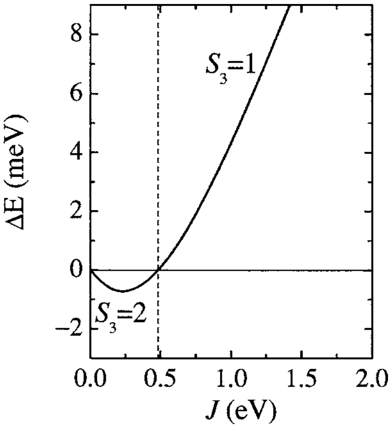

FIG. 10. Energy gap $\Delta E = E_{S=2} - E_{S=1}$ of the molecule 2b as a function of the exchange-coupling constant J (θ=0).

The triplet-singlet gap is simply widened by stronger exchange interactions. The understanding of the dependence on the exchange interaction and the geometry bears the potential of guiding experiments to use more suitable π moiety and radical groups for the application in controllable spin alignment.

IV. SUMMARY

By means of the model Hamiltonian approach, we have clarified the mechanism of spin alignment in the excited states of purely organic molecules. The theoretical model has been applied to describe molecular systems composed of two localized spins and a π-conjugated moiety. We take into account the long-range Coulomb interactions by introducing the PPP model for two types of π moiety: anthracene and biphenyl. We numerically solved the model by the Lanczos algorithm including all the correlation effects. In the anthracene-based molecules (1a and 1b), the lowest excited π moiety induces the ferromagnetic correlation between the localized spins. This spin alignment leads to a metastable high-spin state, which can be generated by photoexcitation and subsequent relaxation processes.

In the biphenyl-based molecules, the spin alignment of the metastable state depends sensitively on the dihedral angle of biphenyl. In contrast to the molecule 2a, the lowest π-excited state is a triplet in the topological isomer 2b if the dihedral angle is zero. If the dihedral angle exceeds a critical value, the lowest π-excited state becomes a spin quintet even in the case of the isomer 2b. This also depends on the strength of the exchange interactions. In the case of weaker exchange coupling, the quintet replaces the triplet as the lowest π-excited state. Our study offers a theoretical basis for understanding photoinduced high-spin states observed in the π-conjugated molecular system.

In this study, the dynamics of spin relaxation has not been touched. We cannot answer quantitatively the lifetime of the lowest π-excited state, although it is believed to be a metastable one. To get a full picture of photoinduced high spin, it is necessary to conduct further studies on the possible relaxations of excited molecules, in which structural relaxations have an important influence on spin alignment as suggested in the present paper.

ACKNOWLEDGMENTS

We are grateful to Professor Y. Teki for valuable discussions. This work was partly supported by NEDO under the Nanotechnology Program.

---

*Corresponding author. Present address: Department of Physics, Osaka University, Machikaneyama 1-1, Toyonaka, Osaka 560-0043, Japan.

[1] K. Itoh, Chem. Phys. Lett. **1**, 235 (1967).
[2] E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, and G. Smolinsky, J. Am. Chem. Soc. **89**, 5076 (1967).
[3] A. Rajca, Chem. Rev. (Washington, D.C.) **94**, 871 (1994).
[4] J. S. Miller and A. J. Epstein, Angew. Chem., Int. Ed. Engl. **33**, 385 (1994).
[5] *Molecular Magnetism: New Magnetic Materials*, edited by K. Itoh and M. Kinoshita (Kodansha Scientific, Tokyo, 2000).
[6] *Magnetism: Molecules to Materials*, edited by J. S. Miller and M. Drillon (Wiley-VCH, Weinheim, 2001), Vols. 1–3.
[7] A. Izuoka, M. Hiraishi, T. Abe, T. Sugawara, K. Sato, and T. Takui, J. Am. Chem. Soc. **122**, 3234 (2000).
[8] J. Nakazaki, I. Chung, M. Matsushita, T. Sugawara, R. Watanabe, A. Izuoka, and Y. Kawada, J. Mater. Chem. **13**, 1011 (2003).
[9] M. Matsushita, T. Nakamura, T. Momose, T. Shida, Y. Teki, T. Takui, T. Kinoshita, and K. Itoh, J. Am. Chem. Soc. **114**, 7470 (1992).
[10] Y. Teki, S. Miyamoto, K. Iimura, M. Nakatsuji, and Y. Miura, J. Am. Chem. Soc. **122**, 984 (2000).
[11] Y. Teki, S. Miyamoto, M. Nakatsuji, and Y. Miura, J. Am. Chem. Soc. **123**, 294 (2001).
[12] Y. Teki, M. Nakatsuji, and Y. Miura, Mol. Phys. **100**, 1385 (2002).
[13] K. Matsuda and M. Irie, J. Am. Chem. Soc. **122**, 7195 (2000).
[14] K. Matsuda and M. Irie, J. Am. Chem. Soc. **122**, 8309 (2000).
[15] N. Tyutyulkov, P. Schuster, and O. Polansky, Theor. Chim. Acta **63**, 291 (1983).
[16] S. A. Alexander and D. J. Klein, J. Am. Chem. Soc. **110**, 3401 (1988).
[17] B. Sinha, I. D. L. Albert, and S. Ramasesha, Phys. Rev. B **42**, 9088 (1990).
[18] S. Li, J. Ma, and Y. Jiang, Chem. Phys. Lett. **246**, 221 (1995).
[19] S. Li, J. Ma, and Y. Jiang, J. Phys. Chem. **100**, 4775 (1996).
[20] S. Li, J. Ma, and Y. Jiang, J. Phys. Chem. A **101**, 5567 (1997).
[21] Z. Fang, Z. L. Liu, and K. L. Yao, Phys. Rev. B **49**, 3916 (1994).
[22] K. Yoshizawa, K. Tanaka, and T. Yamabe, J. Phys. Chem. **98**, 1851 (1994).
[23] K. Nasu, Phys. Rev. B **33**, 330 (1986).
[24] H. Fukutome, A. Takahashi, and M. Ozaki, Chem. Phys. Lett.

133, 34 (1987).

[25] H. Mizouchi, A. Ikawa, and H. Fukutome, J. Phys. Soc. Jpn. **66**, 881 (1997).

[26] D. J. Klein and L. Bytautas, J. Phys. Chem. A **103**, 5196 (1999).

[27] O. Ivanciuc, L. Bytautas, and D. J. Klein, J. Chem. Phys. **116**, 4735 (2002).

[28] O. Ivanciuc, D. J. Klein, and L. Bytautas, Carbon **40**, 2063 (2002).

[29] Y. Chen and H. Chen, J. Phys.: Condens. Matter **13**, 10057 (2001).

[30] S. Yamanaka, T. Kawakami, M. Okumura, and K. Yamaguchi, Chem. Phys. Lett. **233**, 257 (1995).

[31] R. Arita, Y. Suwa, K. Kuroki, and H. Aoki, Phys. Rev. Lett. **88**, 127202 (2002).

[32] N. Mataga, Theor. Chim. Acta **10**, 372 (1968).

[33] A. A. Ovchinnikov, Theor. Chim. Acta **47**, 297 (1978).

[34] D. J. Klein, C. J. Nelin, S. Alexander, and F. A. Matsen, J. Chem. Phys. **77**, 3101 (1982).

[35] E. H. Lieb, Phys. Rev. Lett. **62**, 1201 (1989).

[36] Y. Nagaoka, Phys. Rev. **147**, 392 (1966).

[37] W. T. Borden and E. R. Davidson, Acc. Chem. Res. **14**, 69 (1981).

[38] D. J. Klein and S. A. Alexander, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **232**, 219 (1993).

[39] P. M. Lahti, A. S. Ichimura, and J. A. Berson, J. Org. Chem. **54**, 958 (1989).

[40] P. M. Lahti and A. S. Ichimura, J. Org. Chem. **56**, 3030 (1991).

[41] *Magnetic Properties of Organic Materials*, edited by P. M. Lahti (Marcel Dekker, New York, 1999), pp. 661–701.

[42] H. Sakurai, A. Izuoka, and T. Sugawara, J. Am. Chem. Soc. **122**, 9723 (2000).

[43] Y. Teki, Polyhedron **20**, 1163 (2001).

[44] P. Huai, Y. Shimoi, and S. Abe, Synth. Met. **137**, 1255 (2003).

[45] P. Huai, Y. Shimoi, and S. Abe, Phys. Rev. Lett. **90**, 207203 (2003).

[46] P. Huai, Y. Shimoi, and S. Abe, J. Phys. Soc. Jpn. **73**, 3149 (2004).

[47] P. Huai, Y. Shimoi, and S. Abe, J. Chem. Phys. **122**, 244324 (2005).

[48] R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466 (1953).

[49] J. A. Pople, Trans. Faraday Soc. **46**, 1375 (1953).

[50] J. Fabian, A. Mehlhorn, and R. Zahradnik, J. Phys. Chem. **72**, 3975 (1968).

[51] C. P. Brock and J. D. Dunitz, Acta Crystallogr., Sect. B: Struct. Sci. **46**, 795 (1990).

[52] F. H. Allen, Acta Crystallogr., Sect. B: Struct. Sci. **58**, 380 (2002).

[53] S. Ramasesha, I. D. L. Albert, and B. Sinha, Mol. Phys. **72**, 537 (1991).

[54] H. Cailleau, F. Moussa, and J. Mons, Solid State Commun. **31**, 521 (1979).

[55] S. Ramasesha, D. S. Galvao, and Z. G. Soos, J. Phys. Chem. **97**, 2823 (1993).