

## Direct Observation of a Breit-Wigner Phase of a Wave Function

Jeanette A. Fiss, Ani Khachatryan, Kaspars Truhins, Langchi Zhu, and Robert J. Gordon

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

Tamar Seideman

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

(Received 16 February 2000)

The Breit-Wigner phase of a wave function was obtained by measuring the interference between two independent ionization paths of a molecule. The state of interest was present in only one of the paths, thereby producing a phase shift in the observed signal. An analytical theory was used to determine the phase of the wave function from the observable.

PACS numbers: 33.80.Rv, 32.80.Qk, 82.50.Fv

The relative phase of a wave function is the central ingredient in all quantum mechanical interference phenomena. These include Fano line shapes [1], photofragment and photoelectron angular distributions [2,3], atom interferometry [4], the sculpting of Rydberg wave packets [5], and coherent control of atomic and molecular processes [6,7]. In particular, the phases of continuum wave functions play a central role in scattering theory. The fact that it is the phase that carries the information about the scattering dynamics is explicit in the form of the WKB wave function and in inversion schemes used to extract potential energy functions from spectroscopic data [8].

The phase of a scattering wave function is conveniently separated into a dynamical and a geometric part by partial wave analysis [8,9]. The former contains the signature of the scattering potential, whereas the latter depends on the molecular orientation and on the scattering direction. Dynamical phases arise from long-range scattering effects and/or short-range resonance effects. Long-range forces advance (or retard) the partial waves which compose the scattering wave function as compared with those of a free particle, giving rise to positive (or negative) partial wave phase shifts that vary slowly with energy, on the scale of the de Broglie wavelength. Resonance effects arise from the interference of a quasibound state with the continuum, producing a change of  $\pi$  in the phase of the scattering wave function as energy is scanned through resonance. This phase change, known as a resonance or Breit-Wigner phase, is readily understood by analogy to the classical phase of a forced oscillator.

Although quantum state reconstruction of a wave packet has been demonstrated in many experiments [10], very few studies have determined the phase of a single stationary quantum eigenstate. The relative phases of partial waves of different helicities have been determined in vector correlation experiments [11,12]. In another study, the relative phases of the waves of a scattered electron were measured in an angle-resolved coincidence experiment [13].

We report here the first direct measurement of the Breit-Wigner phase of a predissociating molecule [14]. To measure this phase we constructed what might be called

a “molecular interferometer,” depicted schematically in Fig. 1. As in any interferometric measurement, two phase-coherent pathways connect the initial and final points. Variation of the relative phase of the two paths results in modulation of the detected signal (*vide infra*). In our molecular interferometer, the two pathways consist of one- and three-photon excitation of a molecule to an ionization continuum (Fig. 1a). The relative phase of the

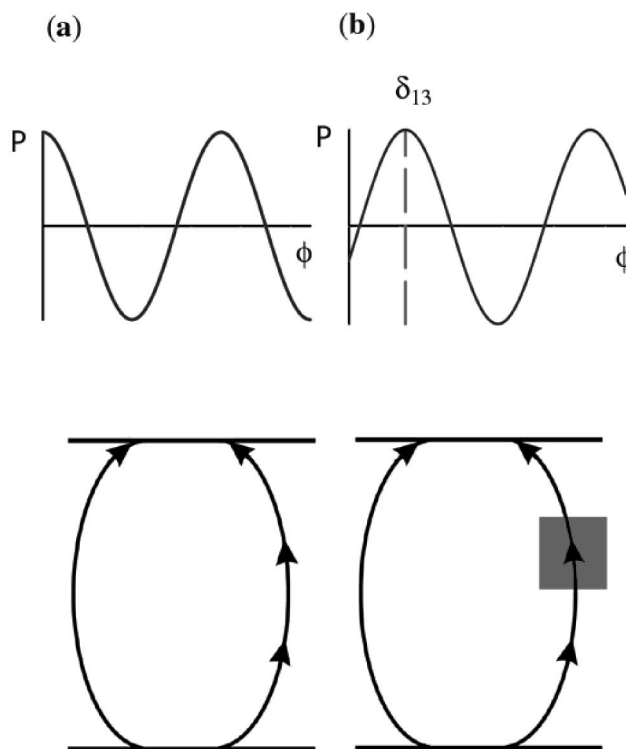


FIG. 1. Illustration of a molecular interferometer. Panel (a) shows that two competing quantum mechanical paths connecting the same initial and final states produce a sinusoidal variation of the product signal that depends on the relative phase of the two paths. In panel (b) an additional phase source is introduced at an intermediate (two-photon) level of the three-photon path. This source could be, for example, a predissociating resonance. The effect of this source is to produce a phase shift of  $\delta_{13}$  in the signal.

two paths is the sum of the relative phase of the laser beams  $\phi$  and the relative phase of the two transition dipole elements, termed the channel phase. The latter phase is obtained as a phase shift in the sinusoidal  $\phi$ -dependence of the signal. Previous work has formulated general criteria under which the continuum at the final level of excitation does not give rise to a phase shift [9,15,16], and in the present work the continuum at the three-photon level was chosen to satisfy these criteria. We now imagine a quasibound state lying at an intermediate level in the three-photon path (Fig. 1b). Because this state is complex (being coupled to a continuum), it introduces a phase to one of the interfering paths, thereby producing a phase shift which equals the phase of the resonance. Previously we exploited the energy dependence of the channel phase to gain unique insight into coupling mechanisms in the dissociation and ionization continua at the final level of excitation (the three-photon level) [16–18]. Here we use the same experimental technology and scattering-based theory to measure the Breit-Wigner phase of an intermediate eigenstate (located at the two-photon level).

The probability of obtaining a product in channel  $S$  by one- vs three-photon excitation is given by [19,20]

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

where  $p_1^S$  and  $p_3^S$  are, respectively, the one- and three-photon transition probabilities for that channel. The remaining term describes the interference between the two paths, where  $\phi = \phi^{(1)} - \phi^{(3)}$  is the relative phase of the two laser fields, and  $\delta_{13}^S$  is the relative phase of the one- and three-photon dipole matrix elements,

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

$D^{(j)}$  being the  $j$ -photon dipole operators,  $E$  the total energy, and  $\hat{k}$  the scattering angles of the products.

The channel phase,  $\delta_{13}^S$ , contains the information that we are seeking. In Refs. [9,15–18] we showed that this phase can arise from a number of distinct physical sources. Specific examples are coupling of the continuum at the three-photon level to other continua and the existence of one or more resonances at the three-photon level. We showed also that the continuum at the three-photon level can be chosen so as not to introduce a phase at all (except possibly for a sign). It is thus possible, by proper choice of the final continuum, to ensure that the value of  $\delta_{13}^S$  will equal (up to  $\pm\pi$ ) the phase of the wave function of the intermediate state, containing no effects of the continuum at the final level of excitation.

Experimentally, one cannot measure  $\delta_{13}^S$  itself but only the *phase lag*,

$$\Delta\delta(A, B) = \delta_{13}^A - \delta_{13}^B, \quad (3)$$

which appears between the modulated signals of two processes (or two arrangement channels),  $A$  and  $B$ . By selecting one of the two processes, say  $S = B$ , such that

$\delta_{13}^B = 0$  or  $\pm\pi$ , the phase lag gives the absolute value of  $\delta_{13}^A$  (modulo  $\pi$ ).

In the present study we measured the Breit-Wigner phase of predissociated intermediate states of hydrogen iodide molecules. 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  $E_{J_g} + 2\omega$ , where  $J_g$  is the total angular momentum of the initial state,  $E_{J_g}$  is the corresponding energy, and  $\omega$  is the frequency of the three-photon field. A partial level scheme of HI showing the relevant levels [21] is given in Fig. 2. The inset shows the rotational levels of the quasibound  $b^3\Pi_1$  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. We used as a reference process (channel  $B$ ) the ionization of  $H_2S$ . The ionization of HI and  $H_2S$  at the three-photon energies considered here contribute at most a sign 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. Although in most experiments only the relative phase of a wave function is observable, here the fact that all other states contributing to the phase lag are real allows us to determine the absolute phase (modulo  $\pi$ ) of the state of interest.

The experimental method has been described previously [22]. Briefly, a molecular beam containing a mixture of HI

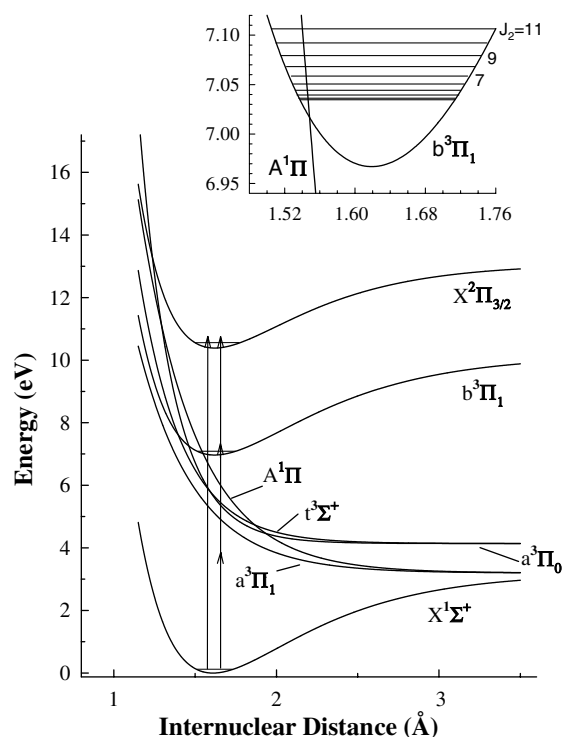


FIG. 2. Excitation scheme of HI. One and three photons are used to produce ground state  $HI^+$  ( $^2\Pi_{3/2}$ ) ions. The  $b^3\Pi_1$  state, located near the two-photon level, is predissociated by several continuum states. The inset shows the rotational levels of the  $b^3\Pi_1$ ,  $v = 0$  state,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

and H<sub>2</sub>S is irradiated by copropagating ultraviolet (UV) and vacuum-ultraviolet (VUV) lasers, which provide the three- and one-photon excitation paths, respectively. The VUV beam is produced from the UV beam by third harmonic generation in a Xe cell, and the relative phase is controlled by passing the beams through a cell containing H<sub>2</sub> gas. The product ions are detected by a time-of-flight mass spectrometer. Typical data showing the modulation and phase lag of the products are found in Ref. [18].

The formalism required for computing the relative phase arising from an intermediate state coupled to a continuum is developed in Ref. [15] and only briefly summarized here. Integration over scattering angles and thermal averaging transform the relative phase in Eq. (2) to the form

$$\delta_{13}^S = \arg \sum_{J_g} W_{J_g} \sum_J \mathcal{T}^{(1)}(J_g | ESJ) \mathcal{T}^{(3)*}(J_g | ESJ), \quad (4)$$

where  $\mathcal{T}^{(j)}$  is a  $j$ -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. Predissociative states in the three-photon process give rise to a complex energy

$$\tan \delta_{13}^S = \frac{\sum_{J_g J_2} A_{J_g J_2} \frac{1}{2} \Gamma_{J_2} [(E_{J_g} + 2\omega - E_{J_2}^R)^2 + \Gamma_{J_2}^2/4]^{-1}}{\sum_{J_g J_2} A_{J_g J_2} (E_{J_g} + 2\omega - E_{J_2}^R) [(E_{J_g} + 2\omega - E_{J_2}^R)^2 + \Gamma_{J_2}^2/4]^{-1}}, \quad (7)$$

where  $A_{J_g J_2}$  is a multiple sum over products of dynamical, geometric, and Boltzmann weighting factors, given explicitly in [15]. In this equation we confined our attention to the  $\delta_\infty = 0, \pm\pi$  case, which is relevant to the HI ionization data presented below [23]. The exact form of Eq. (7) 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  $\delta_{13}^S$ , can be derived by introducing a single (and common [24]) approximation in Eq. (7). 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 [15] that all dynamical factors in the  $A_{J_g J_2}$  cancel out between the numerator and denominator of Eq. (7), obtaining an analytical expression that depends only on the resonance width and the beam temperature. The phase of Eq. (7) reaches an extremum to the red of each resonance position and returns to zero to the blue. The depth of the modulations is determined by the Boltzmann weight factors and hence is sensitive to the rotational temperature. Their widths are determined by the  $\Gamma_{J_2}$  and therefore provide a quantitative measure of the resonance lifetimes.

The experimental results are shown in Fig. 3. In panel (a),  $\delta_{13}^S$  for the ionization of HI (obtained as the phase lag between the HI<sup>+</sup> and H<sub>2</sub>S<sup>+</sup> yield curves) is plotted as a function of UV wavelength. The three-photon UV

denominator in  $\mathcal{T}^{(3)}$ , which translates into an observable phase,  $\delta_{13}^S$ .

With a rotationally selected initial state,  $\delta_{13}^S$  traces in the vicinity of each line position the Breit-Wigner phase of that resonance. That is,

$$\begin{aligned} \delta_{13}^S &= \arg\{\mathcal{T}^{(1)}(J_g | ESJ) \mathcal{T}^{(3)*}(J_g | ESJ)\} \\ &= \delta_\infty - \delta_{\text{res}}(E), \end{aligned} \quad (5)$$

where  $\delta_\infty$  is an asymptotic phase that vanishes (modulo  $\pi$ ) in the absence of the coupling mechanisms discussed below Eq. (3), and

$$\delta_{\text{res}} = -\arg(E - E_{J_2}) = -\tan^{-1}[(\Gamma_{J_2}/2)/(E - E_{J_2}^R)] \quad (6)$$

is the Breit-Wigner phase. In Eq. (6),  $E_{J_2}$  is the complex energy eigenvalue of the  $J_2$  rotational resonance, with  $E_{J_2}^R$  and  $\Gamma_{J_2}/2$  being its real and imaginary parts (the line position and half the linewidth), respectively. The resonance phase,  $\delta_{\text{res}}(E)$ , has a value of  $-\pi$  to the red of the resonance position, reaches  $-\pi/2$  on resonance, and approaches 0 above resonance.

For a thermally averaged parent state, Eq. (5) generalizes as

spectrum of HI<sup>+</sup> is given in panel (b), with the peaks assigned by the O-branch rotational resonances at the two-photon level [25]. In panels (c) and (d) are shown the one-photon VUV ionization spectra of HI and H<sub>2</sub>S. The lack of structure in the VUV spectra demonstrates the absence of resonances at the three-photon level.

The observed  $\delta_{13}^S$  (Fig. 3a) is seen to follow the shape predicted by Eq. (7), providing a direct measure of the Breit-Wigner phase of the quasibound  $b^3\Pi_1$  rotational manifold. The experimental points are the phase of the thermal mixture of superposition states populated by two-photon transitions. The solid curve in Fig. 3a shows a least squares fit of the data to the analytical form of Eq. (7). Allowing up to a linear dependence of the resonance width on  $J_2$ , we find a rotational temperature of 236 K and  $\Gamma_{J_2} = (5.5 + 0.61J_2) \text{ cm}^{-1}$ . (A quadratic expansion of  $\Gamma_{J_2}$  gives a similar quality fit.) The Breit-Wigner phase of individual rotational resonances [see Eq. (6)] obtained from the fit are shown by the dot-dashed curves in Fig. 3a [23]. The increase of  $\Gamma_{J_2}$  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 increases with  $J_2$  [26]. This finding illustrates the fact that the phase of the wave function contains all the dynamical information of the system.

In summary, we have determined the phase of a quasibound wave function. Specifically, we obtained the phase of a three-photon transition dipole matrix element from

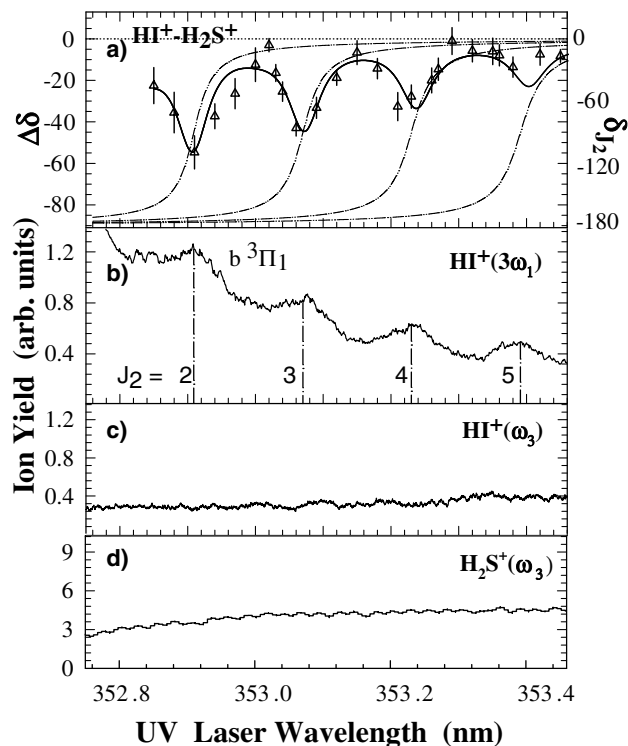


FIG. 3. Phase lag and ionization spectra of HI and H<sub>2</sub>S. Panel (a) shows the observed phase lag between the HI<sup>+</sup> and H<sub>2</sub>S<sup>+</sup> signals. Error bars are a single standard deviation. The solid and dot-dashed curves are explained in the text. Panel (b) is the three-photon UV ionization spectrum of HI, showing the two-photon, O-type rotational branch (indicated by vertical dot-dashed lines) of the  $b^3\Pi_1(v_2 = 0, J_2) \leftarrow X^1\Sigma^+(v_g = 0, J_g)$  transition. Panels (c) and (d) show the one-photon VUV ionization spectra of HI and H<sub>2</sub>S, respectively.

measurement of the relative phase,  $\delta_{13}^S$ , of a one- and three-photon dipole matrix element connecting a bound state with an ionization continuum. From the phase of the three-photon element we calculated the Breit-Wigner phase of a quasibound state located energetically at the two-photon level.

The method described here can be used more generally to measure the absolute phase of a multiphoton transition dipole matrix element. This generalization follows from our ability, based on the results of Ref. [9], to choose a final continuum state that does not contribute (modulo  $\pi$ ) to  $\delta_{13}^S$ . It should be similarly possible to determine the absolute phase of a two-photon transition dipole element by exciting a molecule via a pair of two-photon optical routes. An advantage of the latter scheme is that it does not require the excitation pulses to be phase locked [27]. As discussed in Ref. [15], the availability of both the modulus and the phase of the dipole transition matrix element opens up various exciting possibilities, including direct inversion

of the phase lag spectrum to determine the cross correlation function that underlies the intermediate state dynamics.

We thank the National Science Foundation for its generous support.

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