Supplementary Material: Differential cross sections and collision-induced rotational alignment in the inelastic scattering of NO(X) by Xe

Mark Brouard*,1 Helen Chadwick,1, a) Sean D. S. Gordon,1, b) Cornelia G. Heid,1 Balazs Hornung,1, c) Bethan Nichols,1, d) Jacek Kłos,2 Pablo G. Jambrina,3 and F. Javier Aoiz4

1) The Department of Chemistry, University of Oxford, The Chemistry Research Laboratory, 12 Mansfield Road, Oxford, OX1 3TA, UK

2) Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, USA

3) Departamento de Química Física. Facultad de Ciencias Químicas, University of Salamanca, Salamanca, Spain

4) Departamento de Química Física, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain

(Dated: 17 February 2020)

a) Current address: Department of Chemistry, Swansea University, Singleton Park, Swansea, SA2 8PP, UK
b) Current address: OneSwitch Technologies, Bâtiment C, EPFL Innovation Park, 1015 Lausanne, Switzerland
c) Current address: intellisense.io, 60 Station Road, Cambridge, CB1 2JH, UK
d) Current address: 400 Vermont Ave, Moss Beach, CA 94038, USA
OUTLINE

The Supplementary Material includes details about the method to determine the experimental collision energy (Section I), a brief presentation of the integral cross sections (ICSs; Section II) and differential cross sections (DCSs; Section III) for the final $\epsilon$ $\Lambda$-doublet levels, a discussion of \ell-type rainbow and parity effects (Section III), and finally a presentation and discussion of the collision-induced alignment, focused on the experimental data for the $j_{2+}^{(2)}(\theta)$ polarization dependent differential cross sections (PDDCSs; Section IV).

I. DETERMINATION OF THE EXPERIMENTAL COLLISION ENERGY

The radius of the experimental ion images as a function of $j'$ can be used to determine the collision energy, $E_{\text{coll.}}$.\(^{1,2}\) This method requires high signal intensities, particularly for transitions to high rotational states, in order to accurately determine the image radius. The Newton sphere radius is given in terms of the outgoing velocity by

$$\frac{r_{\text{img}}}{\text{PV}} = |v'_{\text{NO}}| = \frac{m_{\text{Rg}}}{m_{\text{NO}} + m_{\text{Rg}}} \sqrt{\frac{2(E_{\text{Coll}} - \Delta E_{\text{rot}}(j'))}{\mu}},$$

with PV the pixel-to-velocity ratio, a quantity which converts detector pixel number into m s\(^{-1}\). $\Delta E_{\text{rot}}(j')$ is the change in rotational energy of the NO(X) upon excitation and $\mu$ is the reduced mass of the NO + Rg system. The decrease in the image radius continues as $j'$ increases, until all the available kinetic energy has been converted into rotation and the image has become as small as possible. By fitting the experimental image radii, Eq. (1), as a function of $j'$, the pixel-to-velocity ratio and the collision energy can be determined. A plot of the fitted function versus image radius at several different $j'$ is shown in Fig. 1 and yields PV = 11.1 ± 0.2 m s\(^{-1}\) and $E_{\text{coll}} = 519 ± 7$ cm\(^{-1}\).

II. COMPARISON OF INTEGRAL CROSS SECTIONS

A comparison of the ICSs for the various rare gases at a collision energy of 510 cm\(^{-1}\) is shown in supplementary Fig. 2. All transitions shown start in the initial $\epsilon = f$ state. The ICSs for collisions of NO(X) with xenon are larger than for collisions with any of the other rare gases.\(^{3}\) This increase in integral cross section with rare gas atomic number reflects the increasing range of the potential energy surfaces (PESs).\(^{3}\)
FIG. 1. Plot of the radius of the velocity mapped NO(X)–Xe spin-orbit conserving images (red circles) versus the change in rotational state, $\Delta j = j' - j$. The functional form of Eq. (1) (blue continuous line) is fitted to the experimental data to obtain the pixel-to-velocity ratio and the collision energy.

Parity effects$^{3,4}$ (see Section III) are clearly visible in the ICSs for all of the rare gas systems. The integral cross sections oscillate from high to low depending on whether the collision is parity conserving or parity changing.$^3$ This is evident at low $\Delta j (\equiv j' - j)$ in both the spin-orbit conserving and spin-orbit changing transitions. The spin-orbit changing states show the same trends as the spin-orbit conserving ones, but have much smaller integral cross sections.

FIG. 2. Comparison of the ICSs as a function of $\Delta j = j' - j$ for scattering from the $|j = 0.5, \Omega = 0.5, \epsilon = f\rangle$ state into particular $|j', \Omega', \epsilon'\rangle$ final states for different NO(X)–Rg collision systems at a collision energy of 510 cm$^{-1}$. Spin-orbit conserving transitions to final $f$ and $e$ states are shown in the left two panels and the corresponding spin-orbit changing transitions in the two panels on the right. A clear progression of the ICS is seen with increasing atomic number of the rare gas atom, reflecting the increasing range of the PES.
III. DIFFERENTIAL CROSS SECTIONS

The main text presents the differential cross sections (DCSs) for $\epsilon$-conserving ($f \rightarrow f$) transitions for the scattering of NO(X) with Xe at 519 cm$^{-1}$. The $\epsilon$-changing ($f \rightarrow e$) DCSs display a number of similar characteristics and are presented here for both the spin-orbit conserving (supplementary Fig. 3) and the spin-orbit changing manifold (supplementary Fig. 4). As with the DCS data shown in the main text, these figures compare the experimental DCSs with the results of the quantum mechanical (QM) calculations on the ab initio PESs of Klos et al.$^3$ Overall, the agreement between the experimental and QM DCSs is reasonably good, with the poorest agreement found for the high $j'$ spin-orbit changing collisions, which have relatively small integral cross sections, and are thus harder to measure experimentally than the spin-orbit conserving collisions.

A. $\ell$-type rainbows

One striking feature in the $\epsilon$-conserving images shown in the main text and the $\epsilon$-changing images in supplementary Fig. 3 are the pronounced peaks referred to as $\ell$-type rainbows.$^{3,5-9}$ These peaks are visible in the parity changing low $j'$ states, for example at $\theta_R \sim 35^\circ$ for $j' = 5.5 \, f$ in the main text or at $\theta_R \sim 35^\circ$ for the $j' = 4.5 \, e$ state in supplementary Fig. 3. Here, $\ell$ is the magnitude of the orbital angular momentum of the NO–Xe pair. Low-$\ell$ collisions are head-on, while high-$\ell$ collisions are glancing encounters.$^{5-7,10}$ An $\ell$-type rainbow arises from attractive forces between the NO and Xe and, as in atom-atom scattering,$^7$ can be attributed to the focusing of trajectories at scattering angles at the maximum (or minimum if the deflection angle, $\chi$, rather than the scattering angle, $\theta = |\chi|$, is represented) of the classical deflection function. As the NO(X)–Xe PES has a larger attractive limb than the NO(X)–Kr potential, higher rotational states display an $\ell$-type rainbow, allowing it to be seen up to $j' = 5.5 \, f$.$^3$ As was the case with Kr,$^8$ the rainbow in NO(X)–Xe scattering arises from trajectories scattering at impact parameters of $b \geq 4.5$ Å.$^3$ The comparable impact parameters reflect the similar well depths and the importance of the attractive part of the potential in the two systems.

The quasi-classical trajectory (QCT) deflection functions shown in supplementary Fig. 5
FIG. 3. Experimental and fitted velocity-map ion images (top) and corresponding DCSs (bottom), extracted from the fitted images, are shown for the spin-orbit conserving and Λ-doublet changing $|j = 0.5, \Omega = 0.5, \epsilon = f \rangle \rightarrow |j', \Omega' = 0.5, \epsilon' = e \rangle$ transitions in the $\Delta j = 4 - 16$ range. The upper two rows of images are for horizontal (H) polarization, and the lower two rows for vertical (V) polarization of the probe laser. The experimental DCSs represent the average of the DCSs extracted for the two polarizations. The direction of the relative velocity vector is indicated by the white arrow in the top left image. The QM predicted DCSs (red continuous lines) are compared to the experimental parity conserving (blue dashed lines) or parity changing (green dashed lines) DCSs, obtained using a quantum mechanical polarization correction, and the experimental DCSs obtained using the classical kinematic apse model (brown dotted lines).
FIG. 4. Experimental and fitted velocity-map ion images (top) and corresponding DCSs (bottom), extracted from the fitted images, are shown for the spin-orbit and Λ-doublet changing $|j = 0.5, \Omega = 0.5, \rho = f\rangle \rightarrow |j', \Omega' = 1.5, \rho' = e\rangle$ transitions in the $\Delta j = 2 - 11$ range. The upper two rows of images are for horizontal (H) polarization, and the lower two rows for vertical (V) polarization of the probe laser. The experimental DCSs represent the average of the DCSs extracted for the two polarizations. The QM predicted DCSs (red continuous lines) are compared to the experimental parity conserving (blue dashed lines) or parity changing (green dashed lines) DCSs, obtained using a quantum mechanical polarization correction, and the experimental DCSs obtained using the classical kinematic apse model (brown dotted lines).

show that for the Xe system, the glory impact parameter is at $b \sim 4.5$ Å. Above this value, the deflection angle is negative, leading to far-side scattering.

As can be seen from the deflection functions, the rainbow diminishes as $\Delta j$ increases until
FIG. 5. QCT deflection functions from trajectories calculated on the $V_{\text{sum}}$ PES for NO(X) + Xe. The $\ell$-type rainbow is clearly seen as a maximum in the deflection function, corresponding to scattering at the rainbow angle, $\theta_R \approx 35^\circ$.

no such features are obvious at around $\Delta j = 7$. The main reason for this is that the effect of the attractive parts of the potential diminishes for $\Delta j \geq 7$, as large impact parameter collisions can no longer deliver enough torque to access high rotational states. The classically forbidden region occurs for small scattering angles and high impact parameters.

It has previously been observed for krypton scattering with NO(X) that the parity of a transition also plays a significant role in the appearance of the $\ell$-type rainbow. The classical calculations neglect parity effects, and predict an $\ell$-type rainbow for all low $\Delta j$ transitions. However, as in krypton scattering with NO(X), experimentally (and in the QM calculations), the rainbow is only observed for parity changing transitions.

B. Parity effects

Due to the quantum mechanical nature of the collision, the classical picture of a trajectory sampling the potential is no longer appropriate. Individual partial waves can interfere with one another, leading to constructive or destructive interference as a function of the scattering angle. Interference between trajectories scattering off the N-end and O-end can influence the observed differential, and hence integral cross sections. Previous work has shown that a simple four-path model can qualitatively reproduce the observed interference pattern by limiting the scattering to four Jacobi angles that correspond to head-on or side-on collisions at either end of an ellipsoid representing the molecule. Within the model, the scattering amplitudes for the parity conserving and the parity changing transitions are
FIG. 6. Four-path (blue line)$^{1,13}$ and QM (red line) calculations for the NO(X)–Xe collision system at 519 cm$^{-1}$. The top panel shows the DCSs for the parity conserving transitions and the bottom panel the DCSs for the parity changing transitions for $\Delta j = 6, 8, 11, 14$.

given as,

$$f_{i \rightarrow f}^{\text{cons}}(\theta) = 2 + \exp(-i\Delta\phi_N) + \exp(-i\Delta\phi_O),$$

$$f_{i \rightarrow f}^{\text{chan}}(\theta) = \exp(-i(\Delta\phi_N - \pi)) + \exp(-i\Delta\phi_O),$$

with the phase shifts between the N-side (O-side) and the N-end (O-side) of the molecule, $\Delta\phi_N$ ($\Delta\phi_O$), given by$^{1,13}$

$$\Delta\phi_{N/O} = \sqrt{\Delta j_{\theta,N/O}^2 - j'^2 - j}$$
$$\times \left[\frac{\pi}{2} + i \ln \left(1 - \frac{j'^2}{\Delta j_{\theta,N/O}^2} + \frac{ij'^2}{\Delta j_{\theta,N/O}}\right)\right].$$

Here, the values of $\Delta j_{\theta,N/O}$ are the scattering angle dependent functions,

$$\Delta j_{\theta,N/O} = -\frac{i}{2} \Delta j_{\text{max},N/O} \left[\exp \left(+\frac{i}{2}\theta\right) - \exp \left(-\frac{i}{2}\theta\right)\right].$$

The maximum allowed change of the angular momentum, $\Delta j_{\text{max},N/O}$, is related to the wavevector, $k_{uj}$, by $\Delta j_{\text{max},N/O} = 2k_{uj}(A - B)_{N/O}$, where $A_{N/O}$ and $B_{N/O}$ are the major and minor semi-axes (on the N- and O-end of the molecule) obtained from the hard-shell contour of the $V_{\text{sum}}$ potential surface. The values of $(A - B)_N$ and $(A - B)_O$ for NO(X)–Xe are $5.7 \times 10^{-11}$ m and $4.3 \times 10^{-11}$ m, respectively.

Inspection of supplementary Fig. 6 shows that the four-path model qualitatively matches the number and approximate positions of the oscillations in the DCSs. The parity-conserving
transitions (supplementary Fig. 6, top panel) are characterized by multiply peaked DCSs, caused by interference between the different sides and ends of the NO(X) molecule, whereas the parity changing transitions have a single peak caused by interference between the two ends of the NO(X) molecule.

The frequency and number of oscillations is governed by two factors; the anisotropy of the potential encoded in the difference between the A and B semi-axes, and the de Broglie wavelength of the system. The Xe–NO(X) system has the smallest de Broglie wavelength of any of the rare gases for a given collision energy, leading to the appearance of multiple peaks in the DCSs calculated with the four-path model. The simple four-path model is a good indicator for the parity-dependence of the oscillations. Furthermore, it shows that these oscillations arise from interference between trajectories sampling multiple bond axis orientations.

Another parity related phenomenon is the so-called parity pair effect,\(^1,^{15−17}\) where the DCS for a \(j' = n + 0.5f\) state is similar to the DCS of a \(j' = n - 0.5e\) state, but with a slightly different magnitude. This effect can be observed when comparing the experimental images in supplementary Fig. 3 and those shown in Fig. 4 of the main text. Parity pairs can be rationalized in terms of a direct scattering picture,\(^1,^{13,16,17}\) in which the potential matrix elements directly couple the initial and final states, and are proportional to the following terms:

\[
\langle V_{\ell 0} \rangle \propto \frac{1}{2} \left[ 1 - \epsilon^\ell (-1)^{\Delta j + 1} \right] \left( j'lj - \Omega 00 \right) \left( \ell'\ell000 \right) \left\{ j\ell J\ell j'\ell \right\} .
\]  
(6)

Here, the (…) are the 3-\(j\) symbols, and {…} are the 6-\(j\) symbols.\(^{18}\) The equation above holds in the limit of Hund’s case (a) and so works best for low to intermediate rotational states of NO(X). Higher states are best described as being accessed by tiers of virtual transitions.\(^{16}\) Since the parity pairs are coupled by the same matrix elements, the resulting DCSs will be quite similar. In the case of parity changing transitions, both odd and even matrix elements are required to effect the transition, thus, if the odd terms in the potential are zero, these transitions disappear. In a homonuclear molecule, in which the odd terms of the potential are zero, parity changing transitions do not exist.

Compared to inelastic scattering of NO(X) by the lighter rare gases, the parity pair behavior is somewhat less apparent in the case of Xe. For the higher \(\Delta j\) transitions, there is some evidence of parity pairs, but the effect is diminished compared to that in He,\(^{16,17}\) Ne,\(^{19}\) Ar,\(^{1,13}\) and Kr\(^{8,11}\) scattering. This is a consequence of the fact that direct scattering
plays a more minor role in the case of NO(X) + Xe.

Parity effects are also evident in the integral cross sections (see supplementary Fig. 2). Since NO is a near-homonuclear molecule, the parity conserving transitions (those to final states with even/odd $\Delta j$ and $f/e$ spectroscopic index) possess markedly larger DCSs than the parity changing transitions (those to final states with odd/even $\Delta j$ and $f/e$ spectroscopic index). As a consequence, the integral cross sections for parity conserving transitions are significantly larger than for parity changing transitions.

IV. COLLISION-INDUCED ROTATIONAL ALIGNMENT

A. Experimental renormalized PDDCSs

The main text discussed the $\rho_0^{(2)}(\theta)$ renormalized PDDCS to which the experiment is primarily sensitive. Although the experiment is partially sensitive to $\rho_1^{(2)}(\theta)$, the contribution to the observed ion image is very small, only approximately 5% of the total, so although this moment was included in the fit, no meaningful interpretation could be made. The experiment is also sensitive to the $\rho_2^{(2)}(\theta)$ renormalized PDDCSs, which are presented in supplementary Fig. 7.

The experimental normalized difference images tend to be slightly asymmetric about $k$, with greater positive intensity on the side of the image corresponding to slow laboratory motion (the ‘slow side’ of the image). Since the normalized difference images should be symmetric about $k$ due to the removal of the flux-density effects, the enhanced intensity is thought to be due to collisional and/or magnetic depolarization. Molecules scattered to the slow side of the image spend longer in the interaction region as the LAB frame velocities are lower, giving an opportunity for collisional or magnetic depolarization to occur before ionization takes place. If significant depolarization is taking place, the experimental images will slightly underestimate the magnitude of the alignment moments $\rho_0^{(2)}(\theta)$ and $\rho_2^{(2)}(\theta)$. The effect of magnetic depolarization was minimised by placing $\mu$-metal shielding around the interaction region to block stray magnetic fields. The experimental $\rho_2^{(2)}(\theta)$ renormalized PDDCSs, shown in Fig. 7, agree somewhat less well with the results of the QM calculations than the $\rho_0^{(2)}(\theta)$ renormalized PDDCSs shown in the main text. This is to be expected as the experiment is less sensitive to $\rho_2^{(2)}(\theta)$ than to $\rho_0^{(2)}(\theta)$. The main discrepancies are
FIG. 7. The experimentally determined $\rho^{(2)}_{2+}$ renormalized PDDCSs for the NO(X)–Xe collision system, recorded at a collision energy of 519 cm$^{-1}$. The experimental data, with parity conserving transitions shown as blue dashed lines and parity changing collisions as green dashed lines, are compared with the QM PDDCSs (red continuous lines). The grey and blue shaded plots indicate spin-orbit conserving and changing transitions to final $e$ states, respectively; all other plots represent spin-orbit conserving transitions to final $f$ states.

seen for the lowest final rotational states, where the rapid changes in magnitude and lack of intensity in the sideways and backward scattered region make fitting more prone to error. The forward scattered region tends to be the least well reproduced in all the fits. However, in general, the agreement between the QM and the experimental data is good. The $\rho^{(2)}_{2+}(\theta)$ renormalized PDDCS, like the $\rho^{(2)}_{0}(\theta)$ renormalized PDDCS, is also governed primarily by impulsive forces and is only slightly altered by the effects of attractive forces.
FIG. 8. Quantum (red solid lines) and quasi-classical (blue dotted lines) renormalized PDDCSs, \( \rho_{2+}^{(2)} \), for the NO(X)–Xe collision system. The QM renormalized PDDCSs have been summed over the final and averaged over the initial \( \Lambda \)-doublet levels for comparison with the closed-shell QCT results.

B. QCT versus QM renormalized PDDCSs

The \( \rho_{2+}^{(2)}(\theta) \) moments determined from the QM and via quasi-classical trajectory (QCT) calculations are compared in supplementary Fig. 8. As with the QCT and QM data for the \( \rho_0^{(2)}(\theta) \) moments shown in the main text, the QM renormalized PDDCSs have been summed and averaged over \( \Lambda \)-doublets. At low \( \Delta j \), the \( \rho_{2+}^{(2)}(\theta) \) polarization moments obtained from classical calculations compare reasonably well with the QM renormalized PDDCSs. The QCT moments tend to slightly overestimate the degree of alignment in the scattering plane at low scattering angles for \( \Delta j = 4 - 7 \). In general, the agreement with the QCT and QM calculations gets worse with increasing \( \Delta j \), primarily because the QCT \( \rho_{2+}^{(2)}(\theta) \) moments are ill-defined in the classically forbidden region at low scattering angles.

C. Kinematic apse model

Classically, the projection of the angular momentum, \( m_a \), onto the kinematic apse direction can be shown to be rigorously conserved during an impulsive collision.\(^{21,22}\) The
kinematic apse model has been used successfully to produce an alignment correction to the experimental ion images of NO(X) scattering with the rare gases such as He, Ne, and Ar. In the model, the kinematic apse, \( \hat{a} \), lies in the scattering plane and is defined as

\[
\hat{a} = \frac{k - k'}{|k - k'|}. \tag{7}
\]

The renormalized PDDCSs can be obtained from considering the geometry of the scattering system, as described by Hornung et al.\textsuperscript{23,24} The resulting moments are given in terms of the reduced rotation matrices:\textsuperscript{23,24}

\[
\rho_{00}^{\{k\}}(\theta) = \frac{1}{2} [1 + (-1)^k] d_{00}^k (-\beta(\theta)) \langle j' \frac{1}{2}, k|0| j' \frac{1}{2} \rangle \tag{8a}
\]

\[
\rho_{q+}^{\{k\}}(\theta) = (-1)^q \frac{1}{\sqrt{2}} [1 + (-1)^k] d_{0q}^k (-\beta(\theta)) \langle j' \frac{1}{2}, k|0| j' \frac{1}{2} \rangle, \tag{8b}
\]

where \( \langle j' \frac{1}{2}, k|0| j' \frac{1}{2} \rangle \) is a Clebsch–Gordan coefficient and \( d_{0q}^k(\cdot \cdot \cdot) \) is the reduced rotation matrix element. The apse angle, \( \beta(\theta) \), between \( k \) and \( \hat{a} \), appearing in the reduced rotation matrix element, is determined from a set of geometric transforms\textsuperscript{23,24}

\[
\cos \beta(\theta) = \frac{D - \cos \theta}{\sqrt{D^2 + 1 - 2D \cos \theta}}, \tag{9}
\]

with \( D = (E_{\text{coll}} - \Delta E_{\text{rot}})/E_{\text{coll}} \), and \( \Delta E_{\text{rot}} \) the change in rotational energy of the NO(X).

Although collisions of NO(X) with Xe are not strictly hard-shell, as prescribed by the kinematic apse model, the model is surprisingly reliable at predicting the collision-induced rotational alignment of NO(X). A comparison of the apse model calculations with QMHS and rigorous QM calculations is shown in the main text and in supplementary Fig. 9.

The kinematic apse model predicts ‘Frisbee’-like rotation at very low scattering angles (\( \theta \lesssim 5^\circ \)) where \( k \) and \( k' \) are almost parallel.\textsuperscript{20,23} If the collision results in scattering of relatively few degrees (\( 5^\circ \lesssim \theta \lesssim 20^\circ \)), the apse direction is almost perpendicular to \( k \) and the NO(X) rotates in a ‘propeller’-like motion, which, after averaging over the azimuthal angle, results in \( j' \) polarization in the plane of the molecular beams, preferentially parallel to \( k \). This accounts for the rapid rise of \( \rho_0^{\{2\}}(\theta) \) in the low scattering angle region (see Figs. 9 and 10 in the main text). In the sideways to backwards direction, the apse vector \( \hat{a} \) begins to be more parallel to \( k \) again, resulting in more ‘Frisbee’-like rotation, and \( j' \) aligned out of the scattering plane.

In supplementary Fig. 9, the largely impulsive origin of the \( \rho_2^{\{2\}}(\theta) \) moment is again manifested by the qualitative agreement of the kinematic apse model data, the QMHS data
FIG. 9. QM (red continuous line), kinematic apse (blue dotted line) and QMHS (purple dashed line) \( \rho_{2+}^{(2)} \) renormalized PDDCSs for the NO(X)–Xe collision system. The QM renormalized PDDCSs have been summed over the final and averaged over the initial \( \Lambda \)-doublet levels for comparison with the closed-shell QMHS and apse model calculations.

and the results of the full QM calculations. At scattering angles of 0° and 180°, where the apse vector is parallel to \( k \), and \( j' \) roughly perpendicular to it, the \( x \)- and \( y \)-axes of the scattering frame are not unambiguously defined and alignment is equally probable along the two axes, resulting in a net alignment of zero. For small scattering angles (5° \( \lesssim \theta \lesssim 20° \)), with the apse vector roughly perpendicular to \( k \), \( j' \) must point out of the scattering plane, i.e. along the \( y \)-axis, in order for its projection onto the apse to be conserved.

Strong oscillations, that are not present in the QM results, are evident in the \( \rho_{2+}^{(2)}(\theta) \) renormalized PDDCSs from the QMHS calculations. These oscillations tend to occur at high scattering angles in the low \( \Delta j \) transitions, where the \( \rho_{2+}^{(2)}(\theta) \) alignment moment is very small. It is possible that the oscillations arise due to small inaccuracies in the QMHS calculation that are exacerbated at these low values. In addition, the QM and kinematic apse models deviate at low scattering angles, where the attractive region of the potential is dominant. This appears most obvious at high \( \Delta j \), rather than low \( \Delta j \), where attractive forces play a more important role. The deviations indicate that the classical kinematic apse equations are inadequate in the extended classically forbidden region of the higher \( \Delta j \).
FIG. 10. QM DCSs calculated on the NO(X)–Xe potential surface (red solid lines) compared to those performed on the NO(X)–Ar surface with the mass of Xe (blue dotted lines). The features at low scattering angle associated with the attractive part of the PES are considerably more prominent in the Xe potential.

transitions.

D. QM calculations on the NO(X)-Ar surface with Xe mass

Additional quantum scattering calculations were performed on the NO(X)–Ar potential energy surface, using the reduced mass of the NO(X)–Xe system. The DCSs on the NO(X)–Xe potential (with the Xe mass, red lines) are compared to those performed on the NO(X)–Ar potential with the mass of Xe (blue dotted lines) in Fig. 10. Since the Ar potential has a shorter range than the Xe potential surface, the effect of the attractive limb can be easily distinguished. In the \( j' = 3.5f \) state, for example, the \( \ell \)-type rainbow is shifted towards higher scattering angles in the NO(X)–Xe potential, as the strength of the attractive part results in larger deflection angles. For the same reason, the intensity in the forward
scattered region, where glory scattering dominates, is significantly larger in the calculations run on the Xe potential than those run on the Ar potential with the modified reduced mass.

REFERENCES


