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Hunt for geometric phase effects in $\text{H} + \text{HD} \rightarrow \text{HD}(v', j') + \text{H}$

Justin Jankunas,^{1,a)} Mahima Sneha,¹ Richard N. Zare,^{1,b)} Foudhil Bouakline,² and Stuart C. Althorpe³

¹Department of Chemistry, Stanford University, Stanford, California 94305-5080, USA

²Max Born Institute, Max Born Strasse 2a, 12489 Berlin, Germany

³Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

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An attempt has been made to measure the theoretically predicted manifestation of a geometric phase in the differential cross section for the $\text{H} + \text{HD} \rightarrow \text{HD}(v' = 2, j' = 5) + \text{H}$ reaction at a center-of-mass collision energy of 1.44 eV (33.2 kcal/mol). Minute oscillatory differences between calculated differential cross sections that take into account and ignore the effect of geometric phase have proven to be beyond our experimental resolution in spite of the collection of more than 44 000 ions.

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I. INTRODUCTION

From an experimental point of view, the geometric phase (GP) chapter of the voluminous book on $\text{H} + \text{H}_2$ scattering remains to be written. Long ago, Herzberg and Longuet-Higgins¹ showed theoretically that when a system of three 2S atoms is taken around the resulting conical intersection, the electronic wave function changes sign. Physicists, who were more interested in firing electrons around the two sides of a current-carrying solenoid in which the magnetic field is confined inside it, had already been aware of the sign change in the electronic wave function; this is now known as Aharonov-Bohm effect.² The results of these early studies were surprising because they suggested that particles which traverse a field- and force-free region, or in which part of the system undergoes a full 2π rotation,³ may be affected in an experimentally verifiable manner. Mead and Truhlar^{4,5} were the first to calculate the physical consequences of an electronic wave function sign change in the H_3 system, and to recognize the “geometric” nature of this sign change. Berry⁶ worked out explicit expressions for these geometric phase factors; the words “geometric phase” and “Berry’s phase” are synonymous.

Theory claims that inclusion and exclusion of GP in the calculations leads to noticeable differences in the experimental observables. This is not to say that chemical reaction dynamics theorists had a smooth sailing! Transport of nuclear coordinates along a closed loop is particularly interesting in a molecular system. If the total wave function, $\Psi_{\text{total}}(\theta) = \psi_{\text{nuc}}(\theta)\psi_{\text{elec}}(\theta)$, is to remain single-valued upon a 2π rotation of nuclear coordinates around a conical intersection, then the sign change in $\psi_{\text{elec}}(\theta)$ must be accompanied by a corresponding sign change in $\psi_{\text{nuc}}(\theta)$.⁴ This has been termed the Molecular Aharonov-Bohm effect.⁵ Following the seminal work of Mead and Truhlar, Kuppermann and co-workers

computed experimentally measurable quantities that showed differences between GP and non-GP (NGP) calculations. They found pronounced GP and NGP differences in the integral cross sections (ICS) for the $\text{H} + \text{H}_2(v = 0, j - \text{odd/even}) \rightarrow \text{H}_2(v' = 0, j' - \text{odd/even})$ reaction,⁷ and even in the rotational state distributions for the $\text{D} + \text{H}_2(v = 1, j = 1) \rightarrow \text{HD}(v' = 1, j')$ reaction at a collision energy (E_{coll}) of 1.0 eV.⁸ The latter study seemed to explain the disagreement between the experimental results of Kliner *et al.*⁹ and NGP quantum mechanical (QM) calculations, suggesting that the GP effects in the $\text{H} + \text{H}_2$ reaction have been confirmed experimentally. Subsequent theoretical calculations, however, did not reproduce Kliner’s experimental findings nor Kuppermann’s calculations.¹⁰ The work of Kendrick and Althorpe has shown definitively that the GP and NGP differences in the differential cross sections (DCS) of the $\text{H} + \text{H}_2$ reactive scattering for $E_{\text{coll}} < 1.8$ eV are absent.^{11,12} In addition, the so-called “cancellation puzzle,” first posed by Kendrick,¹³ wherein individual J partial waves exhibit GP and NGP differences, but the differences vanish upon summing each J to yield an ICS, has been solved.¹⁴ Subsequent theoretical studies suggested that the GP and NGP differences will be visible in two distinct classes of experiments:^{15–19} (i) at high energies ($E_{\text{coll}} > 4$ eV), DCS will contain marked differences between GP and NGP calculations for any isotopologue of the hydrogen exchange reaction like $\text{H} + \text{D}_2 \rightarrow \text{HD}(v', j') + \text{D}$ at $E_{\text{coll}} > 4$ eV and (ii) at low collision energies ($E_{\text{coll}} < 2.7$ eV), DCS will contain less pronounced GP and NGP differences, as long as the products and reactants are “the same,” or, in other words, the reactive and inelastic pathways are indistinguishable, e.g., $\text{H} + \text{H}_2(v, j - \text{odd/even}) \rightarrow \text{H}_2(v', j' - \text{odd/even}) + \text{H}$, $\text{D} + \text{D}_2(v, j - \text{odd/even}) \rightarrow \text{D}_2(v', j' - \text{odd/even}) + \text{D}$, $\text{H} + \text{HD}(v, j) \rightarrow \text{HD}(v', j') + \text{H}$ etc. In both cases, however, GP and NGP differences come from the interference term between two different scattering pathways. Reactions of class (i) exhibit interference between reactive pathways that wind in opposite senses around the conical intersection, by traversing respectively one and two transition-states (Fig. 1(a)). In the second class of experiments, the interference arises from

^{a)}Present address: Ecole Polytechnique Federale de Lausanne, Institute of Chemical Sciences and Engineering, Lausanne CH-1015, Switzerland.

^{b)}Author to whom correspondence should be addressed. Electronic mail: zare@stanford.edu

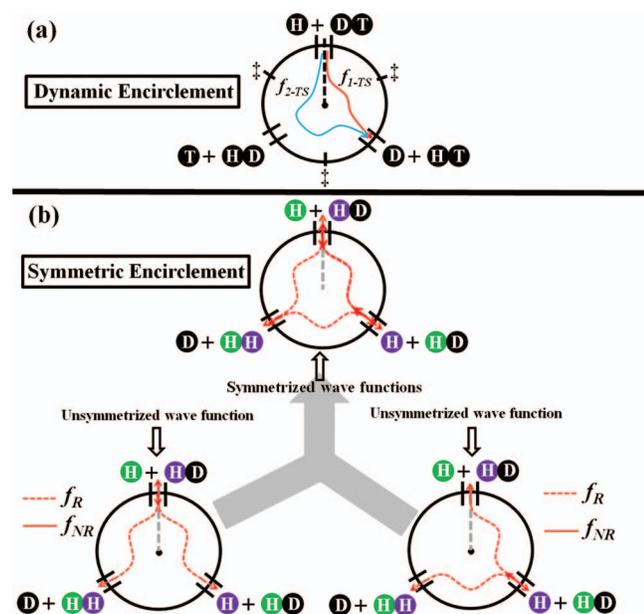


FIG. 1. Schematic illustration of (a) dynamic and (b) symmetric encirclement of the conical intersection in the $\text{H} + \text{H}_2$ chemical reaction, using a hyperspherical coordinate diagram. In the case of a dynamic encirclement, arising from two reaction pathways f_{1-TS} and f_{2-TS} (transition state points are indicated by a double dagger), geometric phase effects can be seen in any isotopologue of the hydrogen exchange reaction including the case of distinguishable nuclei, e.g., $\text{H} + \text{DT} \rightarrow \text{HT}(v', j') + \text{D}$. When dynamic encirclement is negligible, GP effects can still be observed in a reaction wherein the reactants and products are indistinguishable, e.g., $\text{H} + \text{HD} \rightarrow \text{HD}(v', j') + \text{H}$. The encirclement here arises from a proper symmetrization of the total molecular wave function.

a coherent sum of reactive and inelastic scattering (Fig. 1(b)). In both cases the scattering wave function encircles the conical intersection; in the former case “dynamically,” meaning that the superposition of the reaction paths produces the encirclement, and in the latter case “symmetrically,” upon antisymmetrization of the total wave function with respect to exchange of identical nuclei.

Studying the hydrogen exchange reaction at $E_{\text{coll}} > 2.6$ eV is cumbersome for the want of fast enough hydrogen atoms. On the other hand, experiments where reactants and products are identical have a large background from a non-resonant reactant ionization that dramatically reduces the signal-to-noise ratio. Following our recent work on simultaneous measurement of reactive and inelastic scattering in the $\text{H} + \text{HD} \rightarrow \text{HD} + \text{H}$ system,²⁰ we report here the DCS of the $\text{H} + \text{HD} \rightarrow \text{HD}(v' = 2, j' = 5) + \text{H}$ reaction at $E_{\text{coll}} = 1.44$ eV, which is a first thorough attempt to measure minute differences between GP and NGP calculations.

We fit our experimental data to two theoretical curves: NGP and GP DCS, given by

$$\frac{d\sigma^{(NGP)}}{d\Omega} = |f_R|^2 + |f_{NR}|^2 + \frac{1}{2}(f_{NR}^* f_R + f_R^* f_{NR}), \quad (1a)$$

$$\frac{d\sigma^{(GP)}}{d\Omega} = |f_R|^2 + |f_{NR}|^2 - \frac{1}{2}(f_{NR}^* f_R + f_R^* f_{NR}), \quad (1b)$$

where f_{NR} and f_R are non-reactive (inelastic) and reactive scattering amplitudes for the $\text{H} + \text{HD} \rightarrow \text{HD}(v' = 2, j' = 5)$

+ H reaction, respectively. Since the conical intersection is only symmetrically encircled, the sole GP effect is the sign-change in front of the interference term.²¹ By comparing the experimental fit to $\frac{d\sigma^{(NGP)}}{d\Omega}$ and $\frac{d\sigma^{(GP)}}{d\Omega}$, we had hoped to confirm or refute experimentally the presence of GP in the $\text{H} + \text{H}_2$ reaction.

In what follows, Sec. II gives a very brief description of experimental conditions, Sec. III summarizes theoretical methods employed in calculating GP and NGP DCS, Sec. IV presents experimental and theoretical results, and the findings are discussed in Sec. V. Section VI concludes the paper.

II. EXPERIMENTAL

The experimental procedure is almost identical to the one described in Ref. 20; the main parameters can be found in Table 1 of Ref. 20. The only difference between the two studies is a much larger number of $\text{HD}(v' = 2, j' = 5)$ molecules ionized. In summary, one UV laser was used to generate H atoms upon the photodissociation of HBr , and then ionize $\text{HD}(v' = 2, j' = 5)$ reaction products via the $E, F^1\Sigma_g^+ \leftarrow X^1\Sigma_g^+$ transition by means of a [2+1] resonance-enhanced multiphoton ionization (REMPI). The ions were detected on a position-sensitive detector to measure the three-dimensional speed distribution of HD^+ . Laser wavelength was scanned over the Doppler profile of the $\text{HD}(v' = 2, j' = 5)$ reaction product; this we call an “online” scan. A significant background, arising from a non-resonant ionization of $\text{HD}(v = 0, j = 0, 1, 2)$ reactants in the molecular beam, and, to a lesser extent, from a non-resonant ionization of all reaction products, i.e., $\text{HD}(\sum v', \sum j')$, was subtracted by tuning the laser wavelength off the $\text{HD}(v' = 2, j' = 5)$ REMPI line, and performing so-called “offline” scan. The reaction signal was then obtained by subtracting the “offline” scan from the “online” scan. Twelve “online” and 12 “offline” scans were performed in a course of 30 days. The resultant speed distributions were then converted into a DCS via the law of cosines.²⁰ A grand total of 170 698 ions were collected: 107 572 ions during “online” scans and 63 126 ions during “offline” scans. This translated into 44 446 ions after the background subtraction. This is almost five times more than 9176 ions collected for the $\text{HD}(v' = 2, j' = 5)$ state in our previous study.²⁰

III. THEORY

We obtained the exchange-symmetrized DCS of Eq. (1) by computing the (non-exchange-symmetrized) scattering amplitudes f_{NR} and f_R using the ABC code of Skouteris *et al.*²² with the refined Boothroyd-Keogh-Martin-Peterson (BKMP2) potential energy surface.²³ Separate calculations were performed for each initial rotational quantum number $j = 0, 1$, and 2 of the reactant HD molecule, and for each total parity of the triatomic molecule, and repeated for each partial wave up to a total angular momentum $J = 55$. To solve the coupled-channel hyperradial equations, a maximum value of the hyperradius $\rho_{\text{max}} = 25 a_0$ and 250 sectors were used; the coupled-channel basis-set parameters were set to

$E_{\max} = 2.85$ eV, $j_{\max} = 20$, and $k_{\max} = 10$. These parameters were sufficient to achieve convergence of the DCS across the range of collision energies considered here. The convergence was double-checked by comparing the $j = 0$ DCS with the results of wavepacket²⁴ calculations (not shown here); the two sets of results were in very close agreement.

From previous work,^{10,12,14,19,22,23} we know that the non-exchange-symmetrized nuclear wavefunction does not encircle the CI at the collision energies considered here, which are far below the energetic minimum of the conical intersection (CI) at 2.74 eV. Hence geometric phase (GP) effects did not need to be taken into account in the calculations of f_{NR} and f_R . However, the act of symmetrizing the wave function (with respect to exchange of the H-atoms) causes it to encircle the CI (as can be easily demonstrated by sketching the form of the symmetrized wave function in hyperspherical coordinates, see Fig. 1). As a result, GP effects need to be included when superposing f_{NR} and f_R in equation (4). Mead²¹ showed that the sole effect of the GP in such a case is to change the sign of f_{NR} relative to f_R ; see Eq. (1).

IV. RESULTS

Figure 2 presents the experimentally determined DCS for the HD($v' = 2, j' = 5$) product. In what follows we discuss the origin of the theoretical curves to which the experimental results are compared by making a best fit. There are three significant sources of experimental uncertainty: (i) a 0.05 eV spread in the collision energy, (ii) HD($v = 0, j$) reactant rotational state spread ($\sim 33\%$ in $j = 0$, $\sim 37\%$ in $j = 1$, and $\sim 20\%$ in $j = 2$, with trace amounts in $j > 2$), and (iii) photoelectron recoil to HD⁺ ion. For HD($v' = 2, j' = 5$) state, the HD⁺ recoil amounts to 183 m/s, for the particular [2+1] REMPI scheme used. The spread in E_{coll} and j is accounted for by appropriately blurring theoretical predictions. Briefly, theoretical calculations are convoluted with a Gaussian that has a half-width at half-maximum of 50 meV, centered at $E_{\text{coll}} = 1.44$ eV, which accounts for the spread in E_{coll} . Rotational blurring is done by simply weighing theoretical DCSs by the

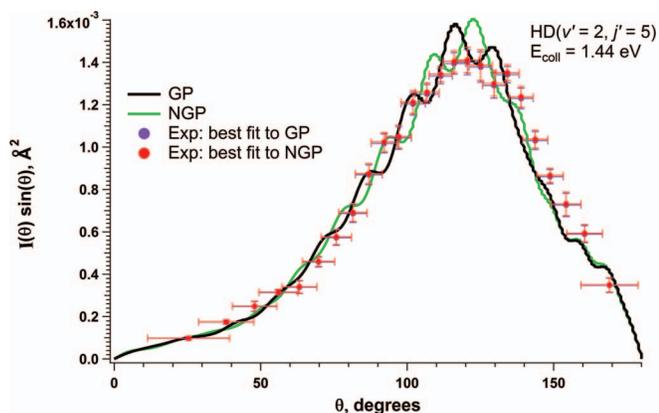


FIG. 2. Experimental and theoretical DCS for $\text{H} + \text{HD} \rightarrow \text{HD}(v' = 2, j' = 5) + \text{H}$ scattering. Green and black curves are NGP and GP blurred calculations (over E_{coll} and j), respectively. Red and purple dots are best fits of experimental data to NGP and GP calculations, respectively. Note that red and purple dots are barely discernible, suggesting that the two fits are very similar.

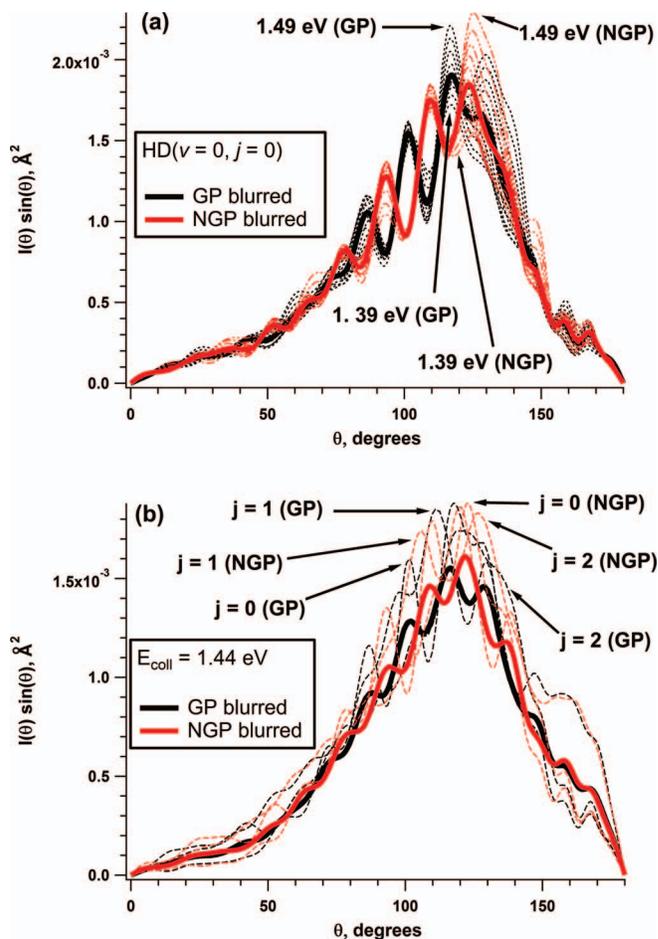


FIG. 3. Effects of (a) collision energy and (b) HD($v = 0, j$) reactant rotational state blurring on theoretical calculations. Dashed-dotted lines in panel (a) correspond to 11 different E_{coll} values centered at $E_{\text{coll}} = 1.44$ eV. Dashed lines in panel (b) correspond to different HD($v = 0, j$) rotational states. In both panels solid red and black lines correspond to averaged (blurred) results. Experimental rotational state spread is seen to have a more deleterious effect of washing out the differences between the GP and NGP.

experimentally measured HD($v = 0, j$) rotational state distributions, *vide supra*.

These effects are illustrated schematically in Fig. 3. The 50 meV spread in E_{coll} does not seem to affect GP and NGP differences to the extent that j averaging does. This is partly caused by the fact that the inelastic DCS for the $\text{H}_a + \text{H}_b\text{D}(v = 0, j = 0, 2) \rightarrow \text{H}_b\text{D}(v' = 2, j' = 5) + \text{H}_a$ process is out-of-phase with the DCS for the $\text{H}_a + \text{H}_b\text{D}(v = 0, j = 1) \rightarrow \text{H}_b\text{D}(v' = 2, j' = 5) + \text{H}_a$ reaction. We have briefly discussed the origins of this peculiar behavior in Ref. 20. Unlike H_2 and D_2 , HD does not exist in *ortho/para* forms; it is therefore not possible to exclude odd or even j rotational levels in the molecular HD beam by using, for example, a paramagnetic catalyst.

Twelve individual measurements of a DCS for the $\text{H} + \text{HD} \rightarrow \text{HD}(v' = 2, j' = 5) + \text{H}$ reaction are shown in Fig. 4. The large black dots represent an average of 12 small red points; an error bar was taken as one standard deviation of 12 measurements. Finally, the HD⁺ photoelectron recoil is taken into account by assuming that 183 m/s is a fundamental limitation of our experimental speed resolution, and

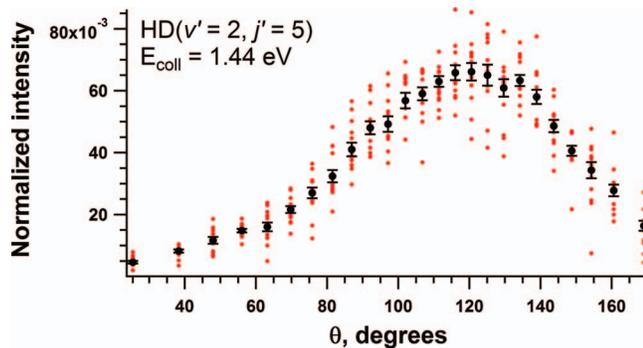


FIG. 4. Twelve independent measurements of the $\text{H} + \text{HD} \rightarrow \text{HD}(v' = 2, j' = 5) + \text{H}$ DCS: each small red dot is an average of roughly 150 ions. Large black dots represent an average of 12 independent measurements at that particular angle, with an associated error (1 standard deviation). Each black dot is therefore an average of roughly 1800 ions.

propagating the error into the angular space. It is easy to show that²⁰

$$\Delta\theta = 2v_{LAB}\Delta v_{LAB}[4u_{COM}^2u_{HD}^2 - (u_{COM}^2 + u_{HD}^2 - v_{LAB}^2)]^{-\frac{1}{2}}, \quad (2)$$

where v_{LAB} , u_{COM} , and u_{HD} are the $\text{HD}(v' = 2, j' = 5)$ speed as measured in the laboratory frame, the center-of-mass speed (COM), and $\text{HD}(v' = 2, j' = 5)$ speed in the COM frame, respectively. For $\text{HD}(v' = 2, j' = 5)$ at $E_{\text{coll}} = 1.44$ eV, $u_{COM} = 4805.9$ m/s, and $u_{HD} = 2663.5$ m/s. We take $\Delta v_{LAB} \sim 183$ m/s. It is clear from Eq. (2), for example, that forward and backward directions in the DCS, i.e., when $v_{LAB}^{MAX} = u_{COM} + u_{HD}$ and $v_{LAB}^{MIN} = u_{COM} - u_{HD}$, will have larger $\Delta\theta$ values because in these regions the denominator of Eq. (2) is smaller. Thus, the experimental DCS with an associated $\Delta\theta$, as well as fully blurred (over E_{coll} and j) theoretical GP and NGP calculations are shown in Fig. 2.

Experimental signal does not directly measure absolute reaction cross sections. Consequently, experimental signal must be multiplied by a constant F to best fit the theoretical data, i.e., a straightforward least-squares fitting

$$S = \sum_{i=1}^N [I(\theta_i)^{theory} - FI(\theta_i)^{experiment}]^2, \quad (3)$$

where $I(\theta_i)^{theory}$ and $I(\theta_i)^{experiment}$ are theoretical and experimental DCS values. F_{best} , the solution of the $\frac{\partial S}{\partial F} = 0$ equation, is substituted into Eq. (3) to yield the residual sum of squares, RSS , i.e.,

$$RSS \equiv \sum_{i=1}^N (I(\theta_i)^{theory} - F_{best}I(\theta_i)^{experiment})^2. \quad (4)$$

F_{best} can also be used in computing the R^2 value, i.e.,

$$R^2 = 1 - \frac{\sum_{i=1}^N (I(\theta_i)^{theory} - F_{best}I(\theta_i)^{experiment})^2}{\sum_{i=1}^N (F_{best}I(\theta_i)^{experiment})^2}. \quad (5)$$

Red and purple experimental dots in Fig. 2 represent the least-squares fit of the experimental data to NGP and to GP

calculations, respectively. Please note that the red and purple dots are barely discernible, suggesting that the two fits, i.e., experiment vs NGP and experiment vs GP, are very similar.

V. DISCUSSION

A mere visual inspection of Fig. 2 seems to suggest that the experiment is not able to resolve minute oscillatory differences between GP and NGP curves. Not trusting our own eyes, we have carried out several statistical tests to gauge how significant the differences between the two fits are. First, the least-squares fitting procedure of our experimental data to theory has generated so-called R^2 values, wherein $R^2 = 1$ means a perfect match. We find that,

$$R_{NGP}^2 = 0.9910,$$

$$R_{GP}^2 = 0.9909.$$

Clearly, both fits, experiment to NGP and experiment to GP, are of extremely high quality, as judged by how close the R^2 values are close to unity. On the other hand, the results do indicate that the fit to NGP is almost imperceptibly better than the GP one. Although a reader may rightly feel that such small differences in the R^2 values are insignificant, we have carried out the familiar two-tailed t -test, to determine whether the differences between the two fits are statistically significant. To this end, we turned to twelve independently measured DCS; small red dots in Fig. 4. The quantity RSS , Eq. (4), is computed for each of these measurements. We then compute the average, $\langle RSS^{GP} \rangle$ and $\langle RSS^{NGP} \rangle$, and standard deviations, σ^{GP} and σ^{NGP} , of the resulting RSS_i^{NGP} and RSS_i^{GP} , where $i = 1, 2, \dots, 12$. These two quantities are used in computing the t value,

$$t = \frac{\langle RSS^{GP} \rangle - \langle RSS^{NGP} \rangle}{\sqrt{\frac{\sigma^{GP}}{12} + \frac{\sigma^{NGP}}{12}}}. \quad (6)$$

We find that $t = 0.517$. In order to say that the two fits are different with a 50% confidence, one needs at least $t = 0.695$, for 12 degrees of freedom. We find therefore that the differences between experiment vs NGP and experiment vs GP fits are statistically insignificant, or, at least, the confidence interval for significant differences is less than 50%.

Even though the experiment was not able to resolve small differences between GP and NGP theoretical calculations, a 30-day effort was dedicated directly to measuring the GP effect in the $\text{H} + \text{H}_2$ reaction. It might be wondered whether the choice of a different product state would have led to a better test. After a careful analysis of theoretical calculations, we compromised on the $\text{HD}(v' = 2, j' = 5)$ state: the particular scattering channel turned out to be an optimum between (i) a rapidly decreasing reaction cross section with increasing GP/NGP differences, (ii) a reasonable ion count rate, and (iii) significant oscillatory GP/NGP differences. Next, we speculate as to why the experimentally measured GP/NGP differences turned out to be so small. As argued in our most recent $\text{H} + \text{HD} \rightarrow \text{HD} + \text{H}$ study,²⁰ experimental resolution cannot be the sole culprit. The GP and NGP oscillations in Fig. 2 have roughly a 10° spacing. The use of 25 bins

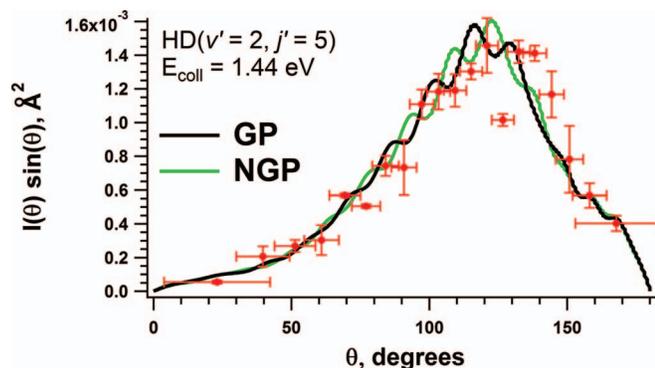


FIG. 5. DCS measurement for the $\text{HD}(v' = 2, j' = 5)$ product from data collected as part of the study reported in Ref. 20, wherein 9176 ions were collected. Both theoretical curves including geometric phase (black) and excluding geometric phase (green) are presented, and the experimental data are fit only to the former.

(experimental data points) in Fig. 2 implies $\sim 4^\circ$ – 5° resolution in the backward and sideways region of the DCS – still less than theoretical oscillations. Instead, we are dealing with a textbook example of “precision and accuracy.” To illustrate the point, we present in Fig. 5 data for the previous DCS measurement for $\text{HD}(v' = 2, j' = 5)$, which has been redrawn in a form not presented in Ref. 20. The old experimental data were based on ~ 9000 ions. The difference between the old and new DCS, Figs. 5 and 2, respectively, is apparent and is twofold: (i) the ordinate error bars have gone down with collection of more ions, i.e., increased precision and (ii) experimental points seem to have “converged” closer to theoretical curves, in other words, accuracy has increased. For example, 9176 were collected previously, and 44 446 were collected for the current study. This suggests a roughly $\sqrt{44\,446/9176} \approx 2.2$ increase in precision – the average ordinate uncertainties in Figs. 2 and 5 are 0.00188 and 0.00471, respectively, i.e., a precision improvement of ~ 2.5 , which is in accord with our predicted improvement. Accuracy has similarly increased, as exemplified by old and new RSS values: $RSS^{GP} = 5.5 \times 10^{-7}$ and $RSS^{NGP} = 5.97 \times 10^{-7}$ for the old data set, and $RSS^{GP} = 2.1 \times 10^{-7}$ and $RSS^{NGP} = 2.1 \times 10^{-7}$ for new data set, respectively, translating into an improvement by a factor of ~ 2.8 . In other words, collecting more ions improves both accuracy and precision, as expected!

Assuming that any additional long-term drifts can be neglected, it is reason to ask: How many ions would we need to collect to see a significant difference between experiment vs GP and experiment vs NGP fits? Let us consider for a moment the precision, or the spread in RSS values for GP and NGP fits. Currently we have used 12 RSS values to compute t -test values. We find that $RSS^{GP} = 8.0 \times 10^{-7}$, $\sigma_{GP} = 5.3 \times 10^{-7}$, and $RSS^{NGP} = 7.0 \times 10^{-7}$, $\sigma_{NGP} = 5.0 \times 10^{-7}$. It is obvious that if the two distributions were modeled as Gaussians, the overlap between the two is nearly unity. One way to say confidently that two distributions are different is to reduce the overlap of two Gaussians. (That is essentially what the t -test measures.) Assuming a $1/\sqrt{N}$ improvement in precision (where N is the number of ions collected), which has so far been borne out experimentally, we can roughly estimate that, for example, to bring down the overlap between two Gaussians to less than

34%, (which, assuming accuracy or mean RSS values do not change appreciably, translates into a healthy 95% confidence interval) one needs to collect ~ 100 times more ions (almost 4.5 million ions). This would take us about 3000 days, or just over eight years – more than an average lifetime of a graduate student! In summary, we do see an improvement in experimental precision and accuracy by collecting more ions in the $\text{H} + \text{HD}$ scattering experiment under our present conditions. We had hoped to see substantial differences between experiment vs GP and experiment vs NGP fits with only 5 times as many ions as in our previous study, which we realize from this study is not possible. Nevertheless, we have demonstrated that precision and accuracy do indeed obey the $1/\sqrt{N}$ law; thus, measuring the GP effect in the $\text{H} + \text{H}_2$ reaction seems to be hypothetically, but not practically, feasible by using the current method. Possibly, the hydrogen-atom Rydberg-tagging method,²⁵ which exhibits a superior angular resolution to that of a Photoloc approach, may be a more sensible approach to distinguishing the GP and NGP theoretical predictions shown in Fig. 2.

Finally, it may be wondered if the time is really ripe for a highly quantitative comparison between theory and experiment for the $\text{H} + \text{H}_2$ reaction. Theory and experiment are not in perfect agreement (see for example the comparison for $\text{HD}(v' = 1, j' = 12, 14)$ reaction products at $E_{\text{coll}} = 1.86$ eV shown in Figs. 3 and 4 of Ref. 20). Moreover, the origin of this disagreement is presently unknown. Thus, it might be questioned whether we have sufficient knowledge to be confident in comparing present theory with present experiment in searching for geometric phase effects. We chose the $\text{HD}(v' = 1, j' = 5)$ reaction product for study precisely, in part, because theory and experiment were already in relatively close agreement, but until the discrepancy between theory and experiment can be better understood and removed, we cannot be entirely sure that we are at the stage where such a comparison is totally unambiguous.

VI. CONCLUSIONS

This year marks the 50th anniversary of the celebrated paper by Herzberg and Longuet-Higgins¹ which marked the beginning of the search for geometric phase effects in molecular systems. Half a century later, the effects of electronic wave function sign change in the H_3 system are yet to be seen experimentally but hope springs eternal. The close overall agreement of theory and experiment (Fig. 2) nevertheless shows how far they both have come in describing this most fundamental scattering system.

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