Direct mapping of the angle-dependent barrier to reaction for Cl + CHD₃ using polarized scattering data

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The transition state, which gates and modulates reactive flux, serves as the central concept in our understanding of activated reactions. The barrier height of the transition state can be estimated from the activation energy taken from thermal kinetics data or from the energetic threshold in the measured excitation function (the dependence of reaction cross-sections on initial collision energies). However, another critical and equally important property, the angle-dependent barrier to reaction, has not yet been amenable to experimental determination until now. Here, using the benchmark reaction of $Cl + CHD_3(v_1 = 1)$ as an example, we show how to map this anisotropic property of the transition state as a function of collision energy from the preferred reactant bond alignment of the backward-scattered products—the imprints of small impact-parameter collisions. The deduced bend potential at the transition state agrees with *ab initio* calculations. We expect that the method should be applicable to many other direct reactions with a collinear barrier.

he textbook Arrhenius rate equation $k = A \exp(-E_a/k_BT)$, where $k_{\rm B}$ is the Boltzmann constant, is widely used to describe chemical reactivity for many chemical processes occurring in both gas and condensed phases¹. Embodied in the expression are two key factors: activation energy E_a and the pre-exponential or steric A factor. The former gives the energetic requirement to overcome the reaction barrier and the latter describes, on intuitive grounds, that a certain collisional geometry will be preferred in breaking and forming chemical bonds². The driving force for the colliding reactants to arrange themselves into such a favourable geometry arises from the anisotropic parts of the intermolecular interactions. Several decades of experimental and theoretical molecular collision studies have culminated in our current understanding of the energetic factor in reaction dynamics^{2–6}. In contrast, comparably less progress has been made in gaining deeper insights into the steric factor at the molecular level^{2,7-9}.

As illustrated in Fig. 1 for an activated collinear $A + BC \rightarrow AB + C$ reaction, near the top of the barrier (the transition state) the system possesses a certain structure orthogonal to the reaction coordinate, which corresponds to the metastable states supported by the bending potential at the saddle point. As such, the reaction barrier height varies with the angle of attack, and these metastable states act as dynamic bottlenecks, which gate the flow of reactive flux from reactants to products. In the context of transition state theory, the steric A factor manifests as the ratio of the partition function (the number of the states that are accessible to the system at a given energy or temperature) of the transition state to those of the two reactants^{1,2}. What governs the partition function of the transition state is the stiffness of the bending potential, leading to the concept of tight-bend or loose-bend transition states². An innovative method of negative ion photodetachment spectroscopy has been developed to probe the transition-state structure spectroscopically¹⁰. By simulating the resolved spectral features, the shape of the reactive potential near the transition state can be examined from the

potential energy surface (PES) used. It remains challenging to design an experimental method enabling direct determination of the shape of the bending potential or the angle-dependent barrier height.

To measure such anisotropic interactions in a scattering experiment, a clear observation of the stereochemical effects will be necessary, which then requires some control to be exercised over the collisional geometry of the interacting species. Typically, one achieves such spatial control by creating and manipulating an anisotropic distribution of the molecular axis of the reactants in the laboratory. A number of powerful techniques employing static electric fields, optical fields or their combinations have been developed and are at the disposal of experimentalists^{9,11,12}. Once the reactants are polarized in space, one searches for differential reactive outcomes under different collisional geometries and compares these with theoretical simulations. With favourable comparisons, one may then glean the critical anisotropic forces that drive the observed steric effects from the PES used in the dynamics calculations. Up to now, this has been the standard and only route to assess the accuracy of the PES through a theory-experiment comparison.

However, the connection between the interaction potential and the observed dynamic attributes is complicated and involves considerable averaging in the dynamics calculations, some of which, the impact parameter for instance, are not yet experimentally controllable. For reactions with polyatomic molecules such as methane, although highly accurate *ab initio* PESs can now be constructed¹³, a full-dimensional quantum dynamics calculation remains a formidable challenge and the less accurate quasiclassical trajectory (QCT) simulation cannot account for the quantum effects (zero-point energy, tunnelling and reactive resonances)¹⁴. It is thus highly desirable to develop an alternative approach capable of retrieving the critical features of the PES directly from measurements for an independent and more stringent test of the theoretically calculated potential.

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Figure 1 | Schematic illustration of how the transition-state structure affects chemical reactivity. Depicted is the reaction profile for an activated reaction of A + BC \rightarrow AB + C with a collinear barrier height E_b . The activated complex or the transition state is denoted as [A-B-C][‡]. The saddle point is a stationary point near the top of the barrier. The potential energy surface curves upwards along the direction orthogonal to the reaction coordinate, forming a bend potential that supports quasi-bound states in regulating the reactive fluxes. At a given collision energy, only those reactants with sufficiently higher E_c (red shaded part) than E_b can (classically) pass through the barrier, and the amount of reactive fluxes (blue shaded part) will depend on the stiffness of the bending potential, and thus the steric factor.

Here, we report a new method to delineate the bending potential at the reactive saddle point almost solely based on experimental data. As can be envisioned from Fig. 1, if we can devise a way to gauge the angular structure of the transition state as a function of collision energy E_c (here we exploit the polarized scattering data to deduce the most probable geometry for reaction), then the angle-dependent barrier can be mapped out. We chose the reaction of $Cl + CHD_3(v_1 = 1) \rightarrow HCl(v = 0) + CD_3(0_0)$ for demonstration. The reaction of Cl + CH₄ (and isotopologues) has been a benchmark for a detailed understanding of polyatomic reactions and possesses a few particularly appealing features for the present exploration. (1) The ground-state reaction proceeds via a direct abstraction mechanism of rebound type with a collinear transition-state structure^{13,15}. (2) Exciting the C-H bond of the reactant promotes reactivity^{16,17}, in line with Polanyi's rules⁴ for a late-barrier reaction. In addition, the excited reaction proceeds via a dual reaction mechanism^{18,19}, where, while the ground-state product pair, $CH_3(0_0) + HCl(v=0)$, is formed by a direct rebound mechanism as the ground-state reaction, the vibrationally excited product pair, $CH_3(0_0) + HCl(v = 1)$, is predominantly mediated by a resonant tunnelling pathway²⁰⁻²². (3) A very detailed study of the stereodynamics of the reaction of an aligned $CHD_3(v_1 = 1)$ with a Cl atom has recently been reported²³⁻²⁶. On the one hand, the deduced polarization-dependent differential cross-sections (PDDCSs) for the $CD_3(0_0) + HCl(v = 1)$ channel do not reveal any obvious angular correlation between the reactant polarization direction and the product recoil angle, as one might anticipate from the time delay in this resonance-mediated pathway. On the other hand, all three anisotropic PDDCSs for the direct-scattered $CD_3(0_0) + HCl(v=0)$ product pair can largely be captured by a venerable line-of-centres (LOC) model^{2,24}, which is essentially a billiard-ball type of collision. The significant implication of the latter finding is that the long-range anisotropic interactions in the reactive entry valley must exert little re-orientation effect on the incoming trajectories, and the short-range anisotropy of the collinear Cl-H-CD₃ configuration near the saddle point is thus responsible for the observed steric effects. We have exploited this particular aspect here to map out the transition-state bending potential directly from the polarized scattering data.



Figure 2 | Imaging the dynamic outcomes in the reaction of Cl + CHD₃(v_1 = 1) with two distinct collisional geometries at E_c = 4.8 kcal mol⁻¹. a, Raw difference (with the IR-off signatures subtracted) images of the probed CD₃(O₀) products are presented for the IR polarization axis (ϵ_{IR}) or the reactive C-H bond being directed either along or perpendicular to the scattering axis **k**. The notation $P(\alpha, \phi)$ denotes the probability density function of reactive events when the ϵ_{IR} direction points along the polar angle α and the azimuthal angle ϕ in a scattering frame with the *z* axis defined by the initial relative velocity vector **k**. The forward scattering angle $\theta = 0^{\circ}$ denotes the initial CHD₃ beam direction in the centre-of-mass coordinate system. **b**, Product speed distributions $d\sigma/du$ with aligned and unpolarized (unp.) reactants. **c**, Top: measured and computed polarized differential cross-sections of the HCl(v = 0) channel for end-on (||) and side-on (\perp) collision geometries. The experimental distributions are the averages of three independent measurements, with statistical errors less than ±5%. Bottom: corresponding unpolarized and sterically preferential (||- \perp) angular distributions, with propagated errors of ±10% for the experimental distributions.

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Figure 3 | **Collisional energy dependency of the steric preference, defined as the ratio of the aligned to the unpolarized reactivity for end-on (||) or side-on (1) attack.** A value of 1.0 means no steric preference and a value greater (smaller) than 1.0 indicates alignment-induced reactivity enhancement (suppression). Experimental error bars indicate ± 1 s.d. **a**,**b**, For the HCl(v = 0) + CD₃(O₀) product channel, theory and experiment agree reasonably well and both indicate higher reactivity for end-on attack and a decline of this differential reactivity with increasing E_c . **c**,**d**, For the HCl(v = 1) product, QCT cannot reproduce the experimental results for this resonance-mediated pathway—a quantum phenomenon.

Results and discussion

Effects of collisional geometry on product distributions. Figure 2a presents two raw images of the $CD_3(0_0)$ products acquired under two distinct polarizations of the infrared excitation laser in the $Cl + CHD_3(v_1 = 1)$ reaction at $E_c = 4.8$ kcal mol⁻¹. Shown here are the difference images, for which the ground-state reaction features (that is, infrared (IR) off) have been subtracted. The sharp forward (0°) peak in the inner ring with a slower speed is assigned, on energetic grounds, to the concomitantly formed HCl(v = 1) products, and the outer ring is ascribed to HCl(v = 0). The general appearances of the two images are strikingly different. The angular distributions of HCl(v=0) show dramatic changes from backward scattering (the || approach) to sideways dominance (the \perp attack), but the relative intensities of the two rings also appear sensitive to reagent alignments. Such strong variations in collision geometries signify enormous steric effects in the reaction. After image analysis (Supplementary Section 1), the resultant product speed distributions were plotted, as presented in Fig. 2b. Also displayed for comparison is the distribution for unpolarized reactants (unp.), that is, $(\sigma_{\parallel} + 2\sigma_{\perp})/3 = \sigma_{unp}$ (ref. 27). The wellresolved two peaks, as labelled, indeed show a remarkable dependency of the correlated HCl-vibrational branching on collisional geometry. Integrating the respective speed distributions then yields the relative polarized cross-section for HCl(v = 0 and 1)channels at the corresponding E_c .

Figure 3 summarizes the E_c dependence of the results for the two channels on collisional geometry. Using the unpolarized crosssection σ_{unp} as a reference, the steric preference of the reactivity with two spatial alignments, \parallel (upper) and \perp (lower), is presented for HCl($\nu = 0$) (Fig. 3a,b) and HCl($\nu = 1$) (Fig. 3c,d) channels. Also shown are the QCT results based on the *ab initio* PES. As is seen in Fig. 3c,d, the QCT fails to reproduce the experimental steric preference for the CD₃(0₀) + HCl($\nu = 1$) channel. This failure is not surprising in that this channel is conceived to proceed via a tunnelling-mediated quantum-resonance pathway, which simply cannot be captured by QCT.

As for the direct-scattered HCl($\nu = 0$) channel shown in Fig. 3a,b, both the observed trend and magnitudes are well reproduced by QCT. Some discrepancy is noted at $E_c \le 2$ kcal mol⁻¹. Similar findings were previously observed^{28,29} in the study of the rotationalmode specificity of CHD₃($\nu_1 = 1$, $|JK\rangle$) + Cl, where the QCT results captured all major features of the experimental findings at higher values of E_c , but failed for $E_c \le 2$ kcal mol⁻¹ due to the change in the reaction mechanism from direct abstraction to a quantum resonance-mediated pathway. The low energy discrepancy, particularly in Fig. 3a, is then ascribed to a significant contribution of the resonance pathway to the ground-state product-pair channel.

Deeper insight into the steric effect is encoded in the polarized angular distribution, as shown in Fig. 2c for the direct HCl(v=0)channel. Two markedly different distributions are observed in the upper panel. The end-on (||) attack yields a predominantly backward-peaking distribution, whereas the side-on (\perp) approach produces mainly sideways-scattered HCl(v=0). The corresponding isotropic and anisotropic components of the two polarized angular distributions are presented in the lower panel. The isotropic one, $(\sigma_{\parallel} + 2\sigma_{\perp})/3$ or σ_{unp} (black symbols), is in excellent agreement with previous reports using unpolarized (or randomly distributed) reagents^{18,19}, and its general shape can be understood within the LOC model as abstracting a peripheral hydrogen atom^{15,24}. The anisotropic distribution $(\sigma_{\parallel} - \sigma_{\perp})$ (the purple dots) displays a feature peaking in the backward direction and becoming negative near 90°, and then gradually increasing to a null value in the forward direction. The QCT calculations corroborate very well with the experimental results, demonstrating the accuracy of the PES used.

The results of HCl($\nu = 0$) at all recorded values of E_c , ranging from 1.3 to 8.6 kcal mol⁻¹, are summarized in Fig. 4a. The patterns

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Figure 4 | E_c -dependent evolution of differential steric preference in the HCl(v = 0) channel. **a**, Normalized, polarized angular distributions for end-on ($\sigma_{||}$) and side-on (σ_{\perp}) approaches. Indicated in a box in each panel is the collisional energy (in kcal mol⁻¹). Each distribution is the average of 3-7 independent measurements, depending on E_c , with typical statistical errors within ±5%. Despite a large disparity in shapes, both geometries yield the same intensity near 90°, as indicated by the green dashed line. **b**, The sign of the normalized anisotropic distribution, $(\sigma_{||} - \sigma_{\perp})/\sigma_{unp}$, gives an immediate impression about the favoured collision geometry. The typical uncertainties are within ±10% from error propagations. **c**, Alignment angle α deduced from the backward-scattered (every 2° angular segment from 168° to 180°) signals within the orange rectangular box in **b**. The horizontal dashed line in each panel represents the average value of the most probable angle α . Deviations of the data points represent errors propagated in calculating angles ρ , with the standard deviations shown in Fig. 5.

of the two polarized angular distributions are distinct. While $d\sigma_{\parallel}/d\cos\theta$ is predominantly backward peaking and becomes broader with increasing E_c , $d\sigma_{\perp}/d\cos\theta$ features a sideways-scattered distribution and protrudes into the forward hemisphere at higher E_c . Two distributions cross each other near 90° (green dashed line), for which the polarized LOC model offered a simple explanation²⁴. As for the normalized anisotropic distribution, $(\sigma_{\parallel} - \sigma_{\perp})/\sigma_{\rm unp}$, Fig. 4b shows that the backward-scattered products favour an end-on approach at all values of E_c , and the steric preference reverses for the forward-scattered products at higher E_c (again, not obvious for $E_c \leq 2$ kcal mol⁻¹).

Unveiling the underlying anisotropic potential property from the polarized scattering data. As shown previously²⁷ and from Supplementary Equations (1) and (2), the normalized anisotropic distribution $(\sigma_{\parallel} - \sigma)/\sigma_{unp}$ can be re-expressed in terms of the reaction polarization moment as $15a_0^2[S_0^2(\theta)/S_0^0(\theta)]/2$, where $a_0^2 = -\sqrt{(2/5)}$ is the reagent polarization moment in the photon frame for the prepared CHD₃($v_1 = 1$, $|JK\rangle = |10\rangle$) state^{24–27}. The physical meaning of the normalized moment $S_0^2(\theta)/S_0^0(\theta)$ is that a positive (negative) value of the polarization moment indicates the reactive propensity for the aligned C-H bond pointing along (perpendicular to) the relative velocity vector (k) of the reactants^{24,30,31}. Although the $S_0^2(\theta)/S_0^0(\theta)$ value provides a clear descriptor for the degree of reactant polarization effects with respect to the reactivity of an unpolarized reagent, it cannot uniquely relate to the direction of the C-H bond axis as seen by the attacking Cl atom. The difficulty in disentangling the correlation between the experimentally controllable infrared polarization axis and the desired direction of attack near the transition state can be traced to the so-called kinematic smearing effect^{32,33}. As illustrated in Fig. 5a, for a given bond axis aligned by IR excitation or angle α , there is an entire range of attack angles ρ that will be sampled at any finite impact parameter *b* due to the random distribution of the azimuthal angles ϕ . Obviously, the larger the *b*, the wider the range of attack angles. Such a kinematic smearing effect, however, can largely be alleviated for collisions with b = 0 (Fig. 5b), which then suggests a simple idea—the angle of attack at a given E_c should be manifested most clearly in the reactivity of small-*b* collisions, and then, by systematically scanning E_c , the angle-dependent barrier to reaction could be mapped out.

The transition state of this reaction is of collinear Cl-H-CD₃ geometry^{15,34}, and the small-*b* collision in a direct encounter is expected to preferentially yield backward-scattered products. Recall that the normalized reactive moment signifies the directional correlation between the reactive C–H bond axis and the **k** vector, and $S_0^2(\theta)/S_0^0(\theta) = a_0^2 P_2(\cos\alpha)$, where $P_2(\cos\alpha)$ denotes the second-order Legendre polynomial^{24,35}. Then, the most probable angle α for the small-*b* collisions can be retrieved from the preferred bond alignment for the backward-scattered products. The orange rectangular box in Fig. 4b indicates the angular range (θ = 168–180°) we used to evaluate the most probable alignment angle α (see Methods).

The remaining task is to relate the alignment angle α , which is controllable in the laboratory frame, to the desired angle of attack ρ at the transition state. With the aid of the *ab initio* calculated



Figure 5 | Strategy to deduce attack angle ρ at the saddle point from the experimentally controllable alignment angle α . **a**, The kinematics smearing effect. Due to the random distribution of the azimuthal angle ϕ about the scattering axis \mathbf{k} , at any finite impact parameter b there is an entire range of attack angles ρ for an experimentally selected alignment angle α . Exemplified are three trajectories at the same α and b, each with a distinct attack angle, ρ_3 for the trajectory of Cl-3, ρ_2 for Cl-2 and ρ = 0 for Cl-1. Obviously, the larger the value of b, the wider the range of ρ sampled for a given α . **b**, For a collinear reaction at $b \approx 0$, the CI atom will meet the molecule at the initially aligned angle α and preferentially yield the backward-scattered products. With the two bond lengths at the saddle point as indicated, simple geometry then gives a unique ρ for a given α . **c**, Plot of the angle-dependent barrier to reaction (Supplementary Table 1 summarizes the three-step results). For the experimentally measured potential, the axes of E and bend angle correspond to E_c and the most probable attack angle ρ for the products in the backward-scattered region, respectively. Two open circles show the results when higher rotational-excited $CD_3(0_0)$ products were probed. Error bars represent ±2 s.d. propagated from Fig. 4c. The blue (red) curve is the theoretical potential as a function of bending angle ρ at the saddle point on the vibrationally adiabatic ground-state (stretch-excited) PES, for which the energy relative to the adiabatically collinear barrier height at $\rho = 0^{\circ}$ is plotted.

bond lengths at the saddle point³⁴, simple geometry leads to a unique bending angle ρ for a given α (Fig. 5b). Figure 5c and Supplementary Table 1 summarize the most probable ρ angles as a function of the E_c of this study. The results display a roughly quadratic dependency of E_c on the most probable bending angle ρ , except for the two lowest values of E_c , for which, again, a resonant complex is formed and thus the angular correlation between the product recoil angle and the initial complex-formation angle will be lost due to the time delay.

The behaviour at higher E_c is reminiscent of the chemical intuition of opening up the attack angles with increasing E_c in a direct reaction². In support of this concept, also depicted in Fig. 5c are the two vibrationally adiabatic bend potentials based on high-level *ab initio* computations at the saddle point (Supplementary Section 2). Although it is debatable which potential—the ground or first stretch-excited—will be more meaningful for such a comparison, their differences are small and both show excellent agreements with this first experimentally derived potential, testifying that the stereodynamics in the backward-scattered region provides a particularly stringent test of the calculated anisotropic property of the collinear transition state.

Conclusions

We have devised an intuitively appealing method to decode the underlying PES property from the polarized scattering data, without resorting to the conventional comparison with dynamics calculations. When applied to a benchmark $Cl + CHD_3(v_1 = 1)$ reaction, the method not only enables a direct mapping of the Cl-H-C bending potential at the transition state, but also vividly deciphers a dual reaction mechanism occurring over different E_c ranges. The premise of this method is to correlate the backward-scattered products with the small-b collisions. Such an intuitive correlation has been a cornerstone in our basic understanding of a direct reaction governed by a collinear barrier². Therefore, the method is expected to be applicable to many other reactions of that class, for which the correlation between small-b collisions and backward-recoiled products is particularly strong. The method needs information on the bond lengths at the saddle point. Because only the relative values of the bond lengths are required, a reasonable estimate may suffice—with some uncertainty—if such information is not available (see the comment in Supplementary Table 1). We used the *ab initio* results in this work for more accurate determination. The derived one-dimensional bend potential here, which is arguably most crucial, is based on the measured polarization moment of $S_0^2(\theta)/S_0^0(\theta)$. Yet, the barrier to reaction is multidimensional in this six-atom system. We surmise that the potential property along other angular degrees of freedom must be imprinted and entangled in the remaining polarization moments, some of which have been measured²⁴⁻²⁶. The challenges ahead are to uncover such information for a full picture and to extend this line of approach to another class of chemical reactions with bent transition-state geometry.

Methods

Experiment. A detailed description of the experiments is provided in Supplementary Section 3. In brief, we performed the experiments using a sourcerotatable, crossed-beam machine equipped with a time-sliced, velocity-mapped ionimaging detector³⁶. Two molecular beams (Cl atom and CHD₃), an IR pump and an ultraviolet (UV) probe laser crossed in the interaction region. The IR laser prepared the ro-vibrationally excited CHD₃($v_1 = 1$, $|JK\rangle = |10\rangle$) reactant and a variable waveplate was used to rotate the polarization direction $\varepsilon_{\rm IR}$ to control the alignment of the reagent's C–H bond^{23,27}. The UV laser probed the dominant ground-state CD₃(0₀) products via a (2 + 1) resonance-enhanced multiphoton ionization (REMPI) scheme. The velocity distribution of the state-tagged CD₃ was measured by a time-sliced, ion-imaging technique for the REMPI ions. Product images were acquired at two particular IR-polarization configurations^{27,31}, corresponding to the collisional geometry with the C–H bond aligned parallel (\parallel or end-on) or perpendicular (\perp or side-on) to the initial velocity vector **k**. We denote the resultant cross-sections σ_{\parallel} and σ_{\perp} , respectively.

Computation. We performed QCT simulations for the Cl + CHD₃(ν_1 = 1, $|JK\rangle = |10\rangle$) reaction using a high-level full-dimensional *ab initio* PES^{34,37}. More than 18 million trajectories were run and analysed at different collision energies with end-on, side-on and random initial orientations of the reactants. Additional computational details are described in Supplementary Section 2.

Mapping the bending potential from the polarized differential cross-sections. After the polarized scattering data were analysed (Supplementary Section 1), we devised a three-step roadmap to unveil the 'experimental' potential directly from the data.

First, re-expressing equations (1) and (2) in Supplementary Section 1 as $(\sigma_{\parallel} - \sigma_{\perp})/\sigma_{\rm unp} = 7.5 a_0^2 G_k [S_0^2(\theta)/S_0^0(\theta)]$ and accounting for the depolarization factor

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 $\begin{array}{l} G_{k} \text{ we obtained the normalized polarization moment $S_{0}^{2}(\theta)/S_{0}^{0}(\theta)$ from the measured $(\sigma_{\parallel} - \sigma_{\perp})/\sigma_{unp}$ in the backward-scattered region, say 168° <math display="inline">\leq \theta \leq 180^{\circ}$ (Fig. 4b)$ (the experimental full angular resolution is <math display="inline">\pm 2.8^{\circ}$). Theoretically, the values of \$(\sigma_{\parallel} - \sigma_{\perp})/\sigma_{unp}\$ should range from 3.0 (the upper limit) to -1.5 (the lower limit)^{25,26}. As shown in Fig. 4b, all experimental data indeed fall within this range. \end{tabular}

Second, the normalized polarization moment $S_0^2(\theta)/S_0^0(\theta)$ in a direct reaction reveals the directional correlation of reactivity between the aligned bond axis and the **k** vector, that is, the most probable alignment angle α for those products recoiled into angle θ . When the transition state is of collinear geometry, collisions at low b are nearly head to head, such that the scattered products will predominantly rebound towards the backward direction. As shown in supplementary section 2 of ref. 24, recognizing that the geometric factors in the full PDDCS expression (equation (2) in ref. 24) are the real part of the orthogonal reduced spherical harmonics, one can then derive each individual polarization moment by multiplying one of the appropriate geometric factors on both sides of the full PDDCS expression to eliminate all other polarization moments. This leads to $S_0^2(\theta)/S_0^0(\theta) = a_0^2 \hat{P}_2(\cos \alpha)$ for a direct collinear reaction, with $P_2(\cos\alpha)$ being the second-order Legendre polynomial³⁵. Hence, the most probable reactant alignment angle α for reactions with $b \approx 0$ can then be deduced from the alignment moment of the backward-scattered products. Figure 4c shows the resultant values of α over the angular range $168 \le \theta \le 180^\circ$. Averaging them yields $\langle \alpha \rangle$ for better statistics and for error estimates.

Third, once the average value of the most probable alignment angle $\langle \alpha \rangle$ for backward-scattered products (namely, reactions with small-b collisions) at a specific $E_{\rm c}$ is determined (Fig. 4c), simple geometry and the use of the *ab initio* calculated bond lengths at the saddle point lead to the desired attack angle $\langle \rho \rangle$ at the transition state at that $E_{\rm c}$ (Fig. 5b). Supplementary Table 1 summarizes the results of this study. The most probable $\langle \rho \rangle$ thus deduced does not appear very sensitive to the exact values of the bond lengths used for this late-barrier reaction (see the comment in Supplementary Table 1) nor the angular range being sampled, as can be seen from Fig. 4c.

Data availability. The data that support the findings of this study are available from the corresponding authors upon request.

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Author contributions

K.L. conceived and designed the experiments. H.P. and F.W. performed the experiments and analysed the data. G.C. performed theoretical calculations. All authors discussed the results and commented on the manuscript. K.L. wrote the paper.

Additional information

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Competing financial interests

The authors declare no competing financial interests.