

Using the Phase of Light as a Photochemical Tool

Robert J. Gordon

*Department of Chemistry (m/c 111), University of Illinois at Chicago, 845 West Taylor Street,
Chicago, IL 60607-7061*

Tamar Seideman

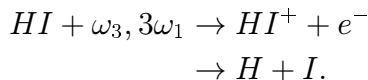
*Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa
K1A-0R6, Canada*

In conventional photochemical and spectroscopic studies, the principle experimental tools are the intensity and frequency of the light source. The phase is usually not considered because absorption and emission cross sections are proportional to the square of the absolute value of the transition dipole matrix element. The phases of the light source and the dipole matrix element enter only if two or more pathways connecting the initial and final states interfere with each other. These paths might be, for example, the absorption of m photons of frequency ω_n and n photons of frequency ω_m having the same total energy. Adding the amplitudes for each path and then taking the square, the probability of obtaining a product S is given by

$$p^S(E) = p_n^S(E) + p_m^S(E) + 2|p_{mn}^S| \cos(\phi + \delta_{mn}^S), \quad (1)$$

where p_n^S and p_m^S are, respectively, the angle averaged probabilities of the m - and n - photon processes, $|p_{mn}^S|$ is the amplitude of the interference term, ϕ is the relative phase of the two electromagnetic fields, and δ_{mn}^S is a channel-specific quantity that depends on the properties of the molecule.

The channel phase, δ_{mn}^S , is a valuable tool for controlling photochemical reactions and for revealing properties of continuum states. The possibility of controlling chemical branching ratios follows directly from Eq. (1). For example, excitation of the hydrogen iodide molecule by one and three photons results in both dissociation and ionization reactions,



The yield of the dissociation channel can be maximized by experimentally setting $\phi = -\delta_{13}^I$, whereas the yield of the ionization channel can be maximized by setting $\phi = -\delta_{13}^{HI^+}$. The ability to discriminate between the two channels is determined by the *phase lag*,

$$\Delta\delta(I, HI^+) = \delta_{13}^I - \delta_{13}^{HI^+}. \quad (2)$$

The emphasis of the present talk is on the molecular information that can be extracted from this new energy-dependent observable, $\Delta\delta$. We have shown that sufficient conditions for δ_{13}^S not to vanish are (i) coupling of continuum S with some other continuum, (ii) interactions of a resonance with the continuum, and (iii) the presence of a quasi-bound state at an intermediate energy. Recently we demonstrated both experimentally and theoretically that δ_{13}^S can be used to measure the absolute phase (modulo π) of a complex wave function. We also found that the phase lag can be used to detect weak transitions that are absent in conventional spectroscopic measurements.