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Geometric phases of electrons due to spin-rotation coupling in rotating C_{60} molecules

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The rapidly rotational motion of C_{60} molecules will provide us with an ingenious way to test Mashhoon's spin-rotation coupling. Since in the low-temperature phase (below 300 K) of C_{60} solid the noncentral intermolecular potential will cause the precession and nutation of rotating frequency of C_{60} molecules, which gives rise to a time-dependent coupling of valency electron spin to the C_{60} rotation, the electron wave functions in rotating C_{60} molecules will acquire geometric phases arising from this time-dependent spin-rotation coupling. The geometric phases of valency electrons in C_{60} molecules is calculated by using the Lewis-Riesenfeld invariant theory in the present paper. It is shown that geometric phases of electrons in C_{60} molecules may be measured through the photoelectron spectroscopy of C_{60}. A physically interesting fact that the information about rotation and precession of C_{60} molecules in the orientational ordered (or disordered) phase may be read off from the photoelectron spectroscopy of C_{60} is also demonstrated. Thus, the measurement of variation of C_{60} rotating frequency through the photoelectron spectroscopy will enable us to obtain the noncentral intermolecular potential, which is helpful in investigating the molecular mechanics of C_{60} solid.

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I. INTRODUCTION

The information on the rotational dynamics of C_{60} molecule in condensed phases has been obtained from nuclear-magnetic-resonance (NMR) studies.[1] Both NMR spectroscopy and quasielastic neutron-scattering experiments[2] indicated the rapid rotation of C_{60} molecules whose rotational correlation time may be picoseconds in the orientationally disordered phase. Historically, many researches were in connection with the molecular dynamics of C_{60} rotation.[3] Heiney *et al.* found from x-ray-diffraction and calorimetrical measurements that solid C_{60} exhibits a phase transition near 249 K from a simple cubic structure at low temperatures to a face-centered-cubic structure at high temperatures.[3–5] These studies suggest that the phase above the transition temperature is characterized by free rotation or rotational diffusion and that the phase below the transition is characterized by jump rotational diffusion between symmetry-equivalent orientations. The correlation time for both phases (orientationally ordered phase below 249 K and orientationally disordered phase above 249 K) were measured to fit with an Arrhenius law, which leads to the fact that in the low-temperature phase the correlation time τ increases by a factor of ~ 40. For example, τ varies from 0.44 to 0.29 ns as the temperature varies between 241 and 254 K.[4] In order to investigate the dynamics of C_{60} rotation, Johnson *et al.* performed detailed measurements of the reorientational correlation time for solid C_{60} over the temperature range 240–331 K and again showed that the correlation time satisfies the Arrhenius behavior.[4] Cheng *et al.* presented molecular-dynamics investigation of orientational freezing in pure solid C_{60} based on a pairwise-additive atom-atom intermolecular potential.[3] Kiefl *et al.* reported the study of the molecular dynamics and electronic structure of μ^{+}-C_{60} radical in a highly crystalline sample of pure C_{60} and showed a signal at room temperature which is a μ^{+}-C_{60} radical in crystalline sample C_{60} undergoing a quasifree rotation.[5] Thus it follows that the molecular dynamics of C_{60} rotation is of great importance, since it is related close to the molecular thermal motion, phase transition, and crystal structure of solid C_{60}.

Generally speaking, in the high-temperature phase (e.g., ranging from 300 K to 2000 K), the noncentral part of the intermolecular potential, which provides the orientational ordering of molecules in the low-temperature phase, vanishes after averaging over all orientations of rapidly rotating molecules.[6,7] Using the standard Lennard-Jones function for the atom-atom interaction between two molecules and averaging, Girifalco obtained the central intermolecular potential for the gaseous and fcc phases of the C_{60} fullerene.[6] By utilizing this Girifalco potential for C_{60} molecules, Zubov *et al.* calculated the saturated vapor pressure and enthalpy of sublimation of the C_{60} fullerite,[8] and Hasegawa *et al.* investigated the solid-fluid phase boundary and phase diagram of C_{60} based on the Monte Carlo method.[9] We can conclude without exaggeration that it has been successful in studying the high-temperature phase diagram of C_{60} by using the Girifalco potential model[6,8,9] and molecular-dynamics (MD) simulation. For example, Caccamo applied the modified-hypernetted-chain theory to the determination of the phase diagram of C_{60} and compared his results with available MD simulation data, and found that the phase diagram obtained was in quite good agreement with previous MD results.[10] Moreover, Caccamo clarified the following physical fact that there truly exists a liquid phase between 1600 and 1900 K. Although the investigation of central intermolecular potentials and high-temperature phase of C_{60} achieves success, to the best of our knowledge, in the literature, the noncentral intermolecular potentials of C_{60} below 300 K gained less attention than they deserved. However, the noncentral intermolecular potentials are indeed essential for the molecular-dynamics simulation of phase diagram in orientationally ordered and disordered phases below 300 K. How can we find

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an effective way to obtain the information about the noncentral intermolecular potentials of C_{60} solid?

Fortunately, since the moment of noncentral intermolecular force provided by one C_{60} molecule will cause the variation of the angular momentum (and hence the rotating frequency) of the other C_{60} molecule about its centroid, and the *time-dependent* rotating frequency may result in a geometric phase (due to the spin-rotation coupling) of valency electrons in this C_{60} molecule. If we can extract the information on the valency electron geometric phases from the photoelectron spectroscopy of C_{60}, then this will provide clue to the physicists on how the noncentral intermolecular force works in C_{60} solid. So, in this paper we will propose an approach to the investigation of noncentral intermolecular potentials and molecular-dynamics of C_{60}. We suggest that both the spin-rotation coupling of electrons and the consequent geometric phases can provide us with an insight into the rotational dynamics, intermolecular interaction, and thermal motion of C_{60} molecules.

Basically, the spin-rotation coupling considered here is one of the gravitational effects since the nature of the inertial force (e.g., the Coriolis force) is the gravitational force according to the principle of equivalence. Mashhoon showed that a particle with an intrinsic spin possesses a gravitomagnetic moment that can be coupled to the gravitomagnetic fields.[11] By using the coordinate transformation of gravitomagnetic vector potentials in Kerr metric from the fixed frame of reference to the rotating frame,[12] it is readily verified that the rotating frequency $\vec{\omega}$ of a rotating frame relative to the inertial frame of reference can be regarded as a gravitomagnetic field.[12] The Hamiltonian of spin-rotation coupling, $H^{\text{s-r}}=\vec{\omega}\cdot\vec{S}$, can be obtained[11–14] by making use of the Dirac equation in the curved space-time,[15] where $\vec{S}$ denotes the spin operator of a spin-$\frac{1}{2}$ particle.

Fleming *et al.* have considered the electron-spin relaxation of C_{60} induced by the coupling of the electron spin to the molecular rotational angular momentum.[16] Since in some certain cases the rotating frequency (e.g., 10^{11} rad/s in orientationally disordered phases[4]) of C_{60} molecule can be compared to the electron Larmor frequency in a magnetic field arising from molecule rotation, it is necessary to consider the gravitational analog of Fleming's case. Moreover, in some cases such as in the low-temperature phase, the precession of C_{60} molecules around cones is faster than the molecular rotation (see, for example, in the following evaluation), and therefore it is also essential to deal with the precessional motion of C_{60} molecules and the consequent geometric phases of valency electrons in molecules.

II. TIME-DEPENDENT SPIN-ROTATION COUPLING

First, we consider the geometric phase of electrons arising from the time-dependent spin-rotation coupling in the rotating C_{60} molecule which undergoes a precessional motion. Note that the gravitational Aharonov-Bohm effect (also termed Aharonov-Carmi effect[17]) due to the Lorentz magnetic force (i.e., the Coriolis force) can be ignored in our following consideration, since Berry's phase, $2m_e\vec{\omega}\cdot\vec{A}$ with $\vec{A}$ being the area vector surrounded by a closed path along which the electron moves, appearing in the gravitational Aharonov-Bohm effect is negligibly small compared with the geometric phase due to the interaction of electron spin with the rotating frame (spin-rotation coupling).

Below 250 K in C_{60} solid, the molecules do not rotate freely and the noncentral part of intermolecular force will give rise to the precession and nutation of angular momentum and rotating frequency of C_{60} molecules. In what follows, the relationship between the rate of change of angular momentum of rotating C_{60} molecules and the time evolution of valency electron wave function undergoing a time-dependent spin-rotation coupling is taken into account.

Since the interaction between C_{60} molecules in solid C_{60} is the van der Waals potential, the coupling is relatively weak and therefore the magnitude of $|\vec{\omega}|$ does not easily alter, except that it gives rise to the variations of the direction of $\vec{\omega}$. By the aid of the above assumptions [e.g., $(d/dt)\vec{\omega}^2=0$], the phenomenological equation for the rotational motion of the C_{60} molecule weakly coupled to its neighbors is derived as

$$\frac{d}{dt}\vec{L}=\vec{B}\times\vec{L}, \tag{2.1}$$

where the effective gravitomagnetic field strength which leads to the precessional motion of C_{60} molecules, reads

$$\vec{B}=\frac{\vec{\omega}\times\dot{\vec{\omega}}}{\omega^2}. \tag{2.2}$$

Here dot denotes the derivative of $\vec{\omega}$ with respect to time t; the angular momentum $\vec{L}$ of the C_{60} molecule is defined to be $\vec{L}=I\vec{\omega}$ with the moment of inertia I being approximately $\frac{2}{3}ma^2$, where m and a (0.355 Å) denote the mass and radius of the C_{60} molecule, respectively. Note that here the rotational angular velocity $\vec{\omega}$ of C_{60} molecules acted upon by intermolecular interactions is *time dependent* due to the molecular thermal motion and thermal fluctuations in solid C_{60}. So, the Hamiltonian describing the coupling of spin of electrons (such as those in the delocalized π bond which has the conjugation effect) to the time-dependent $\vec{\omega}(t)$ is given by $H^{\text{s-r}}(t)=\vec{\omega}(t)\cdot\vec{S}$ and the time-dependent Schrödinger equation governing this electron spin-rotation coupling is

$$H^{\text{s-r}}(t)|\psi_\sigma(t)\rangle=i\hbar\frac{\partial}{\partial t}|\psi_\sigma(t)\rangle. \tag{2.3}$$

For convenience, we set the C_{60} rotating frequency

$$\vec{\omega}(t)=\omega_0[\sin\theta(t)\cos\varphi(t),\sin\theta(t)\sin\varphi(t),\cos\theta(t)], \tag{2.4}$$

where ω_0 is time independent and $\theta(t)$ and $\varphi(t)$ stand for the angle displacements in the spherical polar coordinate system. In order to exactly solve the time-dependent Schrödinger equation (2.3), in what follows use is made of the Lewis-Riesenfeld invariant theory[18] and the invariant-related unitary transformation formulation.[19,20] So, according to the Lewis-Riesenfeld theory[18] an invariant $I(t)$ that satisfies the Liouville–Von Neumann equation $(\partial/\partial t)I(t)+(1/i\hbar)\times[I(t),H^{\text{s-r}}(t)]=0$ should be constructed in terms of the spin operators $S_{\pm}$ and S_3 with $S_{\pm}=S_1\pm iS_2$. Thus the invariant $I(t)$ is of the form

$$I(t)=\tfrac{1}{2}\sin\lambda(t)\exp[-i\gamma(t)]S_{+}+\tfrac{1}{2}\sin\lambda(t)\exp[i\gamma(t)]S_{-}+\cos\lambda(t)S_3, \tag{2.5}$$

where the time-dependent parameters $\lambda(t)$ and $\gamma(t)$ are determined by the following two auxiliary equations:

$$\dot{\lambda}=\omega_0\sin\theta\sin(\varphi-\gamma),$$

$$\dot{\gamma}=\omega_0[\cos\theta-\sin\theta\cot\lambda\,\cos(\varphi-\gamma)], \tag{2.6}$$

with dot denoting the time derivative of $\lambda(t)$ and $\gamma(t)$. Note that insertion of expressions for $I(t)$ and $H^{\text{s-r}}(t)$ into the Liouville–Von Neumann equation yields Eq. (2.6). In accordance with the Liouville–Von Neumann equation, the invariant $I(t)$ possesses *time-independent* eigenvalues, which enables us to obtain the exact solutions of the time-dependent Schrödinger equation (2.3), for it is readily verified that the particular solutions of Eq. (2.3) are different from the eigenstates of the invariant $I(t)$ only by a time-dependent c-number factor.[18] If once the eigenvalue equation of $I(t)$ is exactly solved, then the solutions of the time-dependent Schrödinger equation (2.3) are easily obtained. By utilizing a unitary transformation operator

$$V(t)=\exp[\beta S_{+}-\beta^{*}S_{-}], \tag{2.7}$$

with $\beta(t)=-(\lambda(t)/2)\exp[-i\gamma(t)]$ and $\beta^{*}(t)=-(\lambda(t)/2)\exp[i\gamma(t)]$,[19,21,22] the time-dependent invariant $I(t)$ can be transformed into a time-independent one, i.e., $I_V\equiv V^{\dagger}(t)I(t)V(t)=S_3$, where the time-independent eigenvalue of S_3 is $\sigma=\pm\frac{1}{2}\hbar$ for the electron.

III. GEOMETRIC PHASES OF ELECTRONS IN ROTATING C_{60} MOLECULES

Since $(\partial/\partial t)I_V=0$, the Liouville–Von Neumann equation under this unitary transformation may be rewritten as $[I_V,H_V^{\text{s-r}}(t)]=0$. It follows that $H_V^{\text{s-r}}(t)$ depends only on the third component S_3 of the spin operator of the electron. Further calculation yields

$$H_V^{\text{s-r}}(t)\equiv V^{\dagger}(t)\left[H^{\text{s-r}}(t)-i\hbar\frac{\partial}{\partial t}\right]V(t)=\omega_0[\cos\lambda\cos\theta+\sin\lambda\,\sin\theta\cos(\gamma-\varphi)]S_3+\dot{\gamma}(1-\cos\lambda)S_3. \tag{3.1}$$

This, therefore, means that the particular solution $|\psi_\sigma(t)\rangle_V$ of the time-dependent Schrödinger equation

$$H_V^{\text{s-r}}(t)|\psi_\sigma(t)\rangle_V=i\hbar\frac{\partial}{\partial t}|\psi_\sigma(t)\rangle_V, \tag{3.2}$$

with $|\psi_\sigma(t)\rangle_V=V^{\dagger}(t)|\psi_\sigma(t)\rangle$, is different from the eigenstate of I_V only by a time-dependent c-number factor $\exp((1/i\hbar)[\phi_\sigma^{(\text{d})}(t)+\phi_\sigma^{(\text{g})}(t)])$, where the nonadiabatic noncyclic dynamical phase is

$$\phi_\sigma^{(d)}(t)=\sigma\int_0^t\omega_0\{\cos\lambda(t')\cos\theta(t')+\sin\lambda(t')\sin\theta(t')\cos[\gamma(t')-\varphi(t')]\}dt' \tag{3.3}$$

and the nonadiabatic noncyclic geometric phase is

$$\phi_\sigma^{(\text{g})}(t)=\sigma\int_0^t\{\dot{\gamma}(t')[1-\cos\lambda(t')]\}dt'. \tag{3.4}$$

If the adiabatic cyclic evolution process is taken into consideration, then it is verified that the present calculation is self-consistent. This may be illustrated as follows: in the adiabatic cyclic case, where the parameters $\lambda=\theta=\text{const}$, $\gamma=\varphi$, and the precessional frequency $\dot{\gamma}=\Omega$ is very small, the nonadiabatic geometric phase (3.4) in one cycle ($T=2\pi/\Omega$) is reduced to the expression for Berry's adiabatic cyclic topological phase[23]

$$\phi_\sigma^{(\text{g})}(T)=2\pi\sigma(1-\cos\theta), \tag{3.5}$$

where $2\pi(1-\cos\theta)$ is a solid angle over the parameter space of the C_{60} rotational frequency $\vec{\omega}(t)$. This fact implies that geometric phases possess the topological and global properties of time evolution in time-dependent quantum systems.[21,23]

If the eigenstate of I_V corresponding to the eigenvalue σ is $|\sigma\rangle$, then the eigenstate of the invariant $I(t)$ is $V(t)|\sigma\rangle$. Hence, in accordance with the Lewis-Riesenfeld invariant theory, the particular solution corresponding to σ of Eq. (2.3) reads

$$|\psi_\sigma(t)\rangle=\exp\left\{\frac{1}{i\hbar}[\phi_\sigma^{(d)}(t)+\phi_\sigma^{(\text{g})}(t)]\right\}V(t)|\sigma\rangle. \tag{3.6}$$

The influence of spin-rotation coupling and geometric phases discussed above on the photoelectron spectroscopy in the C_{60} molecule deserves considerations. The total Hamiltonian of an electron in the C_{60} molecule acted upon by the external perturbation (e.g., the radiation fields) can be written as $H=H_0+H^{\text{s-r}}(t)+H'(t)$, where H_0 represents the Hamiltonian of the valency electron in the C_{60} molecule when no spin-rotation coupling and external perturbation exist, and $H'(t)$ describes the external perturbation acting on the electrons. Since H_0 is assumed to be time independent, the eigenvalue equation of H_0 may be written as $H_0\exp[(1/i\hbar)\epsilon_{n,\sigma}t]|\phi_{n,\sigma}\rangle=\epsilon_{n,\sigma}\exp[(1/i\hbar)\epsilon_{n,\sigma}t]|\phi_{n,\sigma}\rangle$. The initial state $|\psi_{n,\sigma}(t=0)\rangle$ of Eq. (2.3) may be taken to be $|\phi_{n,\sigma}\rangle$. Thus, the particular solution of the time-dependent equation $[H_0+H^{\text{s-r}}(t)]|\Phi_{n,\sigma}(t)\rangle=i\hbar(\partial/\partial t)|\Phi_{n,\sigma}(t)\rangle$ is given

$$|\Phi_{n,\sigma}(t)\rangle=\exp\left\{\frac{1}{i\hbar}[\phi_\sigma(t)+\epsilon_{n,\sigma}t]\right\}V(t)|\phi_{n,\sigma}\rangle, \tag{3.7}$$

with $\phi_\sigma(t)=\phi_\sigma^{(d)}(t)+\phi_\sigma^{(\mathrm{g})}(t)$. Note, however, that here the magnetic interactions such as spin-orbit and spin-spin couplings in H_0 have been combined into $H^{\text{s-r}}(t)$ (i.e., this leads to the commutation relation $[H_0,H^{\text{s-r}}(t)]=0$) in order that the exact particular solution can be obtained conveniently via the above unitary transformation method. The solution of the time-dependent Schrödinger equation

$$[H_0+H^{\text{s-r}}(t)+H'(t)]|\Psi(t)\rangle=i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle \tag{3.8}$$

associated with the total Hamiltonian is assumed to be $|\Psi(t)\rangle=\Sigma_{n,\sigma}a_{n,\sigma}(t)|\Phi_{n,\sigma}(t)\rangle$. Substitution of this expression into this time-dependent Schrödinger equation yields

$$i\hbar\frac{d}{dt}a_{m,\sigma'}(t)=\sum_{n,\sigma}a_{n,\sigma}(t)\langle\Phi_{m,\sigma'}(t)|H'(t)|\Phi_{n,\sigma}(t)\rangle. \tag{3.9}$$

Further calculation shows that

$$\langle\Phi_{m,\sigma'}(t)|H'(t)|\Phi_{n,\sigma}(t)\rangle =\exp\left[\frac{1}{i\hbar}\phi_{\mathrm{tot}}(m\sigma',n\sigma;t)\right]H'_{m\sigma',n\sigma}(t), \tag{3.10}$$

where $H'_{m\sigma',n\sigma}(t)=\langle\phi_{m,\sigma'}|V^\dagger(t)H'(t)V(t)|\phi_{n,\sigma}\rangle$ and $\phi_{\mathrm{tot}}(m\sigma',n\sigma;t)=[\phi_\sigma(t)+\epsilon_{n,\sigma}t]-[\phi_{\sigma'}(t)+\epsilon_{m,\sigma'}t]$.

If the initial state is $|\Phi_{k,\sigma}\rangle$, i.e., $a_{k,\sigma}(t=0)=1$, then

$$a_{m,\sigma'}(t)=\frac{1}{i\hbar}\int_0^t H'_{m\sigma',k\sigma}(t')\exp\left[\frac{1}{i\hbar}\phi_{\mathrm{tot}}(m\sigma',k\sigma;t')\right]dt', \tag{3.11}$$

and the transition probability from the state $|\Phi_{k,\sigma}\rangle$ to $|\Phi_{m,\sigma'}(t)\rangle$ is $W_{k\sigma\rightarrow m\sigma'}=a^*_{m,\sigma'}(t)a_{m,\sigma'}(t)$.

Note that the exact solutions of the auxiliary equations (2.6) are often of complicated form. As an illustrative example, here we consider a physically interesting solution to Eq. (2.6), which stands for a typical case where the precessional frequency $\dot{\varphi}$ is constant (denoted by Ω) and the nutational frequency $\dot{\theta}$ vanishing. The explicit expression for this simple solution is

$$\gamma(t)=\varphi(t)=\Omega t,\quad \dot{\lambda}=\dot{\theta}=0, \tag{3.12}$$

where the time independent

$$\Omega=\frac{\omega_0\sin(\lambda-\theta)}{\sin\lambda}. \tag{3.13}$$

Here the C_{60} molecule precesses at an angular velocity Ω about the z axis ($\vec{\omega}$ deviates from z axis by a constant angle θ). Thus it follows that in this case the nonadiabatic noncyclic dynamical phase and the geometric phase of the electron are proportional to time t, i.e.,

$$\phi_\sigma^{(d)}(t)=[\omega_0\sigma\cos(\lambda-\theta)]t,\quad \phi_\sigma^{(\mathrm{g})}(t)=\Omega\sigma(1-\cos\lambda)t, \tag{3.14}$$

respectively, and the total phase difference $\phi_{\mathrm{tot}}(m\sigma',k\sigma;t)$ in transition matrix element $\langle\Phi_{m,\sigma'}(t)|H'(t)|\Phi_{k,\sigma}(t)\rangle$ is therefore of the form

$$\phi_{\mathrm{tot}}(m\sigma',k\sigma;t)=\{(\sigma-\sigma')[\omega_0\cos(\lambda-\theta)+\Omega(1-\cos\lambda)] +(\epsilon_{k,\sigma}-\epsilon_{m,\sigma'})\}t. \tag{3.15}$$

It follows from expression (3.15) that the photon energy absorbed or emitted in the transition process from $|\Phi_{k,\sigma}(t)\rangle$ to $|\Phi_{m,\sigma'}(t)\rangle$ is shifted by $(\sigma-\sigma')[\omega_0\cos(\lambda-\theta)+\Omega(1-\cos\lambda)]$ due to the electron spin-rotation coupling and the consequent geometric-phase effect. Apparently, the energy shifted by the dynamical phase and the geometric phase implies the information (i.e., ω_0, Ω, and θ) about the rotational motion and precession of the C_{60} molecule in condensed phases. This, therefore, means that it is possible for the information on the molecular rotation and precession to be read off in the photoelectron spectroscopy.

IV. POTENTIAL APPLICATIONS TO PHOTOELECTRON SPECTROSCOPY AND RELATED FIELDS

Let us evaluate the precessional frequency Ω and the effective gravitomagnetic field $\vec{B}=\vec{\omega}\times\dot{\vec{\omega}}/\omega^2$. At 283 K it is measured that the molecular reorientational correlation time τ is 9.1 ps, that, is three times as long as the calculated correlation time τ $[\equiv\frac{3}{5}(I/k_BT)^{1/2}$, with k_B and T being Boltzmann's constant and the absolute temperature, respectively] for free rotation (i.e., the unhindered gas-phase rotation) at this temperature.[4] The interaction energy of C_{60} molecule with the angular momentum $\vec{L}$ acted upon by the effective gravitomagnetic field $\vec{\omega}\times\dot{\vec{\omega}}/\omega^2$ is $E=-(\vec{\omega}\times\dot{\vec{\omega}}/\omega^2)\cdot\vec{L}$. As is assumed above, the angular velocity of C_{60} molecule is $\vec{\omega}(t)=\omega_0(\sin\theta\cos\Omega t,\sin\theta\sin\Omega t,\cos\theta)$, and the effective gravitomagnetic field is therefore

$$\vec{B}=\Omega\sin\theta(-\cos\theta\cos\Omega t,-\cos\theta\sin\Omega t,\sin\theta) \tag{4.1}$$

that is, apparently perpendicular to the angular momentum $\vec{L}$. Thus the magnitude of noncentral intermolecular torque acting on the rotating C_{60} molecule is $|\vec{M}|=|\vec{B}\times\vec{L}|=\omega_0\Omega I\sin\theta$ with $I\simeq1.0\times10^{-43}\ \mathrm{Kg\,m^2}$ (Ref. 4) being the moment of inertia of C_{60} molecule. The order of magnitude of $|\vec{M}|$ may be approximately equal to (or less than) the Van der Waals potential energy (0.001–0.1 eV), which may be seen as follows: roughly speaking, the moment of noncentral intermolecular force is the product of the van der Waals force (referring to the noncentral part) and the distance between molecules, the order of magnitude of which is often about the van der Waals potential energy. Since it follows that in the high-temperature phase (orientationally disordered phase), ω_0 may be 10^{11} rad/s, the precessional frequency Ω is therefore compared to ω_0, i.e., $\Omega\simeq|\vec{M}|/I\omega_0$ ranges from 10^{10} to 10^{12} rad/s. However, in the low-temperature phase (orientationally ordered phase), ω_0 decreases (e.g., $\omega_0\sim10^9$ rad/s) and in turn the precessional frequency Ω increases by a factor of $\sim$100. This, therefore, means that in the high-temperature phase the precessional frequency Ω is 10^{12}–10^{14} rad/s. Thus, the precessional frequency of C_{60} molecule is much greater than the rotating frequency ω_0 (which means that in this case the dynamical phases due to the spin-rotation coupling can be ignored) and the frequency shift in the transition matrix element due to geometric phases can be compared to the typical energy of an electron in solid; namely, according to the expression $(\sigma-\sigma')[\omega_0\cos(\lambda-\theta)+\Omega(1-\cos\lambda)]$ for the valency electron energy shift due to the electron spin-rotation coupling, where the precessional frequency $\Omega=10^{12}$–10^{14} rad/s, the valency electron energy shift in orientationally ordered phase is about 0.001–0.1 eV. Hence, it follows that the effects resulting from the spin-rotation coupling and geometric phases in C_{60} molecules deserve further investigations both theoretically and experimentally.

Additionally, it should be pointed out that the photoelectron spectroscopy will suffer several broadening effects such as thermal broadening. It is truly possible that the thermal broadening in C_{60} solid would muss the proposed energy shift. But this problem is not very serious, since below 250 K the thermal broadening is less than 0.01 eV and the valency electron energy shift in the orientationally ordered phase is of the order of magnitude of 0.001–0.1 eV. For the case of 0.1 eV of energy shift, the experimental data of photoelectron spectroscopy will not be affected much by the thermal broadening. In general, the lower is the temperature, the less is the influence of thermal broadening on photoelectron spectroscopy. So, our method can be applicable to the orientationally ordered phase. However, for the orientationally disordered phase, the broadening effect may have a small influence on the photoelectron spectroscopy. For this reason, the experimental scheme to investigate the noncentral intermolecular potential of C_{60} presented here is more suitable for the orientationally ordered phase than the high-temperature phase (orientationally disordered phase).

Thus, in principle, the operating procedure to study the noncentral interaction between C_{60} molecules is as follows.

(i) By making use of the phase/frequency shift formula (3.15), we read off the information (i.e., Ω, ω_0, θ and λ) on the precession and rotation of C_{60}.

(ii) With the help of Eqs. (3.13) and (3.14), one can arrive at the rate of change of rotating frequency of C_{60} molecules and in consequence obtain the so-called gravitomagnetic field strength according to expression (2.2).

(iii) Thus, we obtain the moment of noncentral intermolecular forces acting on the C_{60} molecules by the aid of Eq. (2.1) and consequently derive the noncentral intermolecular potential of C_{60} molecules.

(iv) Based on the above obtained noncentral intermolecular potential, we can consider the molecular dynamics, phase behavior, phase diagram, and crystal structures in C_{60} solid below 300 K.

V. CONCLUDING REMARKS

In general, the interaction between two C_{60} molecules is the sum of the interactions (van der Waals forces) between all of the carbon atoms on one molecule with those of the other. In the gas phase, and in the solid when the temperature is high enough (at least for temperature above 300 K), the noncentral part of the intermolecular forces disappears and therefore the C_{60} molecules rotate rather freely.[6,7] The Girifalco potential applies very well in these cases. In the low-temperature phase where the noncentral intermolecular potential causes the precession of angular momentum of C_{60} molecules and the interaction of valency electron spin with the time-dependent rotation of C_{60} molecules, which will produce electron geometric phases, we suggest an experimental scheme to obtain the information on the noncentral intermolecular potential through the photoelectron spectroscopy of C_{60}.

It is apparently seen that the investigation of the spin-rotation geometric phases of valency electrons in C_{60} molecules is of physical interest, discussed as follows.

(i) It enables us to study the relation between the photoelectron spectroscopy and the rotational motion of C_{60} molecules. Moreover, since geometric phases of electrons in one C_{60} molecule depend on other C_{60} molecules [via the effective gravitomagnetic field strength $\vec{\omega}\times\dot{\vec{\omega}}/\omega^2$ and hence the intermolecular torque $(\vec{\omega}\times\dot{\vec{\omega}}/\omega^2)\times\vec{L}$] and thus imply the information about the thermal motion and rotational dynamics of C_{60}, it is helpful to analyze the condensed phases (and hence the phase-transition behavior) of solid C_{60}.[24]

(ii) For the present, Mashhoon's spin-rotation coupling can be tested only in microwave experiments,[14] since this coupling is relatively weak due to the smallness of the rotational frequency of various rotating frames on the Earth. Fortunately, here the rotational motion of the C_{60} molecule can provide us with an ingenious way to test this weakly gravitational (gravitomagnetic) effect. Since the rotational angular velocity ω_0 of rotating C_{60} molecules is much greater than that of any rotating bodies on the Earth, the C_{60} molecule is an ideal noninertial frame of reference for the electrons in the C_{60} molecule, where the effects resulting from the electron spin-rotation coupling may be easily observed experimentally.

(iii) As was claimed previously, in addition to the Aharonov-Carmi geometric phase due to the Coriolis force (gravitomagnetic Lorentz force),[17] there exists another geometric phase associated with gravitational fields arising from the interaction between the spinning particle and the time-dependent gravitomagnetic fields. In the present paper, the time-dependent gravitomagnetic field strength is just the rotating frequency $\vec{\omega}(t)$ of C_{60} molecules. It may be reasonably believed that, from the point of view of equivalence principle in general relativity, this geometric phase itself appears to possess rich physical significance and should therefore be considered in more detail.

To summarize, we study the C_{60} molecule precession and geometric phases of valency electrons due to the time-dependent spin-rotation coupling in C_{60} molecules. Since in the orientationally ordered phase the precessional frequency of C_{60} is fairly great, the effects of geometric phases will be apparent and even may therefore be read off from the photoelectron spectroscopy, which enables physicists to investigate the noncentral intermolecular potential and hence the rotational dynamics and phase transition of C_{60}. Additionally, the present work will also make possible a test of Mashhoon's spin-rotation coupling by measuring the spin-rotation geometric phases of electrons in C_{60} molecules with rapid rotation. We hope all these physical phenomena and effects would be investigated experimentally in the near future.

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