§23. Molecular Alignment through Non-resonant Multiphoton Transitions in a Microwave Region

Ohtsuki, Y.
(Dept. Chem., Grad. School Sci., Tohoku Univ.)

Controlling molecular alignment and orientation provides macroscopically anisotropic molecular samples. It is a crucial initial step toward a wide range applications that include stereo-dynamics in chemical reactions, elucidation of molecular structures, the control of high-harmonic generation and so on. The control schemes are classified into two categories, adiabatic and non-adiabatic schemes. In the adiabatic scheme, the aligned state is maintained during laser irradiation, which is attributed to a field induced pendular state. On the other hand, the non-adiabatic scheme provides a way to create the aligned state in a field-free manner, which can be more fruitful for many practical applications. This control is done by coherently controlling the rotational states of a molecule, i.e., by wave packet shaping. Besides experimental reports, there have been many theoretical studies, however, most of which focused on the effective induced-dipole interaction averaged over fast optical transitions, i.e., the molecular system follows the square of a pulse envelope function.

We study the intermediate case in which the amplitude as well as relative phases among frequency components of a control pulse plays a role through a case study of an ensemble of non-polar nitrogen molecules [1, 2]. This numerical analysis is motivated recent successful experimental reports, in which closed-feedback loops are equipped. The simulations are done by using optimal control procedure recently developed by us. We adopt a nitrogen molecule that is modeled by a 3D quantum rigid rotor. Controlled rotational wave packets are created through manipulated non-resonant optical transitions induced by polarizability coupling. Optimal pulses are designed to achieve the alignment control at a specified time in the absence/presence of external static fields in zero- and finite-temperature cases, as well as to maintain an aligned state. When the target is chosen so that it maintains an aligned state over a specified time interval, the control mechanism is primarily attributed to a dynamical one [2]. Multiple optimal solutions that lead to virtually the same high control achievement are found.

The molecular system interacts with a time-dependent, linearly polarized electric field, E(t), with frequencies in a microwave region. As there is no resonant coupling with electronic nor vibrational states, the Hamiltonian is expressed as,

$$H = BL^2 - \frac{[E(t)]^2}{2}[(\alpha_{\parallel} - \alpha_{\perp})\cos^2\theta + \alpha_{\perp}], \qquad (1)$$

where B is the rotational constant, L, is the angular moment operator, and θ is the polar angle between the molecular axis and polarization vector of the laser pulse. The dynamical polarizabilty is approximated by static one, the parallel (perpendicular) component of which are denoted by $\alpha_{\parallel}$ ($\alpha_{\perp}$). We measure the degree of alignment by using the average value of the operator, $\cos^2\theta$, and the optimal pulse is designed so that it maximizes the target expectation value, $J = <\psi(t_f)|\cos^2\theta|\psi(t_f)>$ at a specified final time. The iterative solution algorithms reported in our paper are used to perform the simulations.

Figure 1 shows a typical example of the optimal control simulation [2].

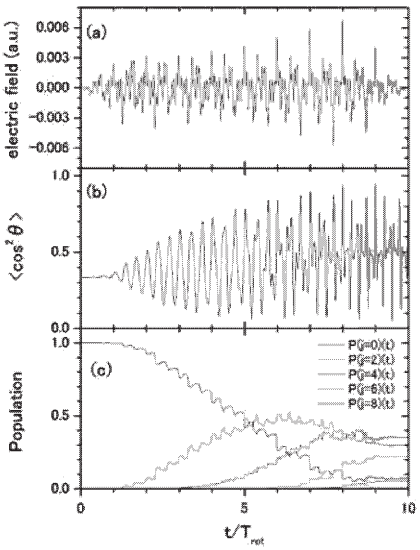

Fig. 1. (a) Optimal pulse as a function of time, (b) time-evolution of the target expectation value, and (c) time-evolution of the 5 rotational states in the case of T=0K. Time is measured in units of the rotational period (8.38 ps).

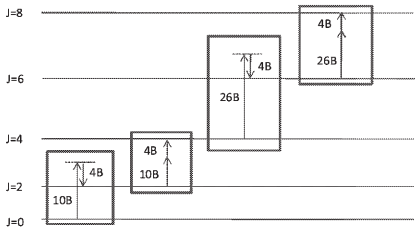

Fig.2. Control mechanisms shown by the power spectrum of the optimal pulse in Fig. 1 (a).

The optimal microwave pulse achieves the high degree of freedom, the expectation value of which id 0.95. The power spectrum of the optimal pulse in Fig. 1 (a) (not shown) consists of 3 frequency components. As shown in Fig. 2, they induce the two-photon absorption and the stimulated Raman processes, resulting in the sequential excitation of the population from the lower state to the higher state as shown in Fig. 1(c). Finally, I emphasize that the present numerical findings include general control features, which are independent on a frequency region.

1) Ohtsuki, Y., Nakagami, K., Phys. Rev. A **77** (2008) 033414.
2) Nakagami, K., Mizumoto, Y., Ohtsuki, Y., J. Chem. Phys. **129** (2008) 194103.