

Alignment is forever - and orientation too: molecules in combined static electric and pulsed nonresonant radiative fields

Long Cai, Jotin Marango, and Bretislav Friedrich

*Department of Chemistry and Chemical Biology, Harvard University
Cambridge, MA 02138, U.S.A.*

The anisotropic polarizability of molecules subject to nonresonant radiation fields has been shown to give rise to directional eigenstates (termed pendular) in which the molecular axis is *aligned* with respect to the electric-field vector [1]. Recently, we have developed a general technique of *orienting* molecules based on the combination of a nonresonant laser field with a static electric field that endows a polar molecule with a pseudo-first-order Stark effect [2]. In a nonresonant laser field, the induced dipole interaction produces a double-well potential, governed by the anisotropy of molecular polarizability and the laser intensity. The pendular energy levels thus occur as tunneling doublets, whose splitting decreases exponentially with the square root of the laser intensity. Adding a static electric field couples the opposite parity members of a given tunneling doublet and produces orientation. Thus often a very weak static electric field can convert second-order alignment by a laser into a strong first-order orientation. The effect occurs for any polar molecules, as only an anisotropic polarizability is required.

The present study deals with the way these directional states are formed in the time-dependent (pulsed) laser fields, required to provide a sufficient intensity. In the reduced form, the corresponding time-dependent Schrödinger equation clocks the time in units of \hbar/B (with B the rotational constant) which defines a “short” and a “long” time for any molecule [3]. In the short-pulse limit (pulse duration $\leq \hbar/B$) the interaction is non-adiabatic and the pendular states recur after the pulse passes over, making it possible and feasible to obtain molecular *alignment and orientation under field-free conditions*; the recurrence period is found to decrease with increasing field strength. In the long-pulse limit (pulse duration $\geq 5\hbar/B$) the interaction is adiabatic and the states faithfully follow the field as if it were static at any instant.

In the non-adiabatic regime, the molecule is described at any time by a superposition of pendular states. As a result, at the end of the laser pulse the wave function maintains the character of a coherent rotational wave packet which gives rise to molecular alignment and orientation at a later time. We present an analysis of the composition of the wave-packets and of the periodic recurrences of the alignment and orientation that take place as a result of the underlying dephasing-rephasing processes.

[1] B. Friedrich and D. Herschbach, Phys. Rev. Lett. **74**, 4623 (1995). [2] B. Friedrich and D. Herschbach, J. Chem. Phys. **111**, 6157 (1999); J. Chem. Phys. **111**, 6157 (1999); J. Phys. Chem. A **103**, 10280 (1999). [3] J. Ortigoso, M. Rodriguez, M. Gupta, and B. Friedrich, J. Chem. Phys. **110**, 3870 (1999).