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[1-4]. 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 ω_m and *m* photons of frequency ω_n, such that $n\,\omega_m = m\,\omega_n$. The overall probability for obtaining a product *S* for the n vs. m photon excitation can be written as

$$P^S = P_m^S + P_n^S + 2P_{mn}^S \cos\left(\phi_{sp} + \delta_{mn}^S\right)$$

where P_m^S is the *n*-photon reaction probability, P_n^S is the *m*-photon probability, P_{mn}^S is the amplitude of a term arising from interference between the two paths, ϕ_{sp} is the spatial phase, which is a property of the radiation field, and δ_{mn}^S is the molecular or channel phase, which is a property of the reactant. The spatial phase can be written as

$$\phi_{sp} = \left(m\phi_n - n\phi_m\right) + \left(mk_n z - nk_m z\right) + \left(m-n\right)\eta\left(z\right)$$

where ϕ_i is the constant phase of the electric field, *z* is the axial coordinate of the field, k_i is the wave number, $\eta(z) = \tan^{-1}(z/z_R)$ is the Gouy phase, and z_R is the Rayleigh range. The first term in ϕ_{sp} is proportional to the difference between the refractive indices at frequencies ω_m and ω_n. The second term is usually assumed to vanish because of momentum conservation. The Gouy phase in the third term describes a π phase shift of a focused laser beam as it propagates through the focal point.[5] It has been demonstrated by Chen and Elliot[6] 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.[7]
The reactions we have studied include the photodissociation and photoionization of vinyl chloride, acetone, and dimethyl sulfide (DMS).

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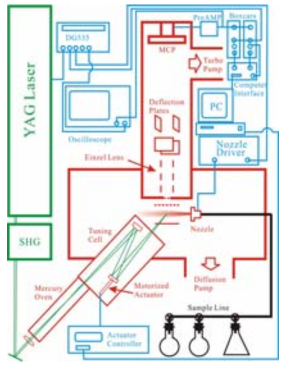
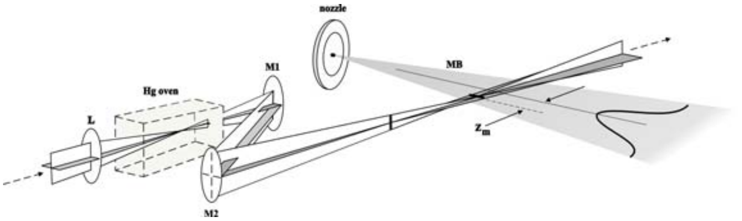
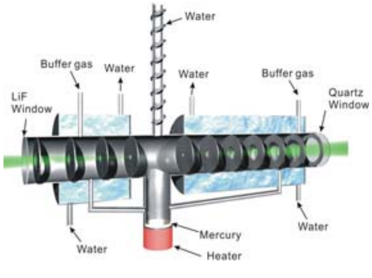
Experimental setup



Schematic drawing of the experimental setup

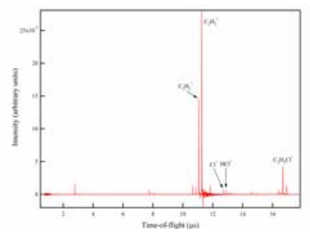


A schematic drawing showing the overlap of the laser and molecular beams. A 532 nm visible laser is focused by a lens (f =76.2 cm) into a mercury oven. Mirrors M1 (f =-5.1 cm) and M2 (f =7.6 cm) are mounted inside the H_2 phase tuning cell (not shown). The two astigmatic foci are separated by 4.6 mm.

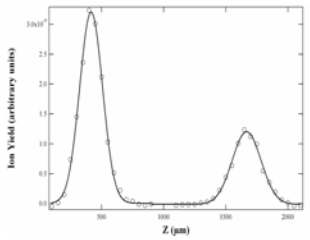


Mercury Oven

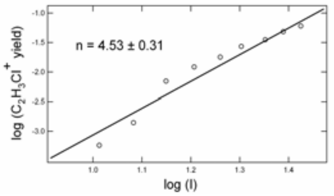
Results



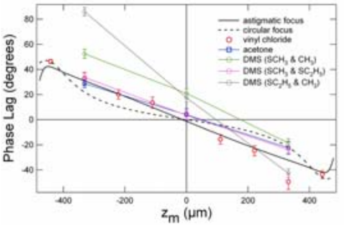
Mass spectrum of vinyl chloride excited with 532 nm irradiation



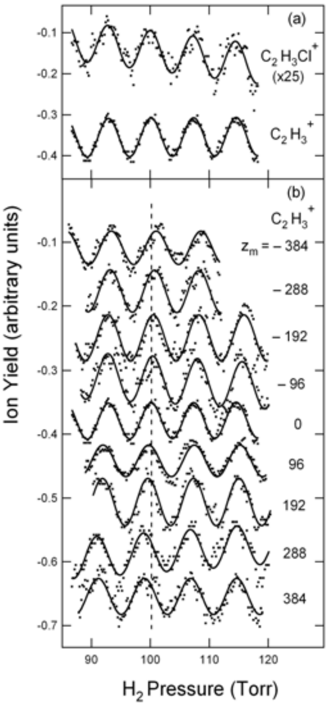
A z-scan of the $C_2H_3^+$ signal showing the two astigmatic foci. The taller peak corresponds to the horizontal focus which is in the plane defined by the laser and the molecular beams.



Intensity dependence of ionization of vinyl chloride

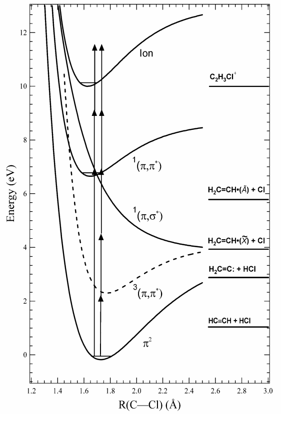


Phase lag as a function of the distance of the molecular beam axis from the focal line of the laser. A positive phase lag corresponds to the parent ion signal leading the fragment. The dashed line is the analytical result for a circular Gaussian focus and a rectangular molecular beam profile. The solid curve is a numerical calculation of the spatial phase, taking into account the astigmatic focus of the laser beam and the Gaussian profile of the molecular beam.



Modulation data for the parent ion and the C_2H_3 fragment. (a) Modulation curves for the laser focused at the center of the molecular beam ($z_m = 0$). (b) Modulation curves for the fragment with the laser focused at various distances (in μm) from the axis of the molecular beam. The modulation curves are shifted so that the parent ion signals (not shown) are in phase with the signal in panel (a). The solid curves are least squares sinusoidal fits to the data. The vertical dashed line is drawn to guide the eye.

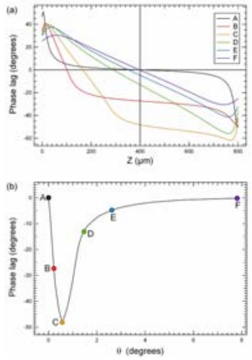
Control Mechanism



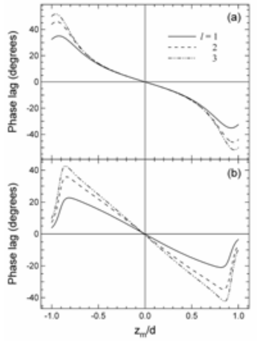
Schematic slice of the potential energy surfaces of vinyl chloride, showing the interfering excitation paths.

$$C_2H_3Cl + \omega_3, 3\omega_1 \rightarrow C_2H_3Cl^*$$
$$C_2H_3Cl^* \rightarrow C_2H_3 + Cl$$
$$C_2H_3Cl^* \rightarrow C_2H_2 + HCl$$
$$C_2H_3Cl^* + 2\omega_1 \rightarrow C_2H_3Cl^+$$

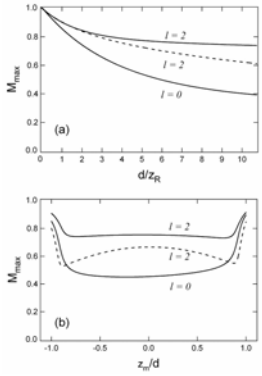
Calculations



Phase lag as a function of separation between the two astigmatic foci.



Phase lag for *l* additional photons in one of the channels assuming either (a) a circular or (b) an astigmatic focus.



Optimized modulation depth, M_{max}, under typical experimental conditions. Panel (a) shows M_{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_{max} as the laser focus is scanned across the molecular beam, with $d/z_R = 7.46$

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 linearly 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.