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Correlated energy transfer in rotationally and spin–orbit inelastic collisions of NO($X^2\Pi_{1/2}, j = 1/2f$) with $O_2(X^3\Sigma_g^−)$

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We present a combined experimental and theoretical study of state-to-state inelastic scattering of NO($X^2\Pi_{1/2}, j = 1/2f$) with $O_2(X^3\Sigma_g^−)$ molecules at a collision energy of 480 cm$^{-1}$, focusing in particular on the observation and interpretation of correlated excitations in both NO and $O_2$. Various final states of the NO radical, in both spin–orbit manifolds, were measured with high resolution using a crossed molecular beam apparatus which employs a combination of Stark deceleration and velocity map imaging. Velocity map imaging directly measures both the angular distribution and the radial velocity distribution of the scattered NO molecules, which probes the kinetic energy uptake or release and hence correlated excitations of NO–$O_2$ pairs. Simultaneous excitations of NO and $O_2$ were resolved for all studied final states of NO. In all cases, the experimental results excellently agree with the results of simulations based on quantum scattering calculations. Trends are discussed by analyzing the scattering wave functions from the calculations.

1 Introduction

It has been a long-standing goal in physical chemistry to probe potential energy surfaces (PESs), which govern intermolecular interactions. The study of inelastic collisions between molecules in the gas-phase is a well-established approach to this end. Combining the velocity map imaging (VMI) technique$^1$ and crossed molecular beam (CMB) technique,$^2$ the rotational energy transfer (RET) in atom-molecule collisions has been extensively studied.$^3$ In bimolecular inelastic collisions, the degrees of freedom of both molecules couple and therefore give rise to much more complex dynamics, when compared to atom-molecule collisions. The added degree of complexity offers opportunities to address dynamical questions including the so-called product pairs, i.e., the simultaneous rotational excitation in both collision partners. By measuring product pairs, detailed information of the RET in both collision partner can be obtained. However, extending atom-molecule inelastic collision studies to bimolecular systems has remained challenging, and RET in bimolecular inelastic collisions is largely unexplored and not well understood.

On the experimental side, the main difficulty of studying bimolecular inelastic collisions compared to atom-molecule systems is the appearance of additional product channels from the simultaneous rotational excitation of both collision partners.

Correlations between excitations of both colliders, referred to as product-pairs, may in principle be probed using VMI. Rotational energy transfer to or from the collision partner will result in a lower or greater kinetic energy, respectively. In VMI, one measures the velocity distribution, such that these different kinetic energies lead to a series of nested spheres,$^4$ whose projections on the two-dimensional detector yield a set of concentric circles. These circles in principle contain the full kinematic information of the collision process, including the integral and differential state-resolved correlated cross sections. It is, however, extremely challenging to experimentally resolve the individual circles, as the experimental blurring associated with, for instance, the collision energy spread and the crushing of spheres on the detector plane is in most cases much larger than the inherent spacing between the circles.$^5$–$^{12}$ Recently, we reported the first observation of rotational product pair correlations in NO–$O_2$ inelastic collisions at a collision energy of 160 cm$^{-1}$,$^1$ by using a Stark decelerator to produce reagent beams of NO with very narrow velocity spread.$^{14}$

Here, we present a joint experimental and theoretical study of state-to-state resolved RET in the inelastic collisions of NO($X^2\Pi_{1/2}, j = 1/2f$) with $O_2(X^3\Sigma_g^−)$. As an extension of our previous experiment,$^{13}$ we study the dynamics at a higher collision energy of 480 cm$^{-1}$ such that excitations of NO to higher rotational states can be probed. Furthermore, we study rotational excitation of NO within the $X^2\Pi_{1/2}$ ($F_1$) manifold, but we also study spin–orbit changing transitions to the $X^2\Pi_{3/2}$ ($F_3$)
through the decelerator, a packet of NO loaded into a 2.6 meter long Stark decelerator. After passing pressure of 3 bar though a NPV. The O\(_2\)(X\(_3\)) is labeled by the quantum number and spin–rotation coupling 40 into three components labeled by a beam of neat O\(_2\) at an intersection angle of 90°.

The O\(_2\) beam is produced by expanding pure O\(_2\) at a typical pressure of 3 bar though a NPV. The O\(_2\)(X\(_2\)) rotational energy level diagram is shown in Fig. 2. Each rotational state is labeled by the quantum number \(N\), and is split by spin–spin and spin–rotation coupling.40 into three components labeled by the quantum number \(j\) with \(j = N - \frac{1}{2}, N, N + \frac{1}{2}\). The initial rotational state distribution of O\(_2\) was probed by measuring a (2 + 1) resonance enhanced multiphoton ionization (REMPI) spectrum. Fig. 2 shows the comparison between the measured spectrum and a spectrum simulated by PGOPHER41 using a rotational temperature of 10 K. From this comparison we conclude that the O\(_2\) molecules emerge from NPV predominantly in the \(N = 1\) state, with a small amount of O\(_2\) in the \(N = 3\) state.

The NO radicals were state-selectively ionized by a (1 + 1′) REMPI scheme using two pulsed dye laser systems. After ionization, the NO ions were collected by VMI optics. The collision energy was calibrated using the method described by Ovlee et al.,28,38 and determined to be 480 cm\(^{-1}\).

2.2 Quantum scattering calculations

Quantum mechanical scattering calculations were performed using the coupled-channels method. The details of the calculations are discussed in detail in ref. 13, and specific details are given here for completeness. The \(ab\) initio coupled potential energy surfaces were taken from ref. 13. These have been calculated using coupled cluster theory for the diagonal potential, and multi-reference configuration for the off-diagonal potential. The transformation to the diabatic representation has been determined using the multiple-property-based algorithm of ref. 42. The basis set used in the scattering calculations was truncated by the requirement \(\int_S \leq 17/2\) and \(N_{SO} \leq 7\), total angular momenta up to \(j = 401/2\) were included, and the radial grid extended from 4.5 to 30\(a_0\) in steps of 0.05\(a_0\). Matching to scattering boundary conditions at the last grid point yields the S-matrices, from which the relevant DCSs are computed. Unlike what is described in ref. 13, we did not use the recoupling approach to compute fine-structure resolved cross sections, as the fine structure is not resolved experimentally and this treatment complicates the subsequent simulations.

We note that channels with \(N_{SO} = 9\) and 11 are also energetically accessible in the experiment, but their inclusion in the scattering calculations was not considered, as this would hugely increase both CPU time and memory requirements.

3 Analysis and simulation

3.1 Analysis method

The experimental scattering images were analyzed as described in more detail in ref. 13. We here only briefly describe the method for completeness, by illustrating the procedure using a scattering image as displayed in Fig. 3a as an example. This image pertains to
excitation of NO into the $j_{\text{NO}} = 13/2f$ state, as is also indicated by the red arrow in the energy level diagram shown in Fig. 4. In the collision process, the collision partner O$_2$ can be excited simultaneously to various rotational states $N'_{\text{O}_2}$, as indicated by the set of colored arrows in Fig. 4. The multiple rings visible in the experimental scattering image correspond to these various scattering channels.

In order to assign the pair-correlated rotational excitations of O$_2$, the radial scattering distribution is analyzed within the angular range enclosed by the two red dashed traces, between $-40^\circ$ and $-5^\circ$, simply by integrating the radial intensity as a function of the radius $R$. This angular window was chosen as the radial resolution and scattering intensities are optimal here, while it avoids the forward scattering region that may be contaminated by unwanted initial population in the primary NO packet. Fig. 3c displays the radial distribution obtained from image a. The various rings can be assigned by comparing the radial distribution with the expected ring positions based on energy and momentum conservation. These positions, referred to as the kinematic cut-off positions, are indicated by the vertical dashed lines, together with the corresponding label $N'_{\text{O}_2}$ for the final rotational state of O$_2$. It is seen that the maximum in intensity of the observed rings in the scattering image is shifted by 1 to 2 pixels inwards with respect to the kinematic cut-off. This shift is a result of both the projection of the three-dimensional Newton sphere onto two-dimensional detection plane and of the velocity spread of O$_2$ beam, and is fully accounted for in simulations of the experiment. For each ring, the angular distribution is analyzed using conventional methods as described before. Briefly, a circular annulus of a few pixels wide is defined. The scattering intensity within this annulus is then integrated, and evaluated as a function of the scattering angle $\theta$.

3.2 Simulation

To compare the experimental results with theoretical predictions, we perform full simulations of the VMI images, based on cross sections from quantum scattering calculations. These simulations take all experimental conditions into account, such as beam spreads, temporal overlap, ionization volume, and spectral width of the laser. The resulting simulated images are analyzed in an identical way as the experimental VMI images, such that radial and angular distributions can be directly compared. Since most O$_2$ molecules in the primary beam reside in the $N'_{\text{O}_2} = 1$ state, we only take this initial state into account in our simulations. For a given final state of NO $j_{\text{NO}}$, we first simulate a scattering image for each of the possible $N_{\text{O}_2} = 1 \rightarrow N'_{\text{O}_2}$ transitions individually.
taking the appropriate DCS for the transition, and finally add all
images together. Since in the quantum scattering calculations
only $O_2$ states up to $N_{O_2} = 7$ could be included, we limit the
simulations for each $J_{NO}$ state to the four product-pair channels
$N_{O_2}' = 1, 3, 5, 7$. It is noted that some experimental images
clearly contain signal for $N_{O_2}' = 9$ and 11 (see Section 4), and
this is thus unaccounted for in the simulations.

As mentioned before, the calculations presented here do not
include the $O_2$ fine structure components $j_{O_2}$. Each rotational
transition, $N_{O_2} \rightarrow N_{O_2}'$, in principle consists of 9 fine-structure-
resolved transitions, $N_{O_2}, J_{O_2} \rightarrow N_{O_2}', j_{O_2}$. These are not resolved
experimentally, but the difference in excitation energy does
contribute to a broadening of the observed rotational transitions.
This effect is therefore also unaccounted for in our simulations.

4 Results and discussion

4.1 Spin–orbit conserving transitions of NO

Fig. 5 displays the experimental and simulated VMI images of
NO molecules for spin–orbit conserving ($F_1 \rightarrow F_1$) transitions.
Excitation of NO up to $J_{NO} = 17/2$ was probed. Both final states
of e and f parity were probed, in so far as isolated REMPI
transitions were available to probe these levels. All images are
presented such that the forward direction appears on the right-
hand side of the images. For low values of $J_{NO}$, small segments
of the images around the forward direction are masked because
of the imperfect state selection of the NO packet. It is seen that
multiple rings are clearly resolved in all images. Furthermore,
the relative intensity of the rings in each image depend strongly on
$J_{NO}$. For $J_{NO} \leq 7/2$, the inner rings in the images are much weaker
than the outermost ring, indicating that elastic scattering of $O_2$ is
preferred over inelastic scattering. For higher values of $J_{NO}$, the inner
rings become more intense and inelastic in $O_2$ gains importance.

Overall, the experimental images show excellent agreement
with the simulated images, both in terms of the relative
intensities of the rings and in terms of the angular distributions.
This is quantified further by the radial profiles presented in
Fig. 6, and by the angular profiles presented in Fig. 7. For
the latter, we only present the angular distributions for the
$N_{O_2} = 1 \rightarrow N_{O_2}' = 1$ outer ring, as for a given value for $J_{NO}$, we
observe only marginal differences in the angular distributions of
the different rings. In the radial distribution for the 11/2e
channel, one can observe an additional outer ring which is
not present in the simulations. This additional ring is an
experimental artefact that is caused by partially overlapping
REMPI transition probing the 5/2f level. It is noted again that
our simulations exclude excitations of $O_2$ into the
$N_{O_2}' = 9$ and 11 levels (although they are clearly visible in the experimental
profiles), and they exclude the fine-structure splitting of the
$O_2$ transitions. The latter one causes the radial profiles to be
consistently broader in the experimental results when compared
to the simulations. From the radial and angular distributions,
interesting trends can be discerned. As $J_{NO}$ increases, inelasticity
in $O_2$ indeed gains significant importance, as was already apparent
from visual inspection of the images in Fig. 5. In addition, the
angular distribution shifts from forward scattered to sideways
scattered. This can be understood by a simple classical picture
of RET, where low amounts of RET are associated with higher impact parameter, \( b \), that tend to be forward scattered, while higher amounts of RET associated with smaller \( b \) tend to lead to sideways or backward scattering. Note that for certain final \( J_{\text{NO}} \) states, a pronounced rainbow feature is observed that is in good agreement with theoretical predictions.

### 4.2 Spin–orbit changing transitions of NO

We now turn to spin–orbit changing \( F_1 \to F_2 \) transitions. Fig. 8–10 show the experimental and simulated scattering images, the radial distributions, and the angular distribution of the outermost \( N_{O_2} = 1 \to N_{O_2} = 1 \) ring, respectively, for \( F_1 \to F_2 \) transitions as a function of \( J_{\text{NO}} \). As for the spin–orbit conserving \( F_1 \to F_1 \) transitions, the agreement between the experiment and simulation is excellent throughout. Similar trends are observed for \( F_1 \to F_2 \) transitions compared to \( F_1 \to F_1 \) transitions. Excitation of O\(_2\) becomes stronger as the final rotational quantum number of NO, \( J_{\text{NO}} \), increases. The angular distribution of the scattered NO molecules shift from forward to sideways scattered as \( J_{\text{NO}} \) increases. Rainbow features, however, are not observed for the scattering channels investigated here.

Although the \( F_1 \to F_1 \) and \( F_1 \to F_2 \) transitions show similar trends as a function of \( J_{\text{NO}} \), it is worth noting that spin–orbit changing transitions require more energy transfer for excitations with the same \( \Delta J = J_{\text{NO}} - J_{\text{NO}} \) when compared to spin–orbit conserving transitions. This offers the intriguing possibility to investigate whether the observed trends are governed predominantly by the transfer of angular momentum or rotational energy. Consider excitation to the rotational states \( 17/2f, F_1 \) and \( 5/2f, F_2 \) of NO. These states are almost energetically degenerate, although there is a significant difference in the angular momenta. The scattering images pertaining to these final states differ qualitatively significantly. For excitation to the \( 17/2f, F_1 \) level, O\(_2\) scatters inelastically and the inner rings carry high intensity. By contrast, for excitation to the \( 5/2f, F_2 \) level, O\(_2\) scatters predominantly elastically and the inner rings are less intense.

### 4.3 Interpretation

To interpret the observations, we analyze the scattering wave functions obtained from the coupled-channels calculations. These wave functions are validated by the comparison of...
theoretical and experimental differential scattering cross sections, and the detailed analysis that the theoretical wave functions permit yields additional insight into the scattering dynamics. We analyze so-called opacity functions, which contain information on the range at which transitions occur, and the vector correlation of the angular momenta of the collisionally-excited molecules. A similar analysis has been performed in our previous study, at lower collision energies, and we here focus on the differences between spin–orbit conserving and changing transitions, which were not probed previously.\textsuperscript{13}

Fig. 8  Experimental (Exp) and corresponding simulated (Sim) images for the spin–orbit changing ($F_1 \rightarrow F_2$) collisions of NO with O$_2$. Images are presented such that the forward direction appears on the right-hand side.

Fig. 9  Radial distributions derived from the experimental (Exp) and simulated images (Sim) from Fig. 8.
4.3.1 Opacity functions. The opacity function is defined as

$$P_{i\rightarrow f}(b) = \frac{k}{2\pi b} \sigma_{i\rightarrow f}(b),$$

where $b = \ell/k$ is the classical impact parameter and $\sigma_{i\rightarrow f}(b)$ is the contribution of a single partial wave, $\ell$, to the cross section for the transition from initial state $i$ to final state $f$. The total cross section is given by

$$\sigma_{i\rightarrow f} = 2\pi \int_0^\infty P_{i\rightarrow f}(b) b db,$$

in the classical limit of continuous $b$, such that the opacity function, $P_{i\rightarrow f}$, can be thought of as the probability of a transition $i \rightarrow f$ for a collision occurring with well-defined classical impact parameter, $b$.

Fig. 11 shows the opacity plots for various spin–orbit conserving transitions of NO and the product pairs $N'_{O_2} = 1, 3, 5, 7$. For nearly elastic transitions, for both $j_{NO}$ and $N'_{O_2}$, there is a dominant contribution to the cross section by impact parameters larger than the classical turning point of the interaction potential, which occurs around $7a_0$. That is, the cross section is dominated by rotational excitation in glancing collisions, rather than head-on collisions. As either or both $j_{NO}$ and $N'_{O_2}$ increases, the collision mechanism becomes more short ranged, and the cross section is dominated by impact parameters $b \lesssim 7a_0$ for which the molecules collide head on. This is completely consistent with our previous study at lower collision energies.\(^{13}\)

Fig. 12 shows similar opacity plots for spin–orbit changing transitions to the NO F\(_2\) manifold. In this case, even for low $j_{NO}$ and $N'_{O_2}$, the cross sections are dominated by short-ranged collisions with impact parameters $b \lesssim 7a_0$. This represents a surprising result as it shows that the range of the collision mechanism is governed by the amount of energy transferred, rather than by the amount of angular momentum transferred. The latter may have been expected as long-range interactions correspond to low rank terms in a tensorial expansion of the PES, and hence directly drive transitions with small changes in the monomer angular momenta only. In addition, the qualitative comparison between the channels that excite NO to the near-degenerate 17/2f, F\(_1\) and 5/2f, F\(_2\) levels, as described above, would have suggested that the amount of angular momentum transferred is more important than the amount of energy transferred.

4.3.2 Vector correlations of $j_A$ and $j_B$. We furthermore analyze the vector correlation of the angular momenta of the collisionally-excited molecules. This is accomplished by computing partial cross sections restricted to specific $j_{AB}$ and $j'_{AB}$, the angular momentum quantum numbers associated with $j_{AB} = j_A + j_B$, the vector sum of the monomer angular momenta. In the initial state,
The above explanation - like torque induced by interactions acting on the point of closest approach - applies to pure rotational excitation. Instead, spin–orbit changing transitions are driven by the off-diagonal potential, which couples the $\Delta = \pm 1$ NO substates, and is induced by non-adiabatic coupling between these asymptotically-degenerate substates.

### 5 Conclusions and outlook

We have presented high-resolution measurements of product pairs for inelastic collisions of state-selected NO radicals with O$_2$ molecules at a collision energy of 480 cm$^{-1}$. Both spin–orbit changing and spin–orbit conserving scattering channels were studied for a large number of final rotational states of NO. In general, the observations are in excellent agreement with the predictions of quantum mechanical coupled-channels scattering calculations, which are based on recently developed NO–O$_2$ PESs. For both spin–orbit conserving and changing transitions of NO, similar correlations of energy transfer in NO and O$_2$ were observed: the higher the energy uptake by NO, the higher probability that O$_2$ is excited to higher rotational states. Interesting differences were also observed. For spin–orbit conserving transitions, near-elastic collisions are dominated by the higher probability that O$_2$ is excited to higher rotational states. By contrast, spin–orbit changing transitions are driven by head-on collisions associated with small impact parameters, even for low amounts of angular momentum transferred. Furthermore, the monomer angular momenta induced in spin–orbit conserving collisions describe a vector correlation, which can be understood classically. For spin–orbit changing transitions, the monomer angular momenta do not display this vector correlation.
Conflicts of interest
The authors declare no competing financial interest.

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