

Imaging quantum stereodynamics through Fraunhofer scattering of NO radicals with rare gas atoms

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Stereodynamics describes how in molecular collisions the vector properties of molecules, such as the directions in which they move and the axes about which they rotate, affect the probabilities (or ‘cross sections’) of specific processes or transitions. The main aspects of stereodynamics in inelastic atom-molecule collisions can often be understood from classical considerations, in which the particles are represented by billiard-ball-like hard objects. In a quantum picture, however, the collision is described in terms of matter waves, which can also scatter into the region of the geometrical shadow of the object and reveal detailed information on the pure quantum mechanical contribution to the stereodynamics. Here, we present measurements of irregular diffraction patterns for NO radicals colliding with rare-gas atoms that can be explained by the analytical Fraunhofer model. They reveal a hitherto overlooked dependence on (or ‘propensity rule’ for) the magnetic quantum number m of the molecules, and a new type of quantum stereodynamics that has no classical analogue or interpretation.

TOC summary: Stereodynamics describes how the vector properties of molecules affect the probabilities of specific processes in molecular collisions. Measurements of irregular diffraction patterns for NO radicals colliding with rare-gas atoms revealed a new type of quantum stereodynamics and a propensity rule for the magnetic quantum number m of the molecules.

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Interactions between individual molecules and atoms play a seminal role in many chemical processes. A widely used method to obtain a detailed knowledge of these interactions, which are captured by the intermolecular potential energy surface (PES), is to study collisions between individual molecules in the gas phase. The essence of understanding a collision is to determine how the reagents in specific initial conditions transform into specific products. The initial conditions include the collision energy and the internal quantum state of the molecules, so called *scalar properties*, but also *vector properties* such as the direction in which the molecules are moving and the orientation of the axis about which they rotate. Experimentally, the last decades have witnessed tremendous progress in controlling the initial conditions, as well as in probing the scalar and vector properties of the products [1–5]. Unraveling the correlation between the pre- and post-collision vector properties reveals the stereodynamics of the interaction, and is one of the long-term goals in understanding the fundamental microscopic principles that underly all chemistry [6–8].

For rotational energy transfer (RET) in atom-molecule collisions, the framework for theoretical descriptions of vector correlations is well established [9–14]. Experimentally, the field has progressed such that correlations between a number of the most relevant vectors needed to describe a collision can now be determined. Among these are two or three-vector correlations between, for instance, the relative velocity vectors (or the translational momenta $\hbar\mathbf{k}$ and $\hbar\mathbf{k}'$) of the two particles and the total angular momenta \mathbf{j} and \mathbf{j}' of the rotating molecule before and after the collision, respectively [4, 8, 15–20]. Measurements of $\mathbf{k}\text{-}\mathbf{j}\text{-}\mathbf{k}'\text{-}\mathbf{j}'$ four-vector correlations, which have often been regarded the pinnacle of the stereodynamics governing RET in atom-molecule collisions [7, 21–23], appear possible in the near future.

The inelastic scattering of an atom with a molecule is a process that is inherently governed by quantum mechanics, and collision cross sections can generally only be described correctly using a full quantum treatment [24–28]. The stereodynamics of the collision, however, is often surprisingly well captured by concepts from classical mechanics. In the most simple description of classically impulsive collisions, representing a large class of systems in RET, the scattering process is treated as a collision between two billiard-ball-like objects, where the object’s edges can to a good approximation be represented by impenetrable, sharp-edged surfaces. The incoming object then scatters by specular reflection, i.e., the angle of incidence to the object’s surface normal is equal to the angle of reflection (see Figure 1). This leads to significant deflection with respect to the direction of the incoming relative velocity, i.e., scattering at large angles. In this “classical regime”, just like billiard balls scattering off each other, the direction of rotation of the molecule after collision with the atom is determined by conservation of angular momentum. It can be shown that in this case,

the projection m_a of \mathbf{j} on the so-called kinematic apse, whose direction is defined by $\mathbf{k}' - \mathbf{k}$ (or the tangent to the surface), is conserved, i.e., $\Delta m_a = 0$ [29, 30]. Indeed, a large body of experiments on the stereodynamics of inelastic processes can be interpreted using this general and rather simple picture [8, 9, 31]. Certainly, differences are found as the classical impulsive approximations break down, and these then yield interesting probes for the true quantum nature of the interaction and the underlying PES [9, 32–35].

Yet, there simultaneously exists a second and fundamentally different mechanism for the particles to deflect upon a collision. In a quantum description of the scattering, the simple billiard-ball-like picture is replaced by the scattering of an incoming wave with wavevector \mathbf{k} that scatters off a sharp-edged object. Following the Huygens principle, the incoming matter waves are diffracted also into the regions of the geometrical shadow of the object. In this region, this process has no classical billiard-ball-like analogy, but is analogous to the diffraction of light by an object which, by Babinet’s principle, yields an identical diffraction pattern as scattering from a slit with an aperture complementary to the shape of the object. The resulting angular distribution is peaked in the forward direction and shows so-called Fraunhofer diffraction oscillations due to interference of waves from opposite sides of the object (see Figure 1). The resulting diffraction pattern therefore directly reflects the non-uniform shape of the object. Within the context of stereodynamics in atom-molecule collisions, a measurement of the diffraction pattern in this “quantum regime” contains information on the anisotropy of the molecule itself, i.e., the shape of the molecule and its orientation with respect to the incoming atom. This yields unprecedented possibilities to experimentally probe the stereodynamics of a collision, without actively controlling all pre-collision conditions.

In 1984, Faubel developed a quantitative model for atom-molecule collisions based on the Huygens principle, and showed that it can also be applied to describe the rotational excitation of a molecule by an atom [36]. Later, Lemeshko and Friedrich used a similar approach to derive an analytical formula for the cross section that also describes the full stereodynamics of the rotational excitation [37–39]. This formula gives the scattering amplitude, the square of which is the cross section, for excitation of a molecule in a rotational state with total angular momentum quantum number j and projection quantum number m to a state with quantum numbers j' , m' , as a function of the scattering angle θ between the initial and final wave vectors \mathbf{k} and \mathbf{k}' [37]. This so-called Fraunhofer model predicts striking irregularities in the diffraction pattern at near-forward-scattered deflection angles, which through analytical expressions can be directly related to $\mathbf{k}\text{-}\mathbf{j}\text{-}\mathbf{k}'\text{-}\mathbf{j}'$ four-vector correlations.

Whereas the stereodynamics for RET in the classical regime has been extensively studied experimentally, the stereodynamics in the quantum regime has proven much harder to capture. Measurements of a diffraction pattern near the object’s classical shadow require extremely high resolution at low deflection angles — the region that is hardest to probe experimentally — and to our knowledge no experiments exist that provide insights into the stereodynamics in this regime. In particular, the cross section patterns resulting from the Fraunhofer model have not been experimentally verified with precision, and the observation of the predicted irregular diffraction patterns has remained elusive.

Here, we present measurements of state-to-state differential cross sections in the quantum regime, using inelastic collisions of rare gas (Rg) atoms with fully state-selected and velocity-controlled NO radicals as a model system. We report the observation of the irregular diffraction patterns at near-forward scattering predicted by the analytical Fraunhofer model. The observed structures are fully reproduced by *ab initio* quantum scattering calculations, and are found to follow a hitherto overlooked quantum mechanical propensity rule for the quantum numbers m and m' , that represent the projection of the angular momenta \mathbf{j} and \mathbf{j}' onto \mathbf{k} , respectively. **This propensity rule implies that a specific Δm transition is much more likely than the other possible Δm transitions.** A theoretical analysis of the stereodynamics in the region of these irregular diffraction structures directly yields information on the shape of NO and the orientation of its bond axis with respect to the atom’s direction of attack, as well as on the plane of rotation of NO after the collision. We find that the Δm propensity rule found here reveals a new type of stereodynamics, that depends not only on the vector properties of the initial and final states, but also on the parity of the molecular wavefunction, including the electronic part. This is a direct manifestation of the pure quantum contribution to the scattering, that has no classical analogue or interpretation.

Results

We studied state-to-state DCSs for inelastic collisions between rare gas atoms and NO radicals, which initially are in the $X^2\Pi_{1/2}$, $v = 0$, $j = 1/2$, f state. The labels $X^2\Pi_{1/2}$, v , and j indicate the electronic, vibrational, and rotational state of the NO radical. Each rotational level is split into two Λ -doublet components with parity labels e and f . Figure 2 shows theoretical differential cross sections for inelastic scattering processes involving various rare gas atoms, exciting the NO radicals from the $j = 1/2$, f state into several rotational levels ranging from $j' = 7/2$ to $j' = 15/2$. Here, θ is the angle between the initial and final wavevectors \mathbf{k} and \mathbf{k}' . These DCSs (red solid curves) were

computed using quantum-mechanical close coupling (QM CC) calculations based on state-of-the-art PESs. A rich diffraction pattern, featuring a series of regular oscillations, is clearly visible in these DCSs. There is, however, one peculiar peak near the forward direction for all collision partners, as indicated by the green arrows. These peaks clearly stand out from the regular diffraction patterns; they exhibit a higher intensity and their positions Θ appear mismatched from the regular oscillatory pattern. As we will show below, these peaks—hereafter referred to as irregular diffraction peaks—obey a hitherto undiscovered Δm propensity rule, yielding unique information on the inherent stereodynamics of the collision process.

We report the experimental observation of these irregular diffraction peaks and we investigate their origin. The experiments were conducted in a high-resolution crossed beam apparatus, in which NO radicals are passed through a Stark decelerator and scatter with a beam of rare gas atoms in a counterpropagating geometry [40], after which state-to-state DCSs are recorded using velocity map [28, 41] ion imaging [42] (VMI). Figure 3 shows the three-dimensional representations of the angular scattering distributions for the systems and final states introduced in Figure 2. The corresponding images that result from simulations of the experiments, using the DCSs from the QM CC calculations as input, are also shown, together with both the DCS extracted from the experimental data and the QM CC computed DCS. Overall, there is excellent agreement between experiment and theory; the irregular diffraction peaks are clearly resolved, and their strikingly distinct appearance in comparison to the regular diffraction pattern is validated experimentally.

Discussion

The origin of the irregular diffraction behaviour at near-forward scattering angles is investigated by calculating the m, m' -composition of the state-to-state scattering cross sections. The possible values for m' range from $-j'$ to $+j'$ in steps of one and the total DCS is a sum of the different Δm contributions. In these calculations, we use the scattering frame as the natural coordinate system, i.e., m and m' are defined as the projection of \mathbf{j} and \mathbf{j}' on the wavevector \mathbf{k} of the reactants, respectively. The m, m' -resolved DCSs are shown in Figure 4 for the seven inelastic systems studied, for each possible value of Δm . Surprisingly, it can be seen in this figure that the irregular diffraction peak is mainly caused by a single Δm contribution, following the propensity rule $\Delta m = j'\epsilon\epsilon' - 1/2$ which will be explained later. Here, ϵ and ϵ' are the spectroscopic parity indices of the initial and final states of the NO molecule, respectively, which take a value of $+1$ for states with e parity and -1 for states with f parity. It should be noted that the initial $j = 1/2, f$ state is an ensemble of

$m = +1/2$ and $m = -1/2$ substates and that the $m \rightarrow m'$ and $-m \rightarrow -m'$ transitions have equal contributions. If we define Δm by assuming that we start from an initial state with $m = +1/2$, we observe, in accordance with the propensity rule, that the irregular diffraction peak for the final states $j' = 7/2, e$, $j' = 9/2, e$, $j' = 11/2, e$ and $j' = 15/2, e$ is governed by $\Delta m = -4, -5, -6$ and -8 , respectively, whereas for the final state $j' = 15/2, f$ it is dominated by $\Delta m = +7$.

The origin of the irregular diffraction peaks, and the Δm propensity rule from which they seem to originate, can be interpreted and fully understood in terms of the Fraunhofer model for RET [36, 37]. This analytical model is based on two distinct approximations: (i) the energy sudden approximation (ESA), in which the rotation of the target molecule during the collision is neglected. This is formally equivalent to omitting the rotational kinetic energy of the molecule from the Hamiltonian. (ii) The approximation of the ESA scattering amplitude by the amplitude for Fraunhofer diffraction by an impenetrable, sharp-edged object. Because of its quantum mechanical nature, this model captures diffraction, interference, and other nonclassical effects [39], which is particularly relevant for scattering angles below $\sim 30^\circ$ and for low Δj excitations. Referring back to Figure 2, the black dashed curves in this figure represent the DCSs predicted by the Fraunhofer model. Although significant scaling of the total scattering cross section is needed (Supplementary section ‘Fraunhofer model’), the Fraunhofer model in general reproduces the behavior of the QM CC computed DCSs at small scattering angles quite well, including the positions of the irregular diffraction peaks. The agreement between the DCSs computed with the Fraunhofer model and QM CC for the various systems and states is discussed in more detail in Supplementary section ‘The irregular diffraction peak’. To validate the use of the Fraunhofer model for these systems, we also performed ESA calculations in which only approximation (i) of the Fraunhofer model is assumed. The results of these calculations show the same qualitative features, but are also in quantitative agreement with the QM CC calculations without any scaling of the DCSs (Supplementary section ‘Energy Sudden Approximation’). Furthermore, we confirmed that the DCSs resulting from the Fraunhofer model and from the calculations with only the ESA approximation follow the same m, m' -composition as the QM CC computed DCSs (Supplementary section ‘Fraunhofer model’). We can therefore conclude that the observed scattering behavior around forward scattering including the irregular diffraction pattern originates from diffraction on a sharp-edged object, and we use the Fraunhofer model to gain further insight into the m, m' -resolved cross sections.

In the Fraunhofer model, the scattering amplitude is given by [37]

$$f_{\epsilon, j, m \rightarrow \epsilon', j', m'}(\theta) = \frac{ikR_0}{4\pi} J_{|\Delta m|}(kR_0\theta) \sum_{\kappa \neq 0} Q(\kappa, j, m, j', m') [(-1)^\kappa + \epsilon\epsilon'(-1)^{\Delta j}], \quad (1)$$

where $J_{|\Delta m|}(kR_0\theta)$ is a Bessel function of the first kind. The coefficients Q are related to the shape of the object from which the incoming wave scatters. This shape is defined by the NO-Rg PES and can be parameterized by a series of Legendre polynomials of order κ (Supplementary section ‘Fraunhofer model’), where $\kappa = 0$ corresponds to a spherical object and the contributions with $\kappa > 0$ describe the deviations from a spherical shape. For the special case of $j = 1/2$ considered here, it follows that each rotational transition is exclusively governed by a single value of $\kappa = j' - 1/2\epsilon\epsilon'$. From the analytical expression in Eq. (1) we can directly derive the possible values of Δm that contribute to the DCS, and calculate their relative contributions. The model predicts that for each rotational transition the largest contribution to the DCS is given by the maximum value $|\Delta m_{\max}|$ for $|\Delta m|$ that can occur (Supplementary section ‘Propensity rule’). Furthermore, a natural distinction between two types of rotational transitions emerges from the analysis. In the first type of transitions with odd values of κ , only odd values for Δm can contribute. This is the case for the final states $j' = 9/2, e$ and $j' = 15/2, f$ presented here. In the second type of transitions with even values of κ , only even Δm play a role, which occurs for the final states $j' = 7/2, e$, $j' = 11/2, e$, and $j' = 15/2, e$ presented here.

Using these rules, we can completely explain the peculiar scattering behavior observed around forward scattering. In the Fraunhofer model, the contribution of a specific Δm transition to the DCS is proportional to $[J_{|\Delta m|}(kR_0\theta)]^2$, where k is the wavenumber of the incoming wave, and R_0 is the radius of the hard-shell target [37]. At $\theta = 0^\circ$, J_0 is the only Bessel function that can contribute and all intensity comes from $\Delta m = 0$. This value for Δm , however, is only allowed for transitions with even values of $j'\epsilon\epsilon' - 1/2$, and indeed a strong scattering peak at $\theta = 0^\circ$ is observed for transitions of the second type. By contrast, a dip at $\theta = 0^\circ$ is observed for transitions with odd $j'\epsilon\epsilon' - 1/2$, reflecting the absence of $\Delta m = 0$ for transitions of the first type.

For $\theta > 0$, also transitions with $|\Delta m| > 0$ start contributing. By the nature of Bessel functions, for each possible value of $|\Delta m|$ the first peak of the Bessel function is the most intense. For higher values of $|\Delta m|$ this first peak is located at larger angles. This explains the position, Θ , of the irregular diffraction peak; it is the first peak of the Bessel function caused by the component with $|\Delta m_{\max}|$, which — according to the rules discussed above — carries maximum intensity (Supplementary section ‘The irregular diffraction peak’). The position of the irregular peak shifts to larger scattering angles with increasing Δj , since a higher value for $|\Delta m_{\max}|$ is possible for such transitions. At smaller scattering angles, different values for $|\Delta m| < |\Delta m_{\max}|$ play a role, but these transitions have a relatively small contribution to the DCS. Together, however, they can result in extra peaks in the region $0 \leq \theta \leq \Theta$.

The occurrence of the irregular diffraction peak can be directly related to a specific orientation of the NO radical with respect to the incoming atom. Let us assume that the incoming wave propagates in the z -direction, see Figure 5. The diffraction pattern is then governed by the projection of the object in the x, y -plane, i.e., the plane perpendicular to \mathbf{k} [36]. Without loss of generality, we can define a coordinate system such that the pre-collision NO bond axis is located in the x, z -plane, and makes an angle β with the z -axis. The influence of the value of β on the diffraction pattern is illustrated in Figure 5 for the NO + Ar, $j' = 11/2, e$ system for which $\kappa = 6$. When $\beta = 0^\circ$, the NO axis points along \mathbf{k} , which results in a circular projection of the molecule’s shape on the x, y -plane. The Fraunhofer model then predicts that the DCS is governed by $\Delta m = 0$ transitions (Supplementary section ‘Stereodynamics’). For $\beta \neq 0$ this projection is no longer circular, and transitions with $\Delta m > 0$ contribute. The anisotropy is maximum for $\beta = \pi/2$, where the maximum value for $|\Delta m|$ has its largest intensity. The Fraunhofer model predicts the largest contribution to the scattering cross section for $|\Delta m| = \kappa$, and, as discussed above, directly explains the irregular diffraction peak and the Δm propensity rule. This result can be interpreted as a direct manifestation of the Huygens principle in molecular collisions: maximum diffraction occurs for the maximum anisotropy of the molecule’s shape. This is the case when the atom strikes the NO radical from the side. Here, \mathbf{r} , the initial orientation of NO relative to the vector \mathbf{k} , is oriented perpendicular to \mathbf{k} .

When the atom scatters from NO in the direction of the irregular peak, Θ , the scattering can thus be associated with a correlation between \mathbf{k} , \mathbf{r} , \mathbf{k}' , and \mathbf{j}' . Note that this correlation reveals information on the reagent orientation, without actively controlling \mathbf{r} in the experiment. In fact, the correlation found here is much more precise than what would have been possible in an experiment where the bond axis is controlled using static electric fields, since the bond axis distribution for oriented molecules in the initial $j = 1/2, f$ state is only mildly anisotropic [19]. This rather surprising situation is a direct consequence of the pure quantum mechanical origin of the stereodynamics studied here.

This quantum mechanical origin is also apparent from the propensity rule $\Delta m = j'\epsilon\epsilon' - 1/2$, which shows that the parity of the NO radical strongly affects the stereodynamics. For instance, for the NO + Xe system, the final state $j' = 15/2, f$ is dominated by the $m = \pm 1/2 \rightarrow m' = \pm 15/2$ ($\Delta m = 7$) transitions, whereas the final state $j' = 15/2, e$ is dominated by the $m = \pm 1/2 \rightarrow m' = \mp 15/2$ ($\Delta m = -8$) transitions. In the first case, the sense of rotation is preserved upon rotational excitation of the molecule, whereas in the second it is reversed. Similarly, collisions that populate the same final state j', ϵ' but originate from either the $j = 1/2, e$ or the $j = 1/2, f$ initial state either preserve or reverse the sense of rotation. Only quantum mechanics can explain this difference: the

energy difference between the nearly degenerate $1/2, e$ and $1/2, f$ states is completely negligible compared to the collision energy, the total angular momenta are obviously identical, but also all vector properties involving either \mathbf{j} , \mathbf{r} , or the spin \mathbf{S} of the two initial states are identical (as derived in the Supplementary section ‘Vector properties for different parity states’). Thus, we conclude that no classical vector correlation model could explain the full stereodynamics in the Fraunhofer regime of these collisions. This sharply contrasts with the situation found in the “classical regime” at larger scattering angles, where the propensity $\Delta m_a = 0$ with respect to the kinematic apse is valid (Supplementary section ‘Kinematic apse frame’). The latter propensity is generally found to be identical for the different parities of the NO radical [31], as is also expected from the billiard-ball-like interpretation of the scattering process in which electronic degrees of freedom and the parity do not play a role. The kinematic apse frame approximations, however, are expected to break down for the non-classical, low scattering angle regime studied here. We indeed found that the irregular peak generally does not follow the apse-related propensity rule (Supplementary section ‘Kinematic apse model’).

Measurements of peculiarities in the diffraction pattern near forward scattering as presented here reveal a new type of stereodynamics of molecular collisions that is very different in nature from the well-known stereodynamics found at larger scattering angles. The effects found here are purely quantum mechanical in nature and have no classical billiard-ball-like interpretation or analogue. Yet, together with a theoretical analysis, they give insights into the stereodynamics of the collision, without actively controlling the orientation of the molecule before the collision, and without actively probing the polarization of the products. They arise naturally from the collision itself, and are captured by a hitherto undiscovered propensity rule for Δm in the scattering frame. These effects can be interpreted in terms of the Huygens principle for the scattering of matter waves from a sharp-edged object.

Methods

The QM CC calculations, the experiments, and the experimental data analysis are extensively described in Ref. [40]. We performed QM CC calculations using a scattering program for open-shell diatom-atom scattering [43]. A channel basis set was used including all NO rotational levels up to $j = 20.5$ and all partial wave contributions up to a total angular momentum of $J = 160.5$ for NO + He and $J = 250.5$ for the other systems to reach convergence. For the propagation of the wavefunction, we used the renormalized Numerov method on a grid in R starting at 3.5 bohr for

NO + He, at 3.0 bohr for NO + Ne, and at 4.5 bohr for NO + Ar, Kr, and Xe, up to 60 bohr for all systems. Here, R is the distance between the rare gas atom and the center-of-mass of the NO molecule. We calculated state-to-state scattering cross sections using V_{sum} and V_{dif} PESs for NO + He [44], NO + Ne [45], NO + Ar [46], NO + Kr [47], and NO + Xe [48] at mean experimental collision energies of 730 cm^{-1} for NO + He, 715 cm^{-1} for NO + Ne, 725 cm^{-1} for NO + Ar, 575 cm^{-1} for NO + Kr, and 490, 500, and 510 cm^{-1} for NO + Xe.

Experimentally, a Nijmegen pulsed valve [49] produced a beam of NO molecules that was passed through a 2.6-m-long Stark decelerator, resulting in a packet of NO molecules in the $X^2\Pi_{1/2}$, $v = 0$, $j = 1/2$, f state with a mean velocity of 350 m/s, a longitudinal velocity spread of 2.1 m/s (1σ), and an angular spread of 0.1° (1σ). This bunch of molecules collided under an angle of 180° with a beam of neat rare gas atoms, produced by a Nijmegen pulsed valve. The scattered NO molecules were state-selectively ionized by an ion-recoil free (1+1') resonance enhanced multiphoton ionization scheme using two tunable dye lasers that crossed each other at right angles and that were directed parallel to the detector plane. The excitation laser made an angle of 45° with both molecular beams and its polarization was parallel to the detector plane. We verified that this polarization only slightly influences the relative intensities, and not the number or positions of peaks. Both lasers were focused to obtain a small ionization volume. The ions were detected using a conventional VMI detector.

The combination of a Stark decelerator and VMI in a counterpropagating beam geometry results in scattering images with unprecedented angular resolution in which diffraction oscillations can be resolved, even for weak inelastic channels with relatively high Δj as studied here [40, 50]. Within our experimental geometry, the Doppler effect caused a slight asymmetry in intensity with respect to the relative velocity vector of the reagents. A correction for the Doppler effect resulted in symmetric images and enabled us to perform the inverse Abel transformation using the BASEX suite of programs [51]. Angular scattering intensity distributions were extracted from the resulting images and were divided by the apparatus function to reveal the DCS of the scattering process. This apparatus function was calculated using simulations of the experiment that take the temporal, spatial and velocity distributions of both molecular beams and the laser geometry into account. The resulting DCS was compared with theoretical predictions.

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Author contributions

Competing financial interests

The authors declare no competing financial interests.

FIG. 1: Illustration of the classical and wave-like regimes that we use to describe stereodynamics in molecular collisions. In a quantum mechanical description of the scattering of hard objects, two different phenomena occur simultaneously. The first one can be interpreted as a classical collision between billiard-ball-like objects and, in quantum mechanics, may be described by an incoming wave being reflected by specular reflection. The outgoing waves (or particles) are mostly deflected to large angles, and produce phenomena such as rainbows [52]. The second type of scattering is purely wave-like in character and is the analogue of light being scattered from an object according to the Huygens principle. An incoming plane wave (black) scatters off the object, producing outgoing waves at much smaller scattering angles with interference patterns characteristic of the shape of the object. These patterns (orange) can be visualized on a screen.

FIG. 2: Differential cross sections for NO radicals colliding with various rare gas atoms resulting from the QM CC calculations (red solid curve) and the Fraunhofer model (black dashed curve). One intense peak near the forward direction stands out from the normal diffraction pattern. This irregular peak is indicated by a green arrow. The DCSs from the Fraunhofer model are scaled, as explained in the Supplementary section ‘Fraunhofer model’. In general, the behavior of the QM CC computed DCSs around forward scattering is reproduced quite well by the Fraunhofer model. We can therefore conclude that the scattering behavior at small angles originates from diffraction of matter waves on a sharp-edged object.

FIG. 3: Angular distributions and differential cross sections for NO radicals colliding with various rare gas atoms. The left column contains three-dimensional representations of the experimental velocity-mapped ion images, whereas the middle column contains the simulated images. The experimental images are corrected for the Doppler effect and the BASEX suite of programs [51] is used to apply an inverse Abel transformation on both the experimental and simulated images to eliminate the blurring caused by the crushing of three-dimensional Newton spheres on a two-dimensional detector. The right column shows the comparison between the DCSs extracted from the measurements (black solid curves) and the QM CC computed DCSs (red dashed curves). Diffraction oscillations are clearly visible in most of the images and DCSs. One intense peak near the forward direction stands out from the normal diffraction pattern. This irregular peak is indicated by a green arrow. Since the inverse Abel transformation creates artificial noise on the center line, we cannot trust the intensity in the forward direction and this intensity is set to zero. The forward direction corresponds to $\theta = 0^\circ$.

FIG. 4: **The m, m' -resolved differential cross sections obtained from the QM CC calculations in the scattering frame.** The thick red line shows the total QM CC computed DCS and the other lines show the m, m' -contributions to this total DCS. The green arrows indicate the irregular diffraction peaks. The insets show parts of the DCSs on an enlarged scale. **The irregular peak is mainly caused by a single Δm contribution, following the propensity rule $\Delta m = j'\epsilon\epsilon' - 1/2$. This propensity can be understood in terms of the Fraunhofer model for rotational energy transfer.**

FIG. 5: **Illustration of the stereodynamics for NO + Ar, $j' = 11/2, e$ collisions, for which $\kappa = 6$, leading to the irregular diffraction peak.** Plane waves with wavevector \mathbf{k} move along the z -axis, and hit an impenetrable object that can have different orientations with respect to \mathbf{k} as indicated by the angle β . Different orientations of the molecule are related to different values for Δm that contribute to the elastic Fraunhofer cross section, I , as defined in Supplementary section ‘Stereodynamics’. This is illustrated in panels *a, c*, and *e*, showing I as function of the scattering angle θ for $\beta = 0, 45$, and 90° , respectively. The scattering angle Θ at which the irregular peak occurs for NO + Ar, $j' = 11/2, e$ is indicated by the green arrow. The corresponding projection of the obstacle on the x, y -plane for $\kappa = 6$ is shown in panels *b, d*, and *f*. Deviations from a circular projection are exaggerated for clarity and indicated by blue (extra area) and red (missing area). Panel *g* graphically shows the relevant vector properties for $\beta = 90^\circ$, illustrating the stereodynamics resulting in the irregular diffraction peak.