3E07

線形紫外レーザーパルス誘起非平面キラル分子における π 電子回転ダイナミクスの理論的研究： コヒーレント角運動量と環電流

（国立台湾大學[1]，国立交通大学[2]，東北大・理[3]）峯尾 浩文[1]，林 聖賢[2]，藤村 勇一[2,3]

Coherent π-electronic-state dynamics of chiral molecule induced by
ultrashort linearly polarized UV pulses: angular mometum and ring current

([1]Institute of Applied Mechanics, National Taiwan University,
Taipei 106 Taiwan, [2]Department of Applied Chemistry, Institute of Molecular Science
and Center for Interdisciplinary Molecular Science, National Chiao-Tung University,
Hsin-Chu 300 Taiwan, [3]Department of Chemistry, Graduate School, Tohoku University,
Sendai 980-857)
Hirobumi Mineo[1], Sheng H. Lin[2], and Yuichi Fujimura[2,3]

In this work we theoretically show behaviors of ring currents in a non-planar Chiral aromatic molecule with two phenol rings combined with a single chemical bond. We remark that this talk is a continuous one of previous talk (3E06): Quantum switching of π–electron dynamics in optically induced nonplanar chiral aromatic molecule (P)-2,2'-biphenol, and use the same molecule.

The electrodynamics induced by a pulse laser $\vec{E}(t)$ can be calculated by solving the equations of motions of the density matrix:

$$\frac{d\rho_{\alpha\beta}(t)}{dt} = -\frac{i}{\hbar}\sum_{\gamma}\left(V_{\alpha\gamma}(t)\rho_{\gamma\beta}(t) - \rho_{\alpha\gamma}(t)V_{\gamma\beta}(t)\right) - \left(i\omega_{\alpha\beta} + \Gamma_{\alpha\beta}\right)\rho_{\alpha\beta}(t)$$

where $\hat{V}(t) = -\vec{\mu}\cdot\vec{E}(t)$, $\vec{\mu}$ is the transition dipole moment operator. $\omega_{\beta\alpha}$ is angular frequency difference between two electronic states α and β. The angular momentum and ring current are given as the expectation values in terms of density matrix elements:

$$\langle O(t)\rangle = n\int d\Omega \int d^3 r_1 \cdots d^3 r_n \delta(\mathbf{r} - \mathbf{r}_1)\left(\mathrm{Tr}\rho_{\beta\alpha}(t)O_{\beta\alpha}(\mathbf{r}_1)\right)$$

where n is the number of electrons, $O_{\beta\alpha}(\mathbf{r}) = \left\langle \Phi_{\alpha}\left|\hat{O}(\mathbf{r})\right|\Phi_{\beta}\right\rangle$, $\hat{O}(\mathbf{r})$ is the single

electron operator. The angular momentum is calculated with the operator

$$\hat{O}(\mathbf{r}) = -i\hbar \sum_{K=L,R} \left(x_K \partial/\partial x_K - y_K \partial/\partial x_K \right) \mathbf{n}_K$$

with $d\Omega = d^3 r$, on the other hand the ring current is given by

$$\hat{O}(\mathbf{r}) = \frac{e\hbar}{2m_e i}\left(\vec{\nabla} - \overleftarrow{\nabla} \right)$$

with $d\Omega = dS$ where $\mathbf{n}_K$ is a unit vector which is perpendicular to a ring K, dS represents an integral over a surface S.

The electronic angular momentum and the resultant ring current are created by a coherent excitation of two electronic excited states using the π pulse laser. These electronic states belong to C_2 point group which have A and B representations. As is similar to a previous talk, in this molecular system we have three electronic excited state a(A), b1(B) and b2(B), and by changing the laser frequency we obtain two coherently excited states a,b1 (b1,b2) which belong to different (same) symmetries. The created ring current at each chemical bond oscillates back and force by a periodicity which is given by the inverse of the energy gap between two coherently excited states.

In Fig. 1 we show the directions of initially created currents by shining $\mathbf{e}_{ab1}^{(+)}$ or

$\mathbf{e}_{b1b2}^{(+)}$ where two coherently excited states are "in-phase". From this figure we find that current or angular momentum transfer through the bridge chemical bond C1-C7 only occurs if two coherently excited states belong to a different representation as is shown in Fig. 1(a). In this case the directions of ring currents and angular momenta on both sides of phenol rings are toward opposite direction. On the other hand if two coherently excited states belong to a same representation B shown in Fig. 1(b), the directions of ring currents and angular momenta on both sides of phenol rings are toward same directions i.e., the created ring currents and angular momenta on both sides behave in a same manner.

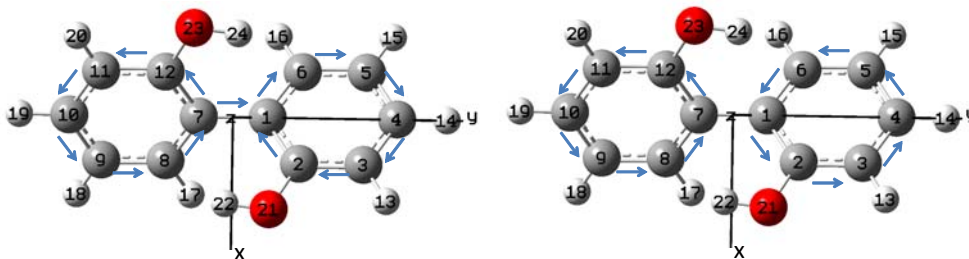(a) *a, b1* excitation (b) *b1,b2* excitation

Fig. 1 Behaviors of the ring currents are plotted where the two coherently excited states are "in-phase".