STARK EFFECT AND TORSIONAL MOTION INTERACTION IN BIPHENYL

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Although the interaction of an electric field with molecular motions has been thoroughly investigated in the case of a rigid molecule,[a] much less results are available for a non-rigid molecule, like the biphenyl molecule, displaying an internal torsional motion strongly coupled to the electric field.

The present paper reports an exact calculation of the rotation-torsion energy levels of a biphenyl molecule interacting with an electric field. This molecule, with formula $(C_6H_5)_2$, consists of two rings which can rotate about the C−C bond, the angle of internal rotation being taken equal to 2γ, with $0 \leq \gamma \leq 2\pi$. This molecule interacts with the electric field through its induced dipole moment, the interaction being described by the γ-dependent polarizability tensor.

The calculation involves computing rotation-torsion energy levels and wavefunctions using the Hamiltonian derived by Merer and Watson[b] for ethylene-like molecules. The γ-dependent electric field interaction Hamiltonian is diagonalized using these wavefunctions as a basis set. The number of energy levels thus obtained being very high, Boltzmannian equilibrium is assumed in order to evaluate average values of several operators related to the molecular orientation, the rotational wavefunction, and the torsional wavefunction.

In the paper, these average values will be calculated for several temperatures in two cases: (*i*) assuming a rigid molecule and setting γ equal to its equilibrium value, approximately $20.2°$, and (*ii*) taking into account the non-rigidity of the molecule and solving the Schrödinger equation as outlined above. The qualitative differences arising in the case of a static electric field and in the case of a fast oscillating circular polarized field will be discussed. The possibility of torsional control of the molecule[c] will also be investigated.

[a] Friedrich and Herschbach, *Phys. Rev. Lett.* **74** (1995) 4623.
[b] Merer and Watson, *J. Mol. Spectrosc.* **47** (1973) 499.
[c] Ramakrishna and Seideman, *Phys. Rev. Lett.* **99** (2007) 103001.