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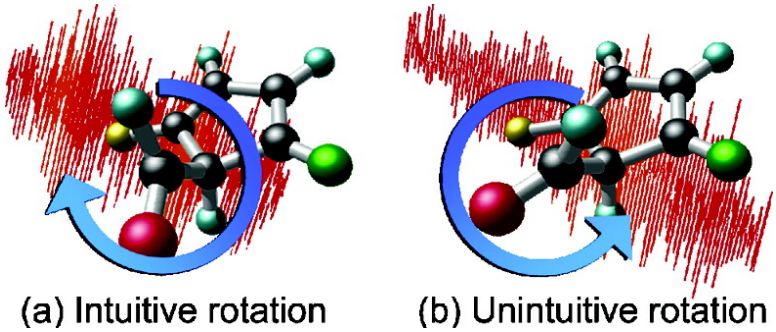

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Quantum Control of a Chiral Molecular Motor Driven by Laser Pulses

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Molecular motors or machines driven by external fields are important in the design of functional molecular devices.[1−8] Optically driven molecular motors are particularly interesting because optical fields have actively controllable parameters, such as central photon frequency, pulse duration, and polarization. One of the main issues in the design of such molecular motors is how to drive them in desired directions by means of lasers. It has been shown that the direction of rotation of chiral molecular motors driven by linearly polarized laser pulses without any optimization procedure depends on their chirality. The direction of rotation of a chiral molecular motor is toward its gentle slope of the asymmetric potential,[9] that is, toward the intuitive direction (see Figure 1). There is no guiding principle for driving a motor in a predesired direction, for example, intuitive or unintuitive direction.

In this paper, we show on the basis of a quantum control theory that chiral molecular motors can be effectively driven in predesired directions by applying linearly polarized laser pulses with optimized electric fields. The theory of quantum control is well-known as an effective method for design of control scenarios for chemical reaction dynamics, and quantum control experiments combined with a genetic algorithm have been carried out.[10−15]

For this purpose, consider (*R*)-2-chloro-5-methylcyclopenta-2,4-dienecarbaldehyde as a simple model for chiral molecular motors, as shown in Figure 1. The aldehyde group is its engine driven by laser pulses propagating in the *z*-direction, and the dihedral angle $O^1-C^2-C^3-H$,[4] α, is a dynamic variable. The direction of the C^2-C^3 bond is set to be parallel to the spatially fixed *z*-axis. Intramolecular mode couplings associated with α were omitted. This can be verified in the zero-order approximation because there are relatively large frequency differences between vibrational and rotational frequencies. This molecule can be fixed on a surface to prevent its molecular rotation[6c,16] or at a space by external forces, such as an electric field.

The Hamiltonian of the molecular motor in a laser pulse of electric field $\boldsymbol{E}(t)$ is expressed within the dipole approximation as $H(t) = H_M - \boldsymbol{\mu}(\alpha)\cdot\boldsymbol{E}(t)$. Here, H_M is the molecular Hamiltonian that consists of the kinetic energy operator and the internal rotational potential function, $V(\alpha)$. $\boldsymbol{\mu}(\alpha)$ is the dipole moment function. $V(\alpha)$ and $\boldsymbol{\mu}(\alpha)$ were evaluated by using an ab initio MO method. The quantum number of the highest excited bound state was estimated to be $n = 53$ by solving the eigenvalue problem of H_M.

The time evolution of the molecular state, $\Psi(t)$, was evaluated by solving the time-dependent Schrödinger equation. In locally optimized control theory,[17] $\boldsymbol{E}(t)$ is determined from the expression $\boldsymbol{E}(t) = -2A\mathrm{Im}\langle\Psi(t)|\hat{W}\boldsymbol{\mu}|\Psi(t)\rangle$, where *A* is a regulation parameter of the laser intensity, and the operator, $\hat{W}$, is a target operator whose expectation value gives the maximum value at a final time, t_f.

Consider now quantum ignition of the motor from the ground state $|0\rangle$ to the internal rotational state $|m\rangle$, where *m* is the rotational quantum number. The final state should be $m < 0$ ($m > 0$) for intuitive (unintuitive) rotation since the intuitive (unintuitive) rotation is in the minus (plus) direction (see Figure 1).

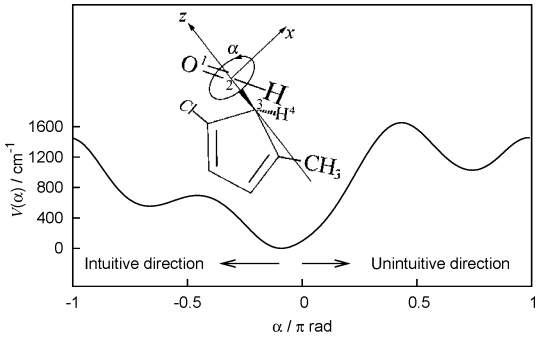

Figure 1. A chiral molecular motor, (*R*)-2-chloro-5-methylcyclopenta-2,4-dienecarbaldehyde, and the potential function of the internal rotation of the aldehyde group. The intuitive (unintuitive) rotational direction indicated by an arrow means that its rotation is toward the gentle (steep) slope of the potential.

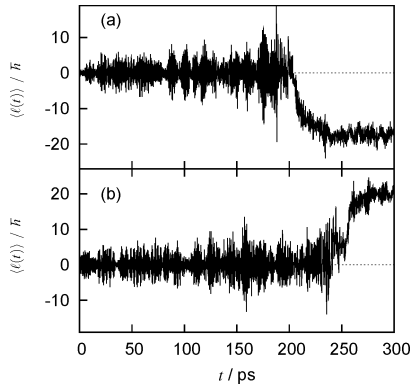

Figure 2. (a) Instantaneous angular momentum, $\langle\ell(t)\rangle$, of the chiral molecular motor driven by controlled laser pulses: (a) rotation in the intuitive direction and (b) rotation in the unintuitive direction. Note that the intuitive rotation is driven earlier than in the unintuitive rotation.

Figure 2 shows the quantum mechanical expectation values of instantaneous angular momentum of the molecular motor $\langle\ell(t)\rangle$ defined as $\langle\Psi(t)|-i\hbar\partial/\partial\alpha|\Psi(t)\rangle$, which were obtained by applying the locally optimized method. The sign and absolute quantity of the expectation value correspond to the direction of the angular momentum and its magnitude, respectively. Figure 2 clearly indicates that rotational directions of the motor are controlled well at the final time of 300 ps. We set $|\Psi(t_f)\rangle = (|66\rangle - i|65\rangle)/\sqrt{2}$ as the target state for an intuitive rotation and $(|66\rangle + i|65\rangle)/\sqrt{2}$ as that for an unintuitive rotation. Here, $|65\rangle$ and $|66\rangle$ are eigenstates whose frequencies are equal to each other within 0.001 cm^{-1}. Thus, these states are practically degenerate in our observation time and correspond to those with rotational quantum numbers $m = \pm 33$.

Figure 3a (3b) shows time frequency resolved spectra of the electric fields, $S(\omega, t)$, by which the motor is driven in the intuitive

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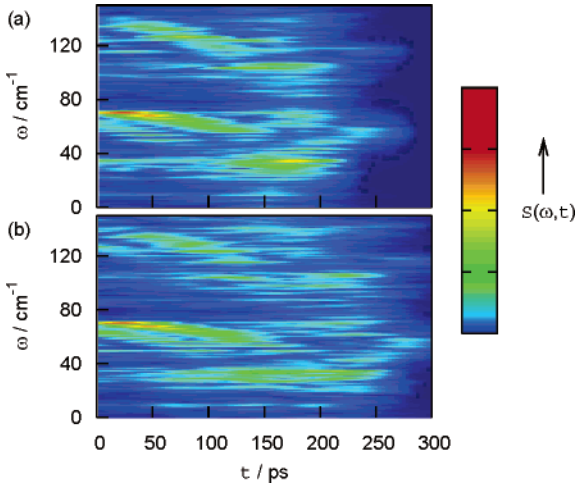

Figure 3. Time frequency resolved spectra of electric fields of laser pulses obtained by using a locally optimized control method: (a) that for the intuitive direction of rotation and (b) that for the unintuitive direction.

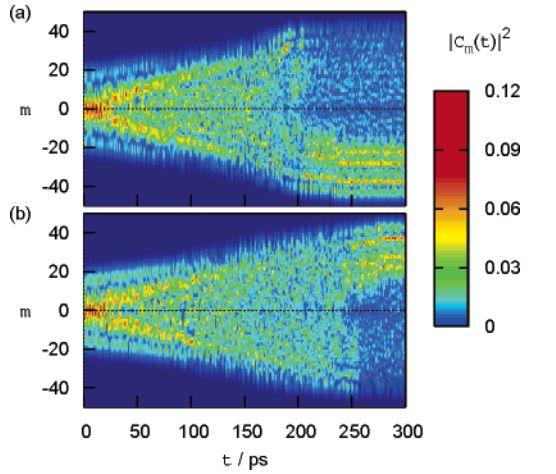

Figure 4. Time-dependent population in an *m*th angular momentum state, $|C_m(t)|^2$: (a) intuitive rotation and (b) unintuitive rotation. The former is characterized by negative values of *m* at the final time, and the latter is characterized by positive values.

(unintuitive) direction indicated in Figure 2a (2b). The designed electric fields are of terahertz (THz) pulses with far-infrared (far-IR) central frequencies. The pulses consist of a sequence of chirped pulses. Note that time difference in the pulse tail end between Figures 3a and 3b: $t_f \approx 220$ and 250 ps, respectively. Results of the detailed analysis will be presented elsewhere.

To clarify the mechanism of unidirectional rotations driven by the controlled laser pulses, we examined when unidirectional motion begins, that is, when a nonstationary rotational state, $|\Psi(t)\rangle$, is created, $|\Psi(t)\rangle = \Sigma C_m(t)|m\rangle$, with only negative (positive) values of *m* in the intuitive (unintuitive) rotational direction.

Figure 4 shows the distribution of time-dependent coefficients, $|C_m(t)|^2$. We can see two dynamic stages; the first stage expresses pendulum motions that are characterized by both negative and positive values of *m*, and the other stage expresses unidirectional motions that are characterized by negative or positive values whose maximum amounts to nearly $|m| \approx 40$. We can see from Figure 4 that the intuitive rotation begins earlier than the unintuitive rotation. This is related to the fact that the intuitive rotation is a favorable motion when laser pulses are used without any optimization procedure. The time difference between these two opposite rotations corresponds to the frequency difference between coherently excited eigenstates of the doorway state. This means that the direction of rotation is determined by the phase of a coherent superposition of the rotational eigenstates created by controlled electric fields. The time required to change the direction of rotations is given by the inverse of the frequency difference between a pair of eigenstates. The relation between the phase of rotational eigenstates and rotational direction can be seen in papers on microwave-kicked diatomic molecules and ratchets.[18]

In conclusion, we have shown on the basis of a quantum control theory that a sequence of linearly polarized, chirped laser pulses of far-IR frequencies can drive predirectional rotational motions of a chiral molecular motor under an idealized condition. Generation and processing of far-IR electric fields are now a hot research subject in THz laser science and technology.[19] Closed loop control procedures combined with a pulse shaper working in the far-IR spectral ranges are required to perform laboratory quantum control of a chiral molecular motor in an optimal and efficient fashion.[11−14]

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References

(1) *Molecular Machine and Motors*; Sauvage, J.-P., Ed.; Springer, Berlin, 2001 (Structure and Bonding, Vol. 99).
(2) Bedard, T. C.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 10662−10671.
(3) Balzani, V.; Gomes-López, M.; Stoddart, J. F. *Acc. Chem. Res.* **1998**, *31*, 405−414.
(4) Tuzun, R. E.; Niod, D. W.; Sumpter, B. G. *Nanotechnology* **1995**, *6*, 52−63.
(5) Sauvage, J.-P. *Acc. Chem. Res.* **1998**, *31*, 611−619.
(6) (a) Vacek, J.; Michl, J. *New J. Chem.* **1997**, *21*, 1259−1268. (b) Vacek, J.; Michl, J. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 5481−5486. (c) Horinek, D.; Michl, J. *J. Am. Chem. Soc.* **2003**, *125*, 11900−11910.
(7) (a) Koumura, N.; Zijlstra, R. W. J.; van Delden, R. A.; Harada, N.; Feringa, B. L. *Nature* **1999**, *401*, 152−155. (b) van Delden, R. A.; ter Wiel, M. K. J.; de Jong, H.; Meetsma, A.; Feringa, B. L. *Org. Biomol. Chem.* **2004**, *2*, 1531−1541.
(8) Mobian, P.; Kern, J.-M.; Sauvage, J.-P. *Angew. Chem., Int. Ed.* **2004**, *43*, 2392−2395.
(9) (a) Hoki, K.; Sato, M.; Yamaki, M.; Sahnoun, R.; González, L.; Koseki, S.; Fujimura, Y. *J. Phys. Chem. B* **2004**, *108*, 4916−4921. (b) Hoki, K.; Yamaki, M.; Koseki, S.; Fujimura, Y. *J. Chem. Phys.* **2003**, *118*, 497−504. (c) Hoki, K.; Yamaki, M.; Fujimura, Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 2975−2978. (d) Hoki, K.; Yamaki, M.; Koseki, S.; Fujimura, Y. *J. Chem. Phys.* **2003**, *119*, 12393−12398. (e) Fujimura, Y.; González, L.; Kröner, D.; Manz, J.; Mehdaoui, I.; Schmidt, B. *Chem. Phys. Lett.* **2004**, *386*, 248−253.
(10) Kohler, B.; Krause, J. L.; Raksi, F.; Wilson, K. R.; Yakovlev, V. V.; Whitnell, R. M.; Yan, Y. J. *Acc. Chem. Res.* **1995**, *28*, 133−140.
(11) Judson, R. S.; Rabitz, H. *Phys. Rev. Lett.* **1992**, *68*, 1500−1503.
(12) Assion, A.; Baumert, T.; Bergt, M.; Brixner, T.; Kiefer, B.; Seyfried, V.; Strehle, M.; Gerber, G. *Science* **1998**, *282*, 919−922.
(13) Rabitz, H.; de Vivie-Riedle, R.; Motzkus, M.; Kompa, K. *Science* **2000**, *288*, 824−828.
(14) Levis, J. R.; Menkir, G. M.; Rabitz, H. *Science* **2001**, *292*, 709−713.
(15) Daniel, C.; Full, J.; González, L.; Lupulescu, C.; Manz, J.; Merli, A.; Vajda, S.; Wöste, L. *Science* **2003**, *299*, 536−539.
(16) Interactions between the aldehyde group and the surface were omitted assuming a large distance between them.
(17) Ohtsuki, Y.; Kono, H.; Fujimura, Y. *J. Chem. Phys.* **1998**, *109*, 9318−9338.
(18) Gong, J.; Brumer, P. *J. Chem. Phys.* **2001**, *115*, 3590−3597; *Phys. Rev. E* **2004**, *70*, 016202-1−016202-6. See also ref 9b for the relation between quantum ratchets and chiral molecular motors driven in specific direction by external fields.
(19) Schmuttenmaer, C. A. *Chem. Rev.* **2004**, *104*, 1759−1779.

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