Directly probing anisotropy in atom–molecule collisions through quantum scattering resonances

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Anisotropy is a fundamental property of particle interactions. It occupies a central role in cold and ultracold molecular processes, where orientation-dependent long-range forces have been studied in ultracold polar molecule collisions1,2. In the cold collisions regime, quantization of the intermolecular degrees of freedom leads to quantum scattering resonances. Although these states have been shown to be sensitive to details of the interaction potential3–9, the effect of anisotropy on quantum resonances has so far eluded experimental observation. Here, we directly measure the anisotropy in atom–molecule interactions via quantum resonances by changing the quantum state of the internal molecular rotor. We observe that a quantum scattering resonance at a collision energy of $k_B \times 270 \text{mK}$ appears in the Penning ionization of molecular hydrogen with metastable helium only if the molecule is rotationally excited. We use state-of-the-art ab initio theory to show that control over the rotational state effectively switches the anisotropy on or off, disentangling the isotropic and anisotropic parts of the interaction.

Anisotropy leaves fingerprints on many atomic and molecular processes, but its contribution is difficult to evaluate and quantify at high energies due to the many quantum states needed to describe the process. For example, the effects of anisotropy can be traced to changes in the angular distribution of products in collisions and half-collisions that are detected with advanced ion imaging techniques4. Numerous experiments have reported orientation effects including the study of bimolecular processes such as the reactive scattering of $\text{H} + \text{D}_2$ (ref. 10), and $\text{F} + \text{CD}_3$ (ref. 11) as well as the inelastic scattering of NO by Ar (ref. 12). Spectroscopic techniques have been successfully used to identify hindered $\text{H}_2$ rotation in an anisotropic potential of van der Waals molecules such as $\text{H}_2\text{O} + \text{H}_2$, and $\text{H}_2\text{HF}$ complexes13,14.

In cold and ultracold molecular processes, where the number of accessible quantum states is greatly reduced, anisotropy effects have so far been studied only in fast reactions. It has been shown that the orientation of the long-range dipole–dipole interaction between molecules can be tuned via external electric fields15. In KRb molecules this method enabled the observation of rethermalization1 and the suppression of a bimolecular chemical reaction1. In addition, the reaction of $\text{N}_2^+ + \text{Rb}$ has been shown to be dominated by the anisotropic charge–quadrupole long-range interaction16.

Similarly, fast Penning ionization reactions have been studied, demonstrating that the rotational state of a molecule defines the type and strength of the effective long-range interaction17. These fast processes are fully described by the long-range interactions alone. At short internuclear separations the Penning ionization occurs with unit probability, acting as a perfect absorber and preventing the formation of outgoing waves. In such a case there is no quantization along the internuclear coordinate that precludes the appearance of quantum scattering resonances.

Experiments that are capable of resolving quantum resonance states allow for collision studies with near spectroscopic precision. For example, isotope shifts have been observed in the Penning ionization of molecular hydrogen isotopologues5. Similar effects between isotopes were observed in rotational state-to-state cross-sections and linked to quantum scattering resonances appearing at different energies8. Feshbach resonances in ultracold anisotropic atom–atom collisions allowed the emergence of chaotic scattering in ultracold Er and Dy to be observed19.

The emergence of discrete quantized metastable states formed during a cold collision provides a new way to study anisotropy. Instead of recording the angular distribution of the collision products, one can conveniently alter the way anisotropy contributes by choosing different rotational quantum states of the interacting molecules. The sensitivity of the orbiting resonances to the molecular degrees of freedom has been theoretically predicted for the reaction $\text{D} + \text{H}_2$ (ref. 20), the reactive scattering of $\text{F} + \text{H}_2$ (ref. 21) and inelastic collisions of $\text{CO} + \text{H}_2$ (ref. 22), for example. This effect has so far eluded experimental investigation due to the insufficient resolution of individual quantum resonance states22. The introduction of merged beam experiments that can reach temperatures as low as 10 mK (refs 3,6) allows for both low enough collision energies and sufficiently high resolutions due to the correlation that develops during the free propagation of a supersonic molecular beam23. This merged beam configuration is used in the current collision measurements, as described in the Methods.

Here we demonstrate the dramatic effect of anisotropy on shape resonances in cold Penning ionization reactions of metastable helium in the $2^3S$ state ($\text{He}^+$) with molecular hydrogen in the rotational ground and first excited states (Fig. 1). In the classical collision regime down to temperatures of several kelvin, $\text{He}^+$ behaves similarly, independent of whether it is in the $j = 0$ or $j = 1$ internal states allow for collision studies with near spectroscopic precision.
measuring the orbiting resonance positions we can independently probe the isotropic and anisotropic parts of the interaction. As the resonance wavefunctions span both the short- and the long-range parts of the potentials, we are able to benchmark first-principles quantum dynamics calculations to within 7 × 10⁻³ cm⁻¹ or 200 MHz precision. This allows for a rigorous comparison with theory and a quantitative evaluation of the different levels of treating electron correlations in electronic structure calculations.

Conveniently, merged beam experiments with molecular hydrogen can be carried out with control over the rotational state of the molecule. A normal molecular hydrogen beam cooled in supersonic expansions consists of 75% ortho-hydrogen and 25% para-hydrogen. It follows from the Pauli principle that the lowest rotational state for para-hydrogen is \( j = 0 \) whereas \( j = 1 \) is the lowest molecular rotational state for ortho-hydrogen. A pure para-hydrogen sample can be prepared by catalytic conversion at cryogenic temperatures, allowing the determination of the state-selected rate coefficient, as has been described previously²⁷.

In Fig. 1, we compare our experimental data to the results of first-principles calculations. A two-dimensional potential energy surface was obtained with the current gold standard of electronic structure theory, the coupled-cluster method with single, double and approximate non-iterative triple excitations [CCSD(T)], and further refined to include higher order correlation effects. Subsequently, the potential energy surface was used in quantum scattering calculations with reactive boundary conditions at short range²⁴. The theoretical results demonstrate that collisions with \( j = 0 \) hydrogen are not sensitive to the anisotropic part of the interaction potential, such that the hydrogen molecule effectively behaves like an atom. Even scaling the anisotropic part, \( V_2 \), by 50% does not introduce an observable change in the rate coefficient, as can be seen in the inset in Fig. 2. In stark contrast the \( j = 1 \) hydrogen rate coefficient is very sensitive to the anisotropy, emerging as shifts in the position of the orbiting resonance

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**Figure 1** | Experimental and theoretical Penning ionization rate coefficients of H₂ molecules in excited and ground rotational states by He⁺. The experimental rate coefficient is shown by the black dots as a function of the mean collision energy in units of temperature. The upper (lower) panel corresponds to \( j = 0 \) (\( j \)) rotationally internal in the \( j = 0 \) (\( j \)) rotational quantum state. Two shape resonances are observed below 5 K for the reaction with ortho-H₂ \( j = 1 \) at 2.37±0.09 K and at 270±20 mK. The \( j = 1 \) lower-energy resonance state corresponds asymptotically to the partial wave \( l = 3 \), whereas the second resonance, which appears both for \( j = 0 \) and \( j = 1 \), corresponds asymptotically to the \( l = 4 \) partial wave. In the reaction with para-H₂ \( j = 0 \), the \( l = 3 \) resonance is absent, whereas the difference in energy of the \( l = 4 \) resonance cannot be distinguished from the \( j = 1 \) case. The results of state-of-the-art first-principles calculations for the reaction with the ground \( j = 0 \) and excited \( j = 1 \) rotational states are depicted by the green, blue and red curves in both panels. The interaction potential obtained with [CCSD(T)/aug-cc-pV6Z + mid-bond, green] alone erroneously predicts a low-energy resonance for para-hydrogen \( j = 0 \) and two low-energy resonances for ortho-hydrogen \( j = 1 \). Including the FCI/aug-cc-pVQZ correction (blue) allows for agreement down to collision energies corresponding to a few hundred millikelvin. Further improvement of the interaction potential is achieved by uniformly scaling the correlation energy by 0.4% (red), resulting in excellent agreement with the measured resonance positions and the overall behaviour of the rate coefficient down to the lowest collision energies probed in the experiment. The calculated rate coefficients are convoluted with the experimental resolution (8 mK) for the lowest collision energies. The error bars indicate the standard error in the rate coefficient and the collision energy, calculated according to 500 measurements per data point.

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**Figure 2** | The theoretical rate coefficients of He⁺ + H₂ in the first excited rotational state \( j = 1 \) for different scaling factors of the leading order anisotropic potential \( V_2 \). The rate resulting from the original potential is depicted by the solid red curve, and the scaling of the anisotropic part by a factor of 1.5, 0.5 and 0.2 is depicted by the blue, magenta and green dashed curves, respectively. As the scaling factor decreases the lower-energy resonance position shifts to lower collision energies. The spectroscopic resolution of the resonance positions can serve as a sensitive measure of the anisotropy in the system. The logarithmic inset shows the rate for the scaling factors of the anisotropic potential by the same factors for the reaction of He⁺ + H₂ in the ground rotational state \( j = 0 \). The rate coefficient remains the same for different scaling factors as the anisotropic potential has a limited contribution to this reaction.
for different scaling factors of the anisotropic potential shown in Fig. 2.

The sensitivity of quantum resonance states to small changes in the interaction allows us to make a meaningful comparison of different levels of treating electron correlations in \textit{ab initio} theory (Fig. 1). In fact, the interaction potential obtained with the ‘bare’ CCSD(T)/aug-cc-pV6Z+mid-bond method is not accurate enough to reproduce the low-energy resonances for collisions with both \( j = 0 \) and \( j = 1 \) \( \text{H}_2 \) (see the green curves in Fig. 1). To account for higher-order electron correlation effects, the full configuration interaction (FCI/aug-cc-pVQZ) contribution beyond CCSD(T) has been calculated and added to the potential. The FCI-corrected potential energy surface performs significantly better (blue curves in Fig. 1), in particular for collisions with \( \text{H}_2 (j = 1) \). However, it still erroneously predicts a resonance in the millikelvin range for \( \text{H}_2 (j = 0) \). To further improve the theoretical model, we have uniformly scaled the correlation energy. This is motivated by the fact that incompleteness of the orbital basis set is the main source of error in the \textit{ab initio} calculations. It particularly affects the correlation energy, whereas the Hartree–Fock energy is almost fully converged in the aug-cc-pV6Z basis set (see Methods for details). In fact, increasing the correlation energy in the interaction potential by merely 0.4% leads to an excellent agreement for the resonance position of \( \text{H}_2 (j = 1) \) and confirms absence of this resonance for \( \text{H}_2 (j = 0) \) (red curves in Fig. 1). The latter can be understood as follows: scaling the correlation energy by 0.4% corresponds to increasing the depth of the isotropic potential by around 0.1 cm\(^{-1}\). This shifts the erroneous resonance obtained with CCSD(T) and CCSD(T) + \( \delta \text{FCI} \) down such that it becomes a truly bound state and does not affect the reaction rate.

A similar comparison of the different levels of theory and experiment could in principle also be performed using rovibrational spectroscopy of bound states. However, while spectroscopic methods measure the spacings between rovibrational states with high precision, these spacings are not sensitive to a global energy shift of the potential. In collisional spectroscopy the spectrum emerges above the dissociation threshold enabling the measurement of the energies of quasi-bound states on an absolute scale. Thus changes in the effective well depth due to the anisotropy are more pronounced in absolute scale measurements of the spectrum (Fig. 3).

To qualitatively understand the role of anisotropy, it is convenient to consider the effective adiabatic interaction potentials. To this end, the interaction potential is expanded into two terms: \( V_j(R) \), the isotropic term where \( R \) is the interparticle separation and \( V_j'(R) \cos \theta \) which describes the angular dependence to first order, where \( \theta \) is the polar angle between the axis of the \( \text{H}_2 \) molecule and the axis joining the \( \text{H}_2 \) centre of mass with the \( \text{He} \) atom. We use an adiabatic theory\textsuperscript{25} inspired by previous works\textsuperscript{26,27} to construct effective potential curves that conserve the total angular momentum \( J \). These potentials asymptotically correlate with a well-defined rotational state of \( \text{H}_2 (j) \) and a well-defined collisional angular momentum, that is, partial wave \( l \). The anisotropy, \( V_j'(R) \), is small in our case compared with the rotational constant for all collision distances, such that mixing of the rotational states of the same parity in the \( \text{H}_2 \) molecule is negligible. Figure 3 compares the three adiabatic potentials that support the lower-energy resonance state that asymptotically correlates with \( j = 0 \) and \( j = 1 \) \( \text{H}_2 \) and orbital angular momentum (partial wave) \( l = 3 \). The black curve corresponding to \( J = 3 \) and \( j = 0 \) \( \text{H}_2 \) is identical to the isotropic part of the interaction potential and includes the centrifugal term. It is deep enough to support a single bound state just below the threshold with a binding energy of \( k_B \times 0.01 \text{K} \), as shown in the inset of Fig. 3. In the case of \( j = 1 \) \( \text{H}_2 \), the anisotropy is responsible for reducing the well depth of the corresponding \( J = 3 \) effective potential, shown in red, enough to raise the bound state above the dissociation threshold (Fig. 3 inset). This state is located below the top of the centrifugal barrier, and is accessible via tunnelling in scattering experiments at a collision energy of \( k_B \times 270 \text{mK} \).

Orbiting resonances amplify minute differences in particle interactions, making them easily detectable in cold collision experiments provided that the energy resolution is sufficiently high. They are a manifestation of the quantization of the intermolecular degrees of freedom, which form a wave matter analogue of an optical cavity. Quantum resonances thus provide an ideal probe to illuminate the different contributions to particle interactions with a sensitivity that is a challenge for current state-of-the-art \textit{ab initio} theory. The sensitivity of quantum resonances to the internal state of a molecule can be exploited in many experiments. Changing the rotational state of a molecule effectively switches the anisotropy of the interparticle interaction on and off, shifts resonance positions and thus dramatically changes the collisional cross-section. Such control over collisional properties can be critical to the success of molecular cooling methods that rely on collisions, such as evaporative or sympathetic cooling.

Figure 3 | Effective potential curves for the reaction of \( \text{He}^* \) and \( \text{H}_2 \) in the ground and excited rotational states. The potential curves are presented as a function of the \( \text{He}^*-\text{H}_2 \) distance in units of bohr radii (\( a_0 \)). All of the curves are asymptotically correlated to partial wave \( l = 3 \) and calculated according to adiabatic theory\textsuperscript{25}. The adiabatic potentials shown in red and black correspond to the total angular momentum \( J = 3 \). The potential of \( j = 0 \) supports one bound state, located below the dissociation threshold at \( k_B \times 0.01 \text{K} \). The contribution of the anisotropic part of the potential in the case of \( j = 1 \) (red curve) causes a reduction of the well depth. This reduction is sufficient to shift the bound state by \( \sim 0.3 \text{K} \) placing it above the dissociation threshold (see the zoomed-in region in the inset), as depicted by the horizontal solid red line, leading to the resonance at 270 mK in the reaction rate coefficient of He\(^* \) + \( \text{H}_2 \) in the excited rotational state (\( j = 1 \)). The grey curve corresponds to two nearly degenerate effective potential curves with a total angular momentum of \( J = 2 \) and \( J = 4 \) and with \( j = 1 \) \( \text{H}_2 \). They support bound states at \( k_B \times 0.18 \text{K} \) below the dissociation threshold and no quasi-bound states. The bound and quasi-bound state wavefunctions for total angular momentum \( J = 3 \) are depicted by the black and red dashed curves, respectively. The resonance state wavefunction spans both the short- and the long-range part of the potential and can therefore be probed in collision experiments.
Methods

Methods, including statements of data availability and any associated accession codes and references, are available in the online version of this paper.

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Author contributions

All authors contributed to all aspects of this work.

Additional information

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Competing financial interests

The authors declare no competing financial interests.
Methods

The experimental set-up, which has been discussed previously\textsuperscript{34,35}, consists of two supersonic beams that are generated by pulsed Even–Lavie valves\textsuperscript{36} placed at a relative angle of 10°. The right beam consists of a nozzle for gas mixtures of H\textsubscript{2} and He. The second beam consists of He, excited to He* using a dielectric barrier discharge\textsuperscript{37} that is located at the exit of the valve and is merged with the straight beam using a 20 cm magnetic guide, leading to zero relative angle between the beams at the detection region. The He* beam velocity is kept constant at 870 m s\textsuperscript{-1} while the H\textsubscript{2} beam velocity is tuned by changing the valve temperature and seeding the H\textsubscript{2} in noble carrier gas mixtures. The collision energy is determined by the relative mean velocity between the beams and the velocity distribution of each beam ranging from 300 K to 10 mK (ref. 23).

The metastable He beam is characterized using an on-axis multichannel plate. The H\textsubscript{2} beam is characterized using a time-of-flight mass spectrometer (TOF-MS)\textsuperscript{38}, which contains an additional ionization element. The TOF-MS is positioned perpendicularly to the beams’ propagation, operating in a multi-pulsed mode, at 4 ms intervals. The reaction product ions are detected with the TOF-MS with the ionization element turned off, while the neutral molecules are characterized with the ionization element turned on. The relative rate coefficient is calculated according to the ratio between the measured signals of the products and reactants at each time interval. The rate coefficient is normalized to an absolute scale according to room-temperature thermal rate measurement of He(2\Sigma\textsubscript{+}) + H\textsubscript{2} (ref. 31).

Rate coefficients were obtained by carrying out coupled-channel quantum reactive scattering calculations using a method\textsuperscript{39} in which only the reactant configuration is explicitly considered, and knowledge of the real value of the interaction energy is sufficient. This approach is based on the assumption that the reaction proceeds irreversibly once the reactants reach a sufficiently short intermolecular distance \(R\), the ‘capture radius’, and that reactive collisions are simulated by imposing appropriate short-range boundary conditions. Such a quantum capture approach is particularly suitable for describing a chemi-ionization process. The incompleteness of the basis set only affects the correlation energy, whereas the Hartree–Fock interaction energy is converged to within 0.01 cm\textsuperscript{-1} in our calculations. Truncation of the basis set results in a shallower potential and an inner turning point that is shifted towards larger intermolecular distances.

The limit of the basis set is estimated assuming a convergence pattern \(A + B^{-1} + C^{-2} + D^{-3}\) for single-geometry calculations in the global minimum with a well depth of 14.30 cm\textsuperscript{-1} and a basis set limit for the CCSD(T) calculations in the global minimum extrapolated from the aug-cc-pV6Z and aug-cc-pV7Z basis sets (in the latter case we could afford for such calculations for T-shape and L-shape geometries) is \(\approx 14.62\) cm\textsuperscript{-1}, whereas extrapolation from the \(X = 5.7, 6.7\) basis set yields the limit \(-14.42\) cm\textsuperscript{-1}. As a conservative estimate, we take the difference between the potential obtained in aug-cc-pV6Z and the basis set limit extrapolated from \(X = 6.7\) as the uncertainty of the potential.

Data availability

The data that support the plots within this Letter and other findings of this study are available from the corresponding author upon reasonable request.

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