THEORY OF MICROWAVE 3-WAVE MIXING OF CHIRAL MOLECULES

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The traditional spectroscopic methods to measure enantiomeric excess, based upon optical rotation or circular dichroism arise from an interference of electric and magnetic dipole contributions of an optical transitions. The later is relativisitic and gets smaller with decreasing frequency and thus these effects have not been previously observed in pure rotational spectroscopy. First introduced by the group at Harvard[1], it is possible to use a 3-wave mixing method (with one of the fields potentially a Stark Field) to distinguish enantiomers if the three wave are nonplaner. In the conceptually simplest form of this experiment, a molecule is polarized with X polarization on a $a \rightarrow b$ transition, and then the resulting ρ_{ab} molecular coherence is transferred to a ρ_{ac} coherence by application of a π pulse on the $b \rightarrow c$ transition. For a chiral molecule with nonzero dipole projections on the three inertial axes, this ρ_{ac} coherence can radiate Z polarized emission at the frequency of the $a \rightarrow c$ transition.

In this talk, I will present the full theory of such experiments, including accounting for dirrection cosine matrix elements and *M* degeneracy. The resulting expressions can be used to calculate the expected size of the signal as a function of the specific transitions used in the $a \rightarrow b \rightarrow c \rightarrow a$ cycle.[2] It will be demonstrated that the maximum size of the ρ_{ac} coherence is nearly that generated by a "$\pi/2$" pulse on the $a \rightarrow c$ transition. However, it is not possible to phase match the emission generated by this polarization due to the requirement that the three fields be orthogonal. Given that in rotational spectroscopy the physical size of the sample produced in a pulsed supersonic jet is comparable to the wavelengths of the microwave fields, the lack of phase matching produces a substantial but not catastrophic loss in the amplitude of the emitted free induction decay field. I will present a proposal to realize an analogy of quasiphase matching to ameliorate the dephasing.

1. D. Patterson, M. Schnell, & JM Doyle, Nature **497**, 475 (2013); D Patterson & JM Doyle, PRL **111**, 023008 (2013)
2. S. Lobsiger *et al*, JCPL **6**, 196 (2015).