Origin of the Phase Lag in the Coherent Control of Photoionization and Photodissociation

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The phase lag associated with coherent control by two-pathway excitation in the presence of autoionizing and/or predissociating resonances is studied experimentally and theoretically. For a mixture of HI and DI, the phase lag $\Delta\delta$ between the two-parent ion signals vanishes to within experimental accuracy, whereas for an HI/H_2S mixture, $|\Delta\delta|$ reaches a maximum in the vicinity of the HI $5s\sigma$ resonance. These and previous observations are all explained within a single theoretical model which clarifies the origins of the phase lag in different atomic and molecular systems. [S0031-9007(98)08101-0]

There has been much recent interest in using the phase of electromagnetic radiation to manipulate the motion of electrons and nuclei [1,2]. The method of coherent control uses two coincident laser fields to induce a transition in an atom, a molecule, or a solid. Control is achieved by varying the relative phase of the two fields so that the induced transition amplitudes interfere constructively or destructively. This method has been used, for example, to control the ionization rate of an atom [3], the dissociation rate of a molecule [4], and the direction of the current generated in a semiconductor [5]. An especially interesting opportunity arises when an excited particle decays into more than one product. In this case, variation of the relative phase of the two fields can be used to control not only the total decay rate but also the branching ratio for the various channels [6].

A much cited example of coherent control is the quantum mechanical interference between one- and three-photon transitions [7]. In this case, the probability of obtaining product S is given by [8]

$$p^S = p_1^S + p_3^S + 2|p_{13}^S|\cos(\phi + \delta_{13}^S), \qquad (1)$$

where p_3^S and p_1^S denote the one- and three-photon transition probabilities, and

$$|p_{13}^S|e^{i\delta_{13}^S} = \int d\hat{k}\,\langle g|\bar{D}^{(3)}|ES\hat{k}^-\rangle\langle ES\hat{k}^-|\bar{D}^{(1)}|g\rangle. \qquad (2)$$

Here $D^{(j)}$ are effective j-photon dipole operators, $\bar{D}^{(j)} = e^{-i\phi^{(j)}}D^{(j)}$, $\phi = \phi^{(1)} - \phi^{(3)}$ is the relative phase of the lasers, E is the total energy corresponding to either three photons of frequency ω_1 or one photon of frequency $\omega_3 = 3\omega_1$, $\hat{k}$ denotes the scattering angles of the photoelectron or photofragment, and δ_{13}^S is referred to as the *phase shift* for channel S. Variation of ϕ produces a modulation in the signal for each channel. For any pair of channels, S and S', a *phase lag* $\Delta\delta(S,S') = \delta_{13}^S - \delta_{13}^{S'}$ appears be-

tween the modulated signals. Because the phase shift is channel specific, it is possible to maximize the yield of product S by setting $\phi = -\delta_{13}^S$. The origin of this phase shift is important for understanding and optimizing control mechanisms and, more significantly, as a route to discovering new molecular properties that could not be inferred from more conventional observables. This is particularly true when the continuum is structured (i.e., in the presence of predissociating or autoionizing resonances), in which case $\langle ES\hat{k}^-|\bar{D}^{(j)}|g\rangle$ is markedly energy dependent, both in magnitude and in phase.

The phase shift in Eq. (1) appeared in the coherent control theory of Brumer and Shapiro [2]. Its very existence, its possible origin, and its significance have been the subjects of controversy in recent literature [9,10]. The first experimental measurement of a phase lag was reported in Ref. [6] for the case of ionization vs dissociation of HI molecules. Further experiments found the phase lag between the ionization and dissociation channels to vary strongly with the transition energy in the vicinity of the $5s\sigma$ resonance of HI and DI [11]. In particular, $|\Delta\delta|$ was found to have a large value far from the resonance and to fall to a steep minimum at the center of the resonance. This phenomenon was explained in terms of a model [11,12] for unimolecular decay into several competing channels, each of which may take place both directly and via a manifold of resonances. Reference [12] relates the structure of the phase lag to the underlying system properties. For the specific case of a single resonance with a direct component, it was shown that near the center of a single resonance the decoupling of the excitation and decay processes causes δ_{13}^S to reach a minimum. The phase lag far from resonance, arising solely from the direct process, is a consequence of the phase of the complex continuum wave function (the so-called "molecular phase"), whereas the structure of the phase lag near the center of the resonance relates to

properties of the resonance state [11,12], as is further explained below.

More recent experiments revealed new and surprising behavior. In the present study we present new data along with theoretical results which provide a global understanding of the origin of the phase shift in different physical scenarios. In particular, we identify two distinct sources of the phase shift. One origin of δ_{13}^S is the phase of the complex transition amplitude, which, under certain circumstances [12], survives integration over scattering angles and leads to a nonvanishing molecular phase. A second, independent source of δ_{13}^S, which has not been previously recognized, is the Breit-Wigner phase of a scattering resonance. As illustrated below, the phase shift in this case displays qualitatively different behavior from that produced by the molecular phase. The identification of this new source of δ_{13}^S resolves a controversy regarding the origin of the phase lag and its implications for control [9,10]. Specifically, it shows that a molecular phase is not required for the appearance of a phase lag.

A key step in unraveling the possible sources of $\Delta\delta$ is to separate the effects of the photodissociation and photoionization channels. It is important to emphasize that the experiment provides only relative phase information. That is, $\Delta\delta$ is the difference between the phase shifts for two channels. For example, for pure HI, the phase lag is the difference between the phase shifts for ionization and dissociation of that molecule; i.e., $\Delta\delta(HI^+, I) = \delta_{13}^{HI^+} - \delta_{13}^{I/HI}$. A way to isolate the effect of ionization is to measure the relative phase shifts for the ionization of two different molecules. Because the absolute phase of the modulated signal for each molecule is not reproducible from run to run, we obtain the relative phase shift by ionizing both molecules simultaneously in a *mixture of gases*. For example, for a mixture of HI and DI, the phase lag between the ionization of the two molecules is $\Delta\delta(HI^+, DI^+) = \delta_{13}^{HI^+} - \delta_{13}^{DI^+}$. We show that for a suitably chosen mixture it is possible to eliminate the effect of the molecular phase and thereby to uncover the contribution from the Breit-Wigner phase. To quantify this argument we derive a general expression for δ_{13}^S and examine its behavior in the limit where molecular phases do not contribute to the phase lag.

The experimental method has been described previously [13]. Briefly, the third harmonic of a dye laser (4 mJ/ pulse) was generated by focusing the ultraviolet (UV) fundamental (ω_1) into a cell containing 5–10 Torr of Xe gas. The relative phase of the UV beam and its vacuum ultraviolet (VUV) third harmonic (ω_3) was varied by passing the copropagating beams through a cell containing 1–10 Torr of H_2 gas. A pulsed (10 Hz) molecular beam, consisting of equal partial pressures of HI and a reference gas, was crossed at a right angle to the laser beams. The density of the molecular beam was always low enough that collisional effects were absent. A pair of Al/MgF$_2$-coated spherical mirrors ($f = 20.3$ cm) mounted in the phase tuning cell focused the two laser beams to a common point within the molecular beam between the electrodes of a time-of-flight mass spectrometer. The ions produced in the reaction region were detected by a microchannel plate mounted at the end of a 1-m-long flight tube.

In a separate experiment, the single-photon (VUV) spectrum of each gas was obtained by focusing the output of the third harmonic generating cell into the main vacuum chamber with a MgF$_2$ lens ($f = 8.9$ cm at 355 nm) at 45° to the molecular beam axis. The VUV focal point was separated from the UV focus by at least 4 cm. The sample gases were introduced into the vacuum chamber at room temperature, and the molecular ions were detected as before.

The gas mixtures used in this experiment were HI + DI and HI + H_2S. Typical modulation data for the HI/H_2S mixture are shown in Fig. 1. The I$^+$ signal, produced from the photodissociation channel of HI, and the parent ion signals, HI$^+$ and H_2S^+, were recorded simultaneously. Modulation of the three signals was produced by variation of the pressure of the H_2 phase tuning gas. The solid curves are least squares fits of the function $a + b\cos[(x - c)/d]$, where x is the H_2 pressure. The phase lag between any pair of channels is given by $\Delta\delta = (c - c')/d$. The single-photon ionization spectra of HI and H_2S are shown in Figs. 2(b) and 2(c). For HI the $5s\sigma$ autoionizing
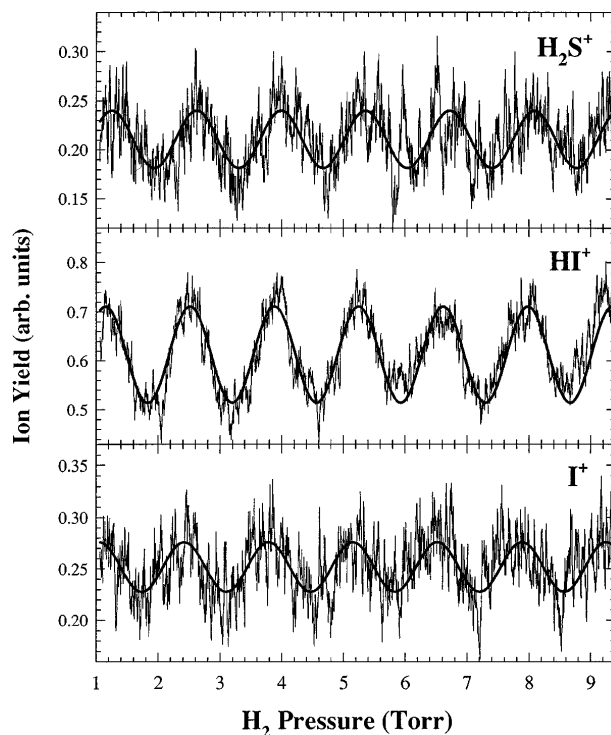

FIG. 1. Modulation curves for H_2S^+, HI$^+$, and I$^+$ recorded at a UV wavelength of 353.80 nm for a mixture of H_2S and HI. The phase lag between HI$^+$ and H_2S^+ is $-25° \pm 3°$, whereas the phase lag between HI$^+$ and I$^+$ is $22° \pm 10°$.
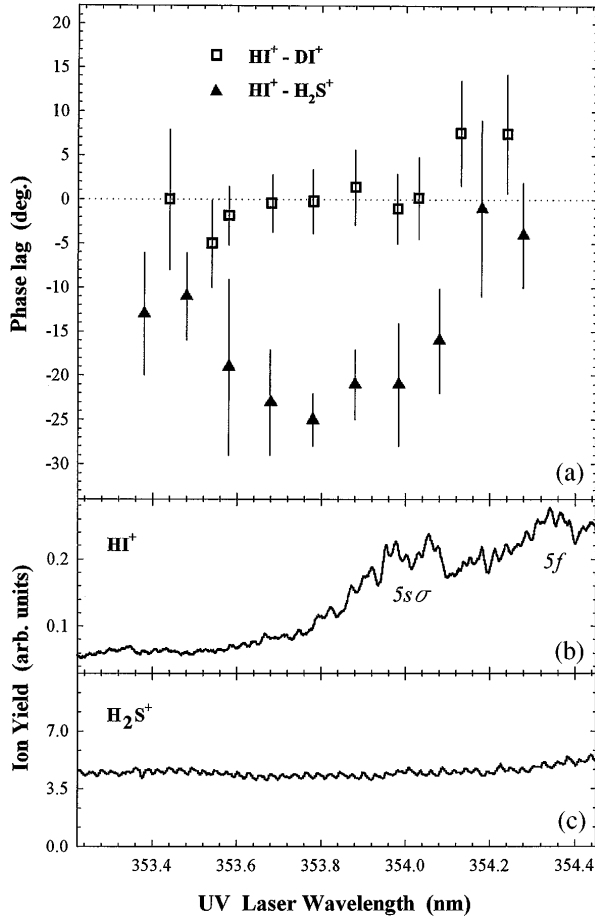
FIG. 2. Phase lags and photoionization spectra. Panel (a) shows the phase lag $\Delta\delta$ between the photoionization of HI and DI (squares) and of HI and H_2S (triangles) in separate gas mixtures. Panels (b) and (c) show the single photon (VUV) spectra of HI and H_2S, respectively. The data points and spectra are each averages of at least ten wavelength scans, and the error bars are 1 standard deviation.

resonance is clearly visible (see Ref. [11] for DI), whereas for H_2S there are no observed resonances at the energies studied.

Previously [11], we found that the phase lags for ionization vs dissociation of both pure isotopomers display a deep minimum near the resonance. In contrast, our new results show that $\Delta\delta(HI^+, DI^+) = 0$ within experimental accuracy. It follows that the strongly energy dependent difference between $\Delta\delta$ observed for pure HI and pure DI arises solely from the dissociation channel. [That is, $\Delta\delta(HI^+, I) - \Delta\delta(DI^+, I) = \delta_{13}^{HI^+} - \delta_{13}^{I/HI} - \delta_{13}^{DI^+} + \delta_{13}^{I/DI} \approx \delta_{13}^{I/DI} - \delta_{13}^{I/HI}$.] Reference [10] showed numerically that the molecular phase for ionization of HI is zero. In Ref. [14] it is shown that, subject to the approximations of Ref. [10], this result applies more generally to linear and symmetric top molecules. Provided that the continuum channels are not coupled directly, the molecular phase for an ionization process vanishes, irrespective

of the angular momentum coupling scheme. The present observations are consistent with these predictions [10,14].

Qualitatively different behavior is observed for ionization of the mixture of HI and H_2S. In this case, $\Delta\delta(HI^+, H_2S^+)$ falls to zero far from the HI resonance and rises to a *maximum* in the vicinity of the resonance. This maximum is blueshifted with respect to the minima of $\Delta\delta(HI^+, I)$ and $\Delta\delta(DI^+, I)$. The finding that $\delta_{13}^{HI^+} \approx \delta_{13}^{H_2S^+}$ off resonance is again consistent with the prediction [10,14] that the molecular phase for ionization is zero. As shown below, the maximum in $\Delta\delta(HI^+, H_2S^+)$ near resonance is explained by a model in which the contributions from the molecular phases vanish.

In order to understand the energy dependence of δ_{13}^S, it is useful to express the transition probability in the general case in terms of the complex-valued one- and three-photon transition amplitudes for both resonance-mediated (at energy $\omega_3 = 3\omega_1$) and direct paths. Equation (1) is rewritten as [12]

$$p^S = \int d\hat{k} |f_{S,d}^{(1)} e^{i\delta_{S,d}^{(1)}} + f_{S,r}^{(1)} e^{i\delta_{S,r}^{(1)}}$$
$$+ e^{i\phi}(f_{S,d}^{(3)} e^{i\delta_{S,d}^{(3)}} + f_{S,r}^{(3)} e^{i\delta_{S,r}^{(3)}})|^2. \quad (3)$$

In Eq. (3) we consider, for clarity, the case of a single resonance, but our results are more general. Here, $f_{S,d}^{(j)}$ and $f_{S,r}^{(j)}$ are the amplitudes for the j-photon-direct and resonance-mediated transitions, and $\delta_{S,d}^{(j)}$ and $\delta_{S,r}^{(j)}$ are the respective phases. The phase $\delta_{S,r}^{(j)}$ may be further partitioned into the sum $\delta_{g-i}^{(j)} + \delta_{i-S} - \delta_i$, where $\delta_{g-i}^{(j)}$ pertains to the transition from the ground state to the resonance, δ_{i-S} is the phase of the matrix element coupling the resonance with the continuum, $\delta_i = \cot^{-1}(-\epsilon)$ is the Breit-Wigner phase, $\epsilon = 2(E - E_i - \Delta_i)/\Gamma_i$ is Fano's dimensionless energy variable [15], E_i is the zero-coupling limit of the resonance eigenvalue, and Γ_i and Δ_i are the resonance width and shift, respectively, due to coupling with the continua.

Evaluating the square in the integrand of Eq. (3), we find that a phase shift may arise from three sets of terms [12]: interference between the direct one- and three-photon paths with amplitude $f_{S,d}^{(1)} f_{S,d}^{(3)}$, interference between the resonance-mediated one- and three-photon paths with amplitude $f_{S,r}^{(1)} f_{S,r}^{(3)}$, and "double" cross terms with amplitudes $f_{S,r}^{(1)} f_{S,d}^{(3)}$ and $f_{S,d}^{(1)} f_{S,r}^{(3)}$. Far from the resonance, only the first set of terms contributes. In the absence of a direct path, δ_{13}^S vanishes in the particular case of an isolated resonance. If both direct and resonance-mediated paths are present, $|\Delta\delta|$ reaches a minimum near the center of the resonance, where the resonance-mediated path dominates (except in the limit where neither direct path carries a phase). This is the structure predicted [12] and observed [11] for pure HI and pure DI.

Qualitatively different behavior is expected in the special case of a purely elastic scattering Hamiltonian. To analyze the form of p^S in that case, we first decompose

the scattering functions in Eq. (2) into partial waves, obtaining (see Ref. [12])

$$\tan \delta_{13}^S = \frac{\sum_{JM} \operatorname{Im} f_{EJM}^{(3)S} f_{EJM}^{(1)S^*}}{\sum_{JM} \operatorname{Re} f_{EJM}^{(3)S} f_{EJM}^{(1)S^*}}, \qquad (4)$$

where $f_{EJM}^{(j)S}$ are j-photon matrix elements coupling the partial waves $|ESJM\rangle$ with the initial state. Partitioning $f_{EJM}^{(j)S}$ into their direct and resonant parts, by analogy to the decomposition of the angle-resolved elements in Eq. (3), $f_{EJM}^{(j)S} = f_{J,d}^{(j)} + f_{J,r}^{(j)} e^{i\delta_{J,r}^{(j)}}$, we have

$$\tan \delta_{13}^S = \frac{\sum_{JM}[-f_{J,r}^{(1)} f_{J,d}^{(3)} \sin \delta_{J,r}^{(1)} + f_{J,d}^{(1)} f_{J,r}^{(3)} \sin \delta_{J,r}^{(3)} - f_{J,r}^{(1)} f_{J,r}^{(3)} \sin(\delta_{J,r}^{(1)} - \delta_{J,r}^{(3)})]}{\sum_{JM}[f_{J,d}^{(1)} f_{J,d}^{(3)} + f_{J,r}^{(1)} f_{J,d}^{(3)} \cos \delta_{J,r}^{(1)} + f_{J,d}^{(1)} f_{J,r}^{(3)} \cos \delta_{J,r}^{(3)} + f_{J,r}^{(1)} f_{J,r}^{(3)} \cos(\delta_{J,r}^{(1)} - \delta_{J,r}^{(3)})]}, \qquad (5)$$

where the index of the magnetic state (which is conserved in a linearly polarized field) and the channel index S have been omitted for clarity of notation. The molecular phases make no contribution in the limit of Eqs. (4) and (5), and, in the absence of the resonant route, δ_{13}^S vanishes.

Equation (5) can be rewritten in terms of generalized j-photon asymmetry parameters $q^{(j)}$ [15] as

$$\tan \delta_{13}^S = \frac{(q^{(1)} + \epsilon)\Sigma^{(1)} - (q^{(3)} + \epsilon)\Sigma^{(3)} + (q^{(1)} - q^{(3)})\Sigma^{(1,3)}}{1 + \epsilon^2 + (1 - q^{(1)}\epsilon)\Sigma^{(1)} + (1 - q^{(3)}\epsilon)\Sigma^{(3)} + (1 + q^{(1)}q^{(3)})\Sigma^{(1,3)}}, \qquad (6)$$

where $\Sigma^{(j)} = \sum_J R_J^{(j)}$, $\Sigma^{(1,3)} = \sum_J R_J^{(1)} R_J^{(3)}$,

$$R_J^{(j)} \equiv \frac{\sum_{J_g,M} n_{J_g} \langle J_g M | \bar{D}^{(j)} | ESJ_i M \rangle}{\sum_{J_g,M} n_{J_g} \langle J_g M | \bar{D}^{(j)} | ESJM \rangle}, \qquad (7)$$

J_g and J_i are the ground state and excited resonance rotational levels, respectively, and n_{J_g} are Boltzmann weights. Because $q^{(j)}$ and $\Sigma^{(j)}$ are, at most, weakly energy dependent, Eq. (6) describes a shifted and asymmetric Lorentzian function. This result agrees with and explains the observed phase lag of HI vs H_2S. In addition to providing qualitative insight, this analysis, in principle, permits the extraction of quantitative system-specific asymmetry parameters $(q^{(j)})$ from the observed phase lag. For the present system, because the identity and form of the zero-order scattering state(s) are unknown, quantitative analysis must await either rotationally resolved phase lag measurements or (partial) electronic structure calculations which would permit evaluation of the overlap elements in Eq. (7).

In conclusion, we have shown that the observed phase lags between the ionization and dissociation of HI and between those of DI are caused by the molecular phases associated with the dissociation channel. This effect is a general phenomenon which typically arises from, and hence provides information about, interactions in the continuum. For the ionization of an HI/H_2S mixture, the phase of the product wave function does not contribute to the phase lag. In this situation the observed phase lag is caused by the occurrence of resonance(s) (in the present case, the autoionizing resonance of HI) and hence conveys information about the resonance properties.

[1] R. J. Gordon and S. A. Rice, Annu. Rev. Phys. Chem. **48**, 595 (1997).

[2] M. Shapiro and P. Brumer, J. Chem. Soc. Faraday Trans. **93**, 1263 (1997).

[3] C. Chen, Y.-Y. Yin, and D. S. Elliott, Phys. Rev. Lett. **64**, 507 (1990).

[4] V. D. Kleiman, L. Zhu, J. Allen, and R. J. Gordon, J. Chem. Phys. **103**, 10 800 (1995).

[5] E. Dupont, P. B. Corkum, H. C. Liu, M. Buchanan, and Z. R. Wasilewski, Phys. Rev. Lett. **74**, 3596 (1995).

[6] L. Zhu, V. Kleiman, X. Li, S. Lu, K. Trentelman, and R. J. Gordon, Science **270**, 77 (1995).

[7] M. Shapiro, J. W. Hepburn, and P. Brumer, Chem. Phys. Lett. **149**, 451 (1988).

[8] P. Brumer and M. Shapiro, Faraday Discuss. **82**, 177 (1986).

[9] T. Nakajima, J. Zhang, and P. Lambropoulos, J. Phys. B **30**, 1077 (1997).

[10] H. Lefebvre-Brion, J. Chem. Phys. **106**, 2544 (1997).

[11] L. Zhu, K. Suto, J. A. Fiss, R. Wada, T. Seideman, and R. J. Gordon, Phys. Rev. Lett. **79**, 4108 (1997).

[12] T. Seideman, J. Chem. Phys. **108**, 1915 (1998).

[13] S. Lu, S. M. Park, Y. Xie, and R. J. Gordon, J. Chem. Phys. **96**, 6613 (1992).

[14] S. C. Althorpe and T. Seideman (unpublished).

[15] U. Fano, Phys. Rev. **124**, 1866 (1961).