What Have we Learned From the Phase Lag in Coherent Control Experiments?

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In coherent control experiments the product signal intensity is modulated by interference between two excitation paths. This modulation is produced by varying the relative phase of the electromagnetic fields used to excited the target. It is observed that the modulated signals for different channels may be out of phase with respect to each other. The phase lag between different channels is energy dependent and contains information about the dynamics of the system. This paper explores different mechanisms that produce such phase lags and assesses what may be learned from them.

I. INTRODUCTION

Interference between competing paths plays a central role in the formulation of quantum mechanics [1] and is responsible for a wide variety of physical phenomena. Examples of processes that depend on quantum mechanical interference are asymmetric spectroscopic lineshapes [2], rainbow scattering [3], photofragment and photoelectron angular distributions [4,5], and atomic and molecular interferometry [6,7]. The key ingredient in all of these phenomena is the relative phases of the wave functions for various paths connecting the initial and final states of a system. The values of these phases are important because they carry the information about the scattering dynamics of the system. This fact is explicit in the semiclassical description of a wave function [8] and in inversion schemes used to extract potential energy functions from spectroscopic data [9].

In the examples cited above, interference is produced by the superposition of two waves having a definite phase relation. The resultant signal is either enhanced or diminished, depending on whether the waves composing it are in or out of phase. As was demonstrated by Brumer and Shapiro over a decade ago [10], this fact can be exploited to control the yields and branching ratios of chemical reactions [11,12]. If the two excitation paths consist of absorption of m and n photons, respectively, then the total (angle-integrated) probability of obtaining product S is given by [10]

$$p^S(E) \;=\; p_n^S(E) \;+\; p_m^S(E) \;+\; 2|p_{mn}^S(E)|\cos(\phi + \delta_{13}^S), \qquad (1)$$

where E is the total energy, and p_m^S and p_n^S are the transition probabilities for the absorption of n and m photons, respectively [1]. The cross term has an amplitude, $2|p_{mn}^S(E)|$, and a phase, $\phi + \delta_{13}^S$, where $\phi = n\phi_m - m\phi_n$ is the relative phase of the electromagnetic fields, and δ_{mn}^S is given by

$$|p_{mn}^S|e^{i\delta_{mn}^S} \;=\; e^{-i\phi} \int d\hat{k}\; \langle g|D^{(m)}|ES\hat{k}^-\rangle\langle ES\hat{k}^-|D^{(n)}|g\rangle, \qquad (2)$$

where $|ES\hat{k}^-\rangle$ is a continuum eigenstate, $|g\rangle$ is the ground state, and $D^{(j)}$ is the j-photon dipole operator. The quantity δ_{13}^S, which we shall refer to as the *channel phase*, depends solely on the properties of the material target.

In a typical coherent control experiment, the laser phase, ϕ, is varied continuously, producing a sinusoidal modulation of the product signals. Because δ_{13}^S depends on the product channel, the modulated signals for any pair of channels, A and B, differ in phase by a quantity,

$$\Delta\delta(A,B) \;=\; \delta_{mn}^A - \delta_{mn}^B, \qquad (3)$$

which we refer to as a *phase lag*. An example is shown in the bottom two panels of Fig. 1 for the ionization and dissociation of HI.

The phase lag is important in control experiments because it provides a tool for altering the branching ratio of a reaction. In recent years it was realized that the value (and energy dependence) of the phase lag is inherently interesting because of fundamental information that it provides about the system. In the present paper we present a catalogue of interference

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[1] In keeping with the convention used in nonlinear optics, we will use subscripts m and n to denote, respectively, the $n-$ and $m-$photon paths, such that $n\omega_m = m\omega_n$. But it will also be convenient to use the parenthetical superscript (j) to denote a $j-$photon transition; e.g., $D^{(3)}$ denotes the three-photon dipole operator.

effects that produce a phase lag, summarizing the main theoretical conclusions and giving, when possible, experimental examples. In addition, we present new data on a "molecular interferometer" that allows one to extract the absolute phase of a wave function.

II. EXPERIMENTAL METHOD

All the experiments discussed here were performed using one- and three-photon excitation, with laser frequencies $\omega_3 = 3\omega_1$. The details of the experiment have been presented elsewhere [13] and need not be repeated here. Suffice it to say that ω_3 was produced from ω_1 by third harmonic generation in a rare gas, thereby establishing a definite phase relation between the two fields. The relative phase of the fields was controlled by passing the laser beams through a gas that has a different index of refraction at the two frequencies. Products from the various reaction channels were measured with a time-of-flight mass spectrometer.

One detail which needs to be emphasized is the method used to isolate individual channel phases. Although the observed phase lag is the difference between two channel phases, by selecting one of the channels, say channel A, to have a real transition amplitude (i.e., $\delta_{13}^B = 0$ or π), it is possible to determine δ_{13}^A absolutely (modulo $\pm\pi$). A convenient way of selecting such a reference channel is to use a gas mixture, one component of which is known empirically to have a zero (or π) channel phase. In our experiments to date we have used the ionization of H_2S as such a reference channel [14]. An example of how this channel is used to isolate $\delta_{13}^{HI^+}$ and δ_{13}^{I} (the channel phases for ionization and dissociation of HI) is shown in Fig. 1.

III. ORIGIN OF THE PHASE LAG

A casual inspection of Eq. (2) might suggest that δ_{13}^S should be zero because the phases of the bra and ket in the integrand cancel. Although such cancelation does occur in a certain limiting case [15], there are many scenarios that produce a non-zero channel phase. Our goal in this section is to provide an overview of these cases, while referring the reader to the literature for the details of their derivation.

Figure 2 is a catalogue of the conditions that might lead to non-zero channel phases. Although the illustrations refer to the specific case of one- vs. three-photon excitation, they may be readily generalized to other pairs of excitation paths. Broadly speaking, there are three types of conditions that lead to non-zero channel phases. First, coupling of the three-photon continuum state to some other continuum introduces a channel phase which has been referred to in some of the literature as a "molecular phase." Second, the existence of resonances at the three-photon level may also produce a channel phase, sometimes referred to as a "resonance phase." Third, resonances at intermediate energies in the three-photon path contribute a Breit-Wigner phase to the overall channel phase.

Figure 2a depicts the limiting case in which there is no channel phase. If there are no resonances present, and if the continuum is not coupled to any other continua, then cancelation occurs and the channel phase vanishes. The continuum in this case produces only elastic scattering. The phase shifts of the component partial waves of the scattered state are independent of coordinates, resulting in a term-by-term cancelation of the phases in a partial wave expansion. An example of this case is seen in $\Delta\delta(HI^+; H_2S^+)$ shown in Fig. 3, where the peaks near 355.0 and 356.0 nm ride on top of a baseline of zero phase lag [16].

If the three-photon continuum is coupled to some other continuum (i.e., if it is inelastic), then term-by-term cancelation of the phases does not occur. Another way of stating this result is to express $|ES\hat{k}^-\rangle$ in Eq. (2) as a linear combination of zero-order continuum states. The integrand then contains cross terms with different bras and kets, so that the phases do not cancel. An example of this case is seen in the dissociation channel of HI in Fig. 3 (i.e., $\Delta\delta(I^+; H_2S^+)$), where the weak structure rides on top of a molecular phase baseline of approx. -120^o.

Panels (c) through (f) of Fig. 1 show the channel phases produced by resonances located energetically at the three-photon level. In case (c), an isolated resonance interacting with a purely elastic continuum gives rise to a maximum at the resonance energy. The relative phase arises from the interference of the direct and resonance-mediated routes and is maximized where interference is constructive. The mechanism is analogous to Young-type interference from four slits. The four pathways in this case are one-photon direct, one-photon resonance-mediated, three-photon direct, and three-photon resonance-mediated excitation. For a rotationally resolved experiment in which the parent state is prepared in a single ro-vibrational level and the resonance vibration is resolved, $\tan\delta^S_{13}$ has the form of a shifted Lorentzian function [17],

$$tan\,\delta^S_{13} = \frac{2(q^{(1)} - q^{(3)})}{\left[\epsilon - \frac{1}{2}(q^{(1)} + q^{(3)})\right]^2 + \left[4 - \frac{1}{4}(q^{(1)} - q^{(3)})^2\right]}; \tag{4}$$

where $q^{(j)}$ is the channel-specific Fano asymmetry parameter [2] for a $j-$ photon transition, $\epsilon = (E - E_0)/2\Gamma$ is the reduced energy shift, E_0 is the resonance energy, and Γ is the width of the resonance. The reader is referred ro Ref. [17] for the general case of many rotational levels. An example of a resonance phase where many rotational levels are present is given by the 356.0 nm peak in Fig. 3, which is produced by the $5d(\pi;\delta)$ resonance of HI [16]. (The smaller peak at 355.0 nm is probably caused by another resonance that has only been tentatively assigned.) Another example is the $5s\sigma$ ionization resonance of HI and DI shown in Ref. [18].

If an isolated resonance is present and the direct process is negligible compared to the resonance-mediated one (case (d)), the phase shift vanishes at the resonance energy. In this limit, the excitation and decay processes decouple, and all memory of the excitation scheme is lost once the molecule reacts. An experimental signature of this case is a *minimum* in $|\delta_{13}^S|$ on resonance, with a non-zero value of the phase lag produced off-resonance by a molecular phase. The reader is referred to Ref. [15] for a derivation of this result. An example of such a "window" is the $5s\sigma$ dissociation resonance for DI shown in Fig. 4 [18]. The strong dip in $\Delta\delta(HI^+; I)$ is also caused by this mechanism; however, the additional structure near 353.7 nm is as yet unexplained.

A more complex pattern is produced in case (f), where coupled resonances interacting with a coupled (i.e., inelastic) continuum produce a structured maximum in δ_{13}^S superimposed on a nonzero, slowly varying background [17]. There are as yet no reported examples of this case. At first it was believed that the $5d(\pi;\delta)$ feature in Fig. 3 is produced by such a coupled resonance; however, in this instance the three-photon resonant-mediated transition is much weaker than the other paths. There results a "three-slit" mechanism, with one-photon direct, one-photon resonance mediated, and three-photon direct paths.

IV. A MOLECULAR INTERFEROMETER

A qualitatively different mechanism is depicted in Fig. 1g. In this case a resonance is present at the two-photon level, making $D^{(3)}$ a complex operator. In the event that there are no molecular or resonance phases present at the three-photon level, the channel phase is identical to the phase of the two-photon state. The system behaves as a "molecular interferometer," with δ_{13}^S providing a measure of the phases of states present in only one arm.

The quantity of interest in this case is the Breit-Wigner phase of a quasi-bound state. The formalism required for computing the relative phase arising from complex intermediates is developed in Ref. [17] and only briefly summarized here. Integration over scattering angles and thermal averaging transform the relative phase in Eq. (2) to the form

$$\delta_{13}^S = \arg \sum_{J_g} W_{J_g} \sum_{J} T^{(1)}(J_g|ESJ)\, T^{(3)*}(J_g|ESJ), \qquad (5)$$

where $T^{(j)}$ is an angle-averaged j-photon transition dipole matrix element, defined in the body-fixed frame, J_g and J are total angular momenta in the initial and continuum states, and W_{J_g} are Boltzmann weights, determined by the rotational temperature of the molecular beam. Complex intermediates in the three-photon process give rise to a complex energy denominator in $T^{(3)}$, which translates into an observable phase, δ_{13}^{S}.

In the case that the rotational levels are well-separated, $B_e \gg \Gamma$ where B_e is the rotational constant, δ_{13}^{S} traces in the vicinity of each line position the Breit-Wigner phase of that resonance. That is,

$$\delta_{13}^{S} = \arg\{T^{(1)}(J_g|ESJ)T^{(3)*}(J_g|ESJ)\} = \delta_{\infty} + \delta_{\mathrm{res}}(E); \tag{6}$$

where δ_{∞} is an asymptotic phase that that reduces to $\pm\pi$ in the absence of the coupling mechanisms discussed in the previous section, and

$$\delta_{\mathrm{res}} = -\arg(E - E_{J_2}) = -\tan^{-1}[(\Gamma/2)/(E - E_{J_2}^{R})] \tag{7}$$

is the Breit-Wigner phase, E_{J_2} being the complex energy eigenvalue of the J_2 rotational resonance and $E_{J_2}^{R}$ its real part (the line position). The Breit-Wigner phase has a value of $-\pi$ to the red of the resonance position, reaches $-\pi/2$ on resonance, and approaches 0 above resonance. The energy dependence of δ_{res} for an isolated rotational level is plotted in Fig. 5a.

For a thermally averaged parent state, Eq. (6) generalizes as [17]

$$\tan\delta_{13}^{S} = \frac{\sum_{J_gJ_2} A_{J_g;J_2}\frac{1}{2}\Gamma_{J_2}[(E_{J_g} + 2\omega - E_{J_2}^{R})^2 + \Gamma_{J_2}^2/4]^{-1}}{\sum_{J_gJ_2} A_{J_gJ_2}(E_{J_g} + 2\omega - E_{J_2}^{R})[(E_{J_g} + 2\omega - E_{J_2}^{R})^2 + \Gamma_{J_2}^2/4]^{-1}}, \tag{8}$$

where $A_{J_g;J_2}$ is a multiple sum over products of dynamical, geometric, and Boltzmann weighting factors, given explicitly in [17], and δ_{∞} is set equal to zero. The exact form of Eq. (8) depends (through the $A_{J_g;J_2}$) on the ground, intermediate, and continuum potential energy surfaces and is thus useful only in cases where this information is available. A fully analytical expression, which does not rely on knowledge of the electronic structure of the molecule and also provides better insight into the origin and structure of δ_{13}^{S}, can be derived by introducing a single (and common [19]) approximation in Eq. (8). Namely, we neglect the dependence of the body-fixed eigenfunctions and the corresponding eigenvalues on the total angular momentum. Within this approximation, it is readily shown [17] that all dynamical factors in the $A_{J_gJ_2}$ cancel out between the numerator and denominator of Eq. (8), obtaining an analytical expression that depends only on the resonance width and the beam temperature.

Model calculations of δ_{res} for a thermal mixture at 200 K are presented in Fig. 5b-d for a range of Γ values. Throughout the range the overall S shape of the phase is evident. For the broadest case considered ($\Gamma = 3B_e$ in Fig. 5b), the O- and S-type rotational branches are evident as weak oscillations far from resonance, whereas the P-, Q-, and R-branches strongly overlap. For the sharpest case considered ($\Gamma = 0.3B_e$ in Fig. 5d), all the rotational branches are well resolved.

In an experimental study we measured the Breit-Wigner phases of complex intermediate states of hydrogen iodide molecules [21]. These states are members of the rotational manifold of the $b^3\Pi_1$ Rydberg state that are located energetically at two-thirds of the ionization energy, i.e., at $E_{J_g} + 2\omega_3$. A partial level scheme of HI showing the relevant levels is given in Fig. 6. The inset shows the rotational levels of the quasi-bound $b^3\Pi_1$ state, which is predissociated by the $A^1\Pi$ continuum state. The lasers are tuned away from any three-photon resonances, so that only a direct transition to the ionization continuum occurs. The ionization of HI and H_2S at the three-photon energies considered here do not contribute to the phase lag, and hence $\Delta\delta(HI^+; H_2S^+)$ is a direct measure of the absolute phase of the two-photon resonant states of HI.

The experimental results are shown in Fig. 7. In panel (a), δ_{13}^S for the ionization of HI (obtained as the phase lag between the HI^+ and H_2S^+ yield curves) is plotted as a function of the three-photon wavelength. The three-photon spectrum of HI^+ is given in panel (b), with the peaks assigned by the O-branch rotational resonances at the two-photon level [20]. In panels (c) and (d) are shown the one-photon ionization spectra of HI and H_2S. The lack of structure in the one-photon spectra demonstrates the absence of resonances at the three-photon level.

The observed δ_{13}^S (Fig. 3a) is seen to follow the shape predicted by Eq. (8), providing a direct measure of the Breit-Wigner phase of the quasi-bound $b^3\Pi_1$ rotational manifold. The solid curve in Fig. 3a shows a least squares fit of the data to the analytical form of Eq. (8). Allowing up to a linear dependence of the resonance width on J_2, we find a rotational temperature of 236 K and $\Gamma_{J_2} = (5.5 + 0.61J_2)$ cm^{-1}. (A quadratic expansion of Γ_{J_2} gives a similar quality fit.) The Breit-Wigner phases of individual rotational resonances [see Eq. (7)] obtained from the fit are shown by the dot-dashed curves in Fig. 7a. The increase of Γ_{J_2} with J_2 is indicative of a rotational perturbation coupling the $b^3\Pi_1$ state to the continuum and is consistent with our spectroscopic observation that the branching ratio of predissociation vs. ionization in creases with J_2 [22].

IV. FUTURE DIRECTIONS

The theoretical and experimental results summarized in this paper demonstrate how the phase lag obtained in coherent control experiments can be a powerful tool for studying the properties of the continuum. The availability of both the phase and modulus of the dipole transition matrix element opens up various exciting possibilities for future research. One of these is the direct inversion of the phase lag spectrum to determine the cross correlation function that underlies the intermediate state dynamics. Another direction that we are exploring is use of the phase lag to detect spectroscopic transitions that are too weak to observe by conventional absorption spectroscopy. Finally, with a more complete understanding of its physical origin, we are better equipped to exploit the phase lag as a tool for coherent control.

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[1] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw Hill, New York, 1965).

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

[3] M. S. Child, *Molecular Collision Theory*(Dover, Mineola, 1975)

[4] H. Park and R.N. Zare, J. Chem. Phys. 106, 2239 (1997).

[5] T. Seideman, J. Chem. Phys. 107, 7859 (1997).

[6] M.S. Chapman et al., Phys. Rev. Lett. 74, 4783 (1995).

[7] M. Arndt, O. Nairz, J. Vos-Andreae, C. Keller, G. van der Zouw, and A. Zellinger, Nature 401, 680 (1999).

[8] J. J. Sakurai, *Modern Quantum Mechanics* (Addison Wesley, Reading, 1995).

[9] R.G. Newton, *Scattering Theory of Waves and Particles*, (McGraw-Hill , New York, 1966).

[10] P. Brumer and M. Shapiro, Faraday Disc. 82, 177 (1986).

[11] R.J. Gordon and S.A. Rice, Ann. Rev. Phys. Chem. 48, 595 (1997).

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

[13] L. Zhu, V. Kleiman, X. Li, S. Lu, K. Trentelman, and R.J. Gordon, Science270, 77 (1995).

[14] J.A. Fiss, L. Zhu, R.J. Gordon, and T. Seideman, Phys. Rev. Lett. 81, 65 (1998).

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

[16] J. A. Fiss, A. Khachatrian, L. Zhu, R. J. Gordon, and T. Seideman, Disc Faraday Soc. 113, 61 (1999).

[17] T. Seideman, J. Chem. Phys. 111, 9168 (1999).

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

[19] W. M. McClain and R.A. Harris, in *Excited States*, E. C. Lim, ed., (Academic, New York, 1977), Vol. 3, pp1-56.

[20] J. A. Fiss, L. Zhu, K. Suto, G. He, R. J. Gordon, *Chem. Phys.* 233, 335 (1998).

[21] J.A. Fiss, A. Khachatrian, K. Truhins, L. Zhu, R. J. Gordon, and T. Seideman (submitted).

[22] A. Khachatrian, K. Suto, L. Zhu, and R. J. Gordon, unpublished results.

Fig. 1. Modulation curves for H_2S^+, HI^+ and I^+ for a mixture of H_2S and HI. The wavelength of the $!_1$ ¯eld is 353.80 nm. Taken by permission from Ref. [14].

Fig. 2. Schematic drawing showing di®erent sources for the channel phase, $\pm^S_{13}$. (a) In the case that the continuum potential induces only elastic scattering, $\pm^S_{13}$ vanishes. (b) If the continuum is coupled to a second continuum, $\pm^S_{13}$ is a smooth, nonzero function of energy. (c) An isolated resonance that interacts with a purely elastic continuum gives rise to a maximum at the resonance energy. The relative phase arises from the interference of the direct and resonance-mediated routes and is maximized where interference is constructive. (d) In the case that an isolated resonance interacts with a coupled continuum, the phase shift is nonzero o®-resonance and falls to a minimum on-resonance. (e) Although an isolated resonance with no direct route to the continuum does not produce a phase, coupled resonances give rise to a nonzero $\pm^S_{13}$ regardless of the availability of a direct route. (f) Coupled resonances interacting with a coupled (i.e., inelastic) continuum produce a structured maximum in $\pm^S_{13}$ superimposed on a nonzero, slowly varying background. (g) A qualitatively di®erent source of a relative phase is a resonance located at an intermediate energy in the three-photon path. In the case that the continuum at the three-photon level is elastic, $\pm^S_{13}$ is the Breit-Wigner phase of the intermediate resonance.

Fig. 3. Phase lag spectrum (top panel) for the photodissociation and photoionization of HI (circles) and for the photoionization of a mixture of HI and H_2S (triangles) in the vicinity of the 5d(¼; ±) resonance of HI. The bottom panel is the one-photon ionization spectrum of HI. Taken with permission from Ref. [16].

Fig. 4. Phase lag spectrum (top panel) for the photodissociation and photoionization of HI (open circles) and DI (closed circles)in the vicinity of the 5s¾ resonance. The bottom two panels are the one-photon ionization spectrum of HI and DI. Taken with permission from Ref. [18].

Fig. 5. Model calculation of the Breit-Wigner phase for a Boltzmann ensemble of molecules for various values of the temperature, T, and resonance width, ¡. The abscissa is the displacement of the energy from the 0 ¡ 0 transition divided by the rotational constant of the excited state. The rotational constant was taken to be 6.427 cm^{i}1 for both the ground and excited states, and a § ! § ! ¦ ! ¦ three-photon transition was assumed. (a)T=1 K, ¡ = 3B_e. In this case only the S(0) transition occurs. (b)T=200K, ¡ = 3B_e. (c)T=200K, ¡ = 1B_e. (d)T=200K, ¡ = 0:3B_e.

Fig. 6. Excitation scheme of HI. One and three photons are used to produce ground state $HI^+(^2\Pi_{3/2})$ ions. The $b^3\Pi_1$ state, located near the two-photon level, is predissociated by several continuum states. The inset shows the rotational levels of the $b^3\Pi_1, v = 0$ state, which are predissociated by the $A^1\Pi$ continuum state.

Fig. 7. Phase lag and ionization spectra of HI and H_2S. Panel (a) shows the observed phase lag between the HI^+ and H_2S^+ signals. The solid curve is a least squares fit of Eq. (8) to the data. The dot-dashed curves are the Breit-Wigner phases of individual rotational resonances, deduced, using Eq. (8), from the data. Panel (b) is the three-photon ionization spectrum of HI, showing the two-photon, O-type rotational branch of the $b^3\Pi_1(v_2 = 0, J_2) \leftarrow X^1\Sigma^+(v_g = 0, J_g)$ transition. Panels (c) and (c) show the one-photon ionization spectra of HI and H_2S, respectively.