Effects of the Gouy Phase on the Coherent Control of Chemical Reactions

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Introduction
Various methods have been used to control the outcome of a chemical reaction. The Brumer and Shapiro approach, analogous to the Young's two-slit experiment, is referred to as coherent phase control. In the most commonly studied scenario of coherent phase control, the two excitation paths are the absorption of n photons of frequency $\omega_n$ and m photons of frequency $\omega_m$, such that $n \omega_n = m \omega_m$. The overall probability for obtaining a product $S$ for the n vs. m photon excitation can be written as

$$P_n = P^0_n + 2 P^0_m \cos \phi + \delta_{n,m}$$

where $P_n$ is the n-photon reaction probability, $P^0_m$ is the m-photon probability, $\phi$ is the amplitude of a term arising from interference between the two paths, $\phi$ is the spatial phase, which is a property of the radiation field, and $\delta_{n,m}$ is the molecular or channel phase, which is a property of the reactant.

The spatial phase can be written as

$$\phi = (m \phi_n - n \phi_m) + (m k_z - n k_z) z + (m - n) \phi(z)$$

where $\phi$ is the constant phase of the electric field, z is the axial coordinate of the field, $k_n$ is the wave number, $\phi(z) = \tan^{-1}(2k_z R)$ is the Gouy phase, and $k_z$ is the Rayleigh range.

The first term in $\phi$ is proportional to the difference between the refractive indices at frequencies $\omega_n$ and $\omega_m$. The second term is usually assumed to vanish because of momentum conservation. The Gouy phase in the third term describes a phase shift of a focused laser beam as it propagates through the focal point. It has been demonstrated by Chen and Elliot for the one- vs. three-photon excitation of mercury atoms, but this phase shift has never been used to control the branching ratio of a reaction.

We demonstrate here how the Gouy phase can be exploited to control the branching ratio, even in the absence of a molecular phase $\phi$. The reactions we have studied include the photodissociation and photoionization of vinyl chloride, acetone, and dimethyl sulfide (DMS).

Experimental setup

Results

A schematic drawing showing the overlap of the laser and molecular beams. A 532 nm visible laser is focused by a lens (f = 76.2 cm) into a mercury oven. Mirrors M1 (f = 7.6 cm) and M2 (f = 7.6 cm) are mounted inside the H$_2$ phase tuning cell (not shown). The two astigmatic foci are separated by 4.5 mm.

Calculations

Control Mechanism

Optimized modulation depth, $M_{\text{max}}$, under typical experimental conditions. Panel (a) shows $M_{\text{max}}$ at the center of the molecular beam ($z_m = 0$) as a function of the ratio of the molecular beam radius to the Rayleigh range. Panel (b) shows the variation of $M_{\text{max}}$ as the laser focus is scanned across the molecular beam, with $\delta_{lR} = 1.746$.

Conclusions

It is shown that phase control of bound-to-continuum transitions in molecules having large densities of states is achievable with modulation depths as large as 42%. The main finding of this study is that the Gouy phase of a focused laser beam may be used to control the branching ratio of a photo-induced reaction. This phase, which was not included in previous formulations of coherent phase control, adds linearity to the refractive and molecular phases in the interference term. A necessary and sufficient condition for this phase to serve as a control parameter is that the product yields have different intensity dependences.