CHEMICAL PHYSICS

Molecular square dancing in CO-CO collisions

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Knowledge of rotational energy transfer (RET) involving carbon monoxide (CO) molecules is crucial for the interpretation of astrophysical data. As of now, our nearly perfect understanding of atom-molecule scattering shows that RET usually occurs by only a simple “bump” between partners. To advance molecular dynamics to the next step in complexity, we studied molecule-molecule scattering in great detail for collision between two CO molecules. Using advanced imaging methods and quasi-classical and fully quantum theory, we found that a synchronous movement can occur during CO-CO collisions, whereby a bump is followed by a move similar to a “do-si-do” in square dancing. This resulted in little angular deflection but high RET to both partners, a very unusual combination. The associated conditions suggest that this process can occur in other molecule-molecule systems.

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If art follows nature, then the square dance call “swing your partner, do-si-do” must have been inspired by “dance moves” laid out during the collision of two CO molecules, where despite a considerable “swing” (conversion of translational to rotational energy), both molecules leave the encounter moving forward. Up to now, the dance moves for rotational energy transfer (RET) in atom-molecule scattering have been described as being annoyingly predictable (1): Large swings are always accompanied by about-face or backward scattering. Advanced experimental methods, particularly velocity map imaging (VMI) (2), can now expose details of molecule-molecule scattering with a resolution sufficient to recognize new collision processes involving unexpected motion, as shown in this report. Although the likelihood of the unexpected process observed here depends strongly on the initial collision geometry, we show that it is responsible for production of up to 20% of high-energy rotational states.

Our current understanding of RET, which is the most probable energy-exchange process during a molecular collision, is nearly perfect for atom-diatom collisions, based in detail on accurate fully quantum calculations and in general on simple and precise models that treat the collision as a point mass colliding with a hard-shell ellipsoid scaled to the shape of the molecule. Along with predicting the directionality of scattering, these models also lead to the exponential energy gap law (EGL) (3), where the probability of collision-induced transfer is found to be proportional to \( \exp(-\Delta E) \), with \( \Delta E \) being the energy difference between the ground and excited rotational states and \( C \) being a constant. The EGL ascribes a much lower probability of rotational excitation to higher \( j \) levels, where \( j \) is the rotational quantum number. A key question is whether this picture always applies to molecule-molecule scattering.

Because a single collision can cause rotational excitation of both collision partners in molecule-molecule interactions, the ideal RET experiment provides for each possible product-pair the directionality of scattering, also known as the pair-correlated differential scattering cross section (PC-DCS). This measurement is now possible when using crossed molecular beam scattering (4) combined with VMI, where each molecular beam has a narrow (5) or ultra-narrow and controlled (6) velocity distribution and contains only the lowest \( j = 0 \) rotational state of the molecule of interest. Nascent product molecules in a chosen final \( (j') \) state are then converted to ions by resonant laser ionization, and their velocity distribution is mapped using VMI with high speed and angular resolution onto a two-dimensional image (7-9). Our study explores (nearly) identical-molecule scattering, which offers conceptual and computational advantages over mixed molecules. We characterize RET in the collision system \( ^{13}\text{CO}(j = 0) + ^{12}\text{CO}(j = 0) \rightarrow ^{13}\text{CO}(j') + ^{12}\text{CO}(j'') \), where, for practical reasons, specific \( j' \) rotational quantum levels of \( ^{13}\text{CO} \) product molecules are detected. Besides being of fundamental interest, CO-CO scattering is relevant in the pure CO atmosphere of exotic exoplanets (10) and in cometary atmospheres, where the CO is the second most abundant molecule after \( \text{H}_2\text{O} \). CO has a small dipole moment and forms a dimer with two stable, end-on antiparallel geometries with relatively small binding energies of about 125 cm\(^{-1}\) (11). The CO-CO center-of-mass distance is substantially larger for the geometry when the C ends are closer than when the O ends are closer, because the C end is effectively larger than the O end. We show that the latter property also has interesting effects in CO-CO collisions.

We report here the scattering of \( ^{12}\text{CO}(j = 0) \) with \( ^{13}\text{CO}(j = 0) \) to form \( ^{13}\text{CO}(j = 15) \), where the experiment yields the PC-DCS for each \( j' \) level of \( ^{13}\text{CO}(j' = 0, 1, 2, \ldots, j'_{\text{max}}) \) paired with \( ^{12}\text{CO}(j' = 15) \). However, in this so-called “heavy-heavy” collision system where the CO rotation energy spacing is much smaller than the collision energy, only partial (but sufficient) resolution of the product-pair DCSs was possible. Note that full resolution of PC-DCSs for collisions of NO with \( \text{O}_2 \) and \( \text{ND}_2\text{D}_2 \) have been recently reported, both at a lower collision energy than that of the present system.

Crossed beam scattering with identical molecules poses severe overlap problems that were solved here using a beam of \( ^{13}\text{CO} \) and selective \( ^{12}\text{CO} \) ionization. Moreover, we detected final states that were too high in energy to be populated by collision of \( ^{13}\text{CO} \) with the carrier gas used for rotational-state-cooling of CO in the partner beam, as described in the supplementary materials (SM). The conditions that avoided overlap allowed detection of \( ^{13}\text{CO}(j' > 10) \) final states from CO-CO scattering at a 1460-cm\(^{-1}\) collision energy, which, for a “heavy-heavy” system, has too many open channels at present for analysis by fully quantum theory. Quasi-classical trajectory (QCT) analysis on an accurate CO-CO potential energy surface (14, 15), proven to be reliable for CO-He and CO-Ar collisions in previous publications (16, 17), was used here to simulate the scattering process. The QCT results were confirmed at a lower collision energy by fully quantum close-coupling (CC) calculations and compared with those from a previous fully quantum theory study on CO-CO (18) described in the SM.

Details of the experiment and analysis methods are presented in the SM. Raw velocity map images of \( ^{13}\text{CO}(j' = 15) \) molecules formed by scattering with CO and with \( \text{N}_2 \) for comparison (fig. S1) showed an obvious difference of “extra” signal in the forward scattering region around high \( j' = j'' \), hereafter labeled as forward-scattered symmetric excitation (FSSE), which was present for \( ^{13}\text{CO}-\text{CO} \) but missing for \( ^{13}\text{CO}-\text{N}_2 \). After correcting the raw images for ionization laser polarization sensitivity and the density-flux transform, the experimental data are plotted in Fig. 1 in \( (j', \theta) \) coordinates, where the image radius is converted to the \( j' \) position. FSSE signal peaked at \( j' = 15 \), which was seen only in the CO + CO data, as indicated by an arrow in both the experimental plot (Fig. 1, left) and the corresponding theoretical prediction (Fig. 1, right). An explanation for why FSSE is absent for the kinematically similar CO + \( \text{N}_2 \) system was provided by the QCT analysis, as described later in the text.

The dotted diagonal lines shown in Fig. 1 indicate regions of atom-molecule-type behavior for inelastic scattering, where conversion
of translational energy to an increasingly larger amount of rotational energy required an increasingly “head-on” collision with the target molecule, and thus a smaller impact parameter (the distance of closest approach that would have occurred without any interaction). Small-impact parameter collisions result in scattering toward increasingly larger (backward) angles. The longer dotted diagonal line follows the ridge of the primary rainbow (a build-up of trajectories that pass the threshold for rotational excitation \(j\)), whereas the shorter dotted line, at larger scattering angles, follows the expected secondary rainbow.

Figure 1 shows satisfactory agreement, including the FSSE signal, between experiment and QCT. A full description of the QCT results, including the FSSE versus EGL relative yields in CO-CO RET at 1460- and 500-cm\(^{-1}\) collision energies, is presented in the SM section. The \((j, j’ = 15, 15)\) pair-correlated differential cross section with forward scattering angles of 30° or less originated predominantly from trajectories with an impact parameter between 3.0 and 3.5 Å. More than half of the trajectories leading to forward scattering were very similar to the prototypical trajectories shown in movie S1 and sketched in Fig. 2. For comparison, movie S2 shows non-FSSE collisions producing (15, 5) products.

Three unusual features in Fig. 2 characterized FSSE: (i) initial collision geometry, (ii) abruptness of RET, and (iii) the do-si-do movement. The collision geometry is shown in the middle region of Fig. 2 as a series of stills at time positions A to F, from a visual molecular dynamics (19) visualization of a prototypical \((j, j’ = 15, 15)\) trajectory. The most effective initial geometry was where the two C ends collide, with an impact parameter of 3.2 Å. Forward scattering was most probable when both the molecular axes were in the same collision plane \((\theta = 0)\), defined with respect to the internuclear separation vector \(\mathbf{R}\). The interaction energy curve in Fig. 2 shows that collision at point \(B\), 240 fs, was abrupt and accounted for the translation to RET, with both molecules rotating individually and in the same sense. Most notable in Fig. 2 was the relatively constant value of the center-of-mass distance between the diatoms \((R)\) from \(-240\) to \(-600\) fs, which was roughly half of a CO \((j = 15)\) rotational period. The average speed here was \(\pm 492\) m/s, so near-zero recoil means that the molecules swing around each other with little repulsion or additional torque to reach the O-end facing or back-to-back (do-si-do) configuration. In square dancing, a feature of the do-si-do is that both pairs of feet point outward, avoiding tripping. In the case of CO-N\(_2\), FSSE was not possible because of “tripping” by the ellipsoidal N\(_2\) partner. Two ovoids, colliding first at their large ends, are needed for FSSE. As shown in fig. S5C, FSSE was not due to the displaced center of mass in CO but rather a size (electronic volume) effect of the potential energy surface. Following the do-si-do, which allows RET far beyond EGL predictions, the rotationally excited molecules departed in the forward-scattering direction.

FSSE collisions showed two sequential interactions, where the first, C-C end, collision resulted in translation to RET, whereas the second interaction at the O-O end reoriented the recoil direction of the two molecules as they separated, without changing the rotational energy. Viewing the process in reverse, the O-O-end interaction first swings the molecules around closer to each other so that when they slam together on the C-C ends, all rotation energy is up-converted to faster linear motion. QCT yielded a final impact parameter \(b_t = 4.0 \pm 0.1\) Å, a value that is 25% larger than the expected value of 3.2 Å.

**Fig. 1.** Contour plot of experimental and theoretical PC-DCSs for \(^{13}\)CO + CO and \(^{13}\)CO + N\(_2\) inelastic scattering to the \(j’ \left(^{13}\text{CO}\right) = 15\) final state. (Left) Partially resolved experimental PC-DCSs with scattering angle on the horizontal axis; the vertical axis indicates the final rotational state of the CO or N\(_2\) coproduct, \(j’(\text{CO or N}_2)\), which ranges from the low states \([j’(\text{CO or N}_2) = 0 \text{ to } 6]\) at the bottom to the higher states at the top, up to \(j’_{\text{max}}(\text{CO or N}_2) = 19\). The \(j’(\text{CO or N}_2) = 0 \text{ to } 6\) signals are not resolved. (Right) Theoretical PC-DCSs fully resolved in the individual final rotational state of coproduct CO or N\(_2\), with \(j’(\text{CO or N}_2)\) convoluted over the experimental uncertainty. The arrow in both panels for \(^{13}\)CO + CO indicates the region of the unexpected forward-scattered high \(j’ = j’\) signal, which is not observed for the kinematically similar \(^{13}\)CO + N\(_2\) scattering.
At a lower collision energy (500 cm⁻¹), QCT predicted the same FSSE process, peaking at \((j', f') = (8, 8)\), with forward scattering being most probable at \(b_i = 3.0\) Å. FSSE occurred for both collision energies with roughly 60% conversion of translational to rotational energy. Fully quantum CC calculations at 500 cm⁻¹ confirmed an amount of rotational excitation for near-symmetric excitation similar to that at 1460 cm⁻¹ collision energy, peaking even closer to forward scattering than the QCT results (fig. S8). CC calculations also revealed a propensity for collisions resulting in even values of final \(j\) (fig. S7), reflecting the nearly homonuclear diatomic nature of CO.

Pair-correlated excitation cross sections observed previously for NO-O₂ collisions (22) also deviate from EGL behavior in that strong excitation in both the NO and O₂ molecules is prefered over excitation in one collision partner only, even though the total amount of energy transfer is higher. Opacity function analysis showed that the inelastic channels for high rotational-state excitation were governed by short-range head-on collisions and that only the long-range contributions follow "normal" behavior (22).

CO-CO is not a particularly unusual collision system. We suggest that FSSE-like behavior is also possible in mixed-molecule scattering systems that match the criteria found here: (i) large ends colliding first and (ii) an abrupt energy transfer coupled with a swing around toward the small-end configuration before departure. Potential energy surfaces with minor topological features compared with the collision energy could allow the pathway observed here for CO-CO scattering. As molecule-molecule scattering is explored in higher detail with new methods, more unusual molecular dance moves could be expected.

REFERENCES AND NOTES
20. Z. F. Sun, M. C. van Hemert, J. Loreau, A. van der Avoird, A. G. Suits, D. H. Parker, Molecular square dancing in CO-CO collisions dataset, Dryad (2020); https://doi.org/10.5061/dryad.8g96mkp0.

ACKNOWLEDGMENTS
We thank B. v. d. Meerakker, G. C. Groenenboom, and R. J. A. Scheidsbach for discussion. R. J. A. Scheidsbach, C. K. Bishwakarma, G. Sarma, and L. Gerritsen developed the theoretical methods used in this work. Funding: The experimental part of this work was funded by the Dutch National Science Foundation (NWO) under grant number TOP 715.013.002 and the Dutch Astrochemistry Network DANNI under grant number 648.000.024. A.G.S. acknowledges support from the U.S. National Science Foundation (NSF) under award number CHE-1955239. Author contributions: The experimental work and data analysis were carried out by Z.F.S., A.G.S., and D.H.P. Theoretical calculations were done by M.C.V.H., J.L., and A.v.d.A. All authors contributed to interpreting the results and writing the manuscript. Competing interests: None declared. Data and materials availability: All data are available in the main text or in the supplementary materials and at Dryad (20).

SUPPLEMENTARY MATERIALS
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Experimental Methods
Theoretical Methods
Supplementary Text
Figs. S1 to S8
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References (21–31)
Data S1
Movies S1 and S2
19 March 2020; accepted 22 May 2020
10.1126/science.aar2729

Fig. 2. Trajectory details for two colliding CO\((j = 0)\) molecules, ending with both \(j = 15\). \(R_{CC}\) and \(R_{OO}\) are internuclear distances, and \(R\) is the center-of-mass distance between the two diatoms. The dihedral angle \(\phi\) is 180° when the molecular axes are coplanar and antiparallel, and \(\theta_a\) and \(\theta_b\) are the angles between the \(R\) vector and the bond directions of molecules \(a\) (traveling up in the figure) and \(b\) (traveling down), respectively. In the top panel, \(\delta\) is the angle between \(R_{CC}\) and \(R_{OO}\) in the figure) and \(b\). In the figure, (respectively). Molecular rotation begins at position \(B\) and reaches the angle values shown under each position. Collision energy is 1460 cm⁻¹. See text and SM (movie S1) for more details.

Fig. 3. Cartoon of scattering-angle reorientation.
With the collision geometry at position \(A\) in Fig. 2, or its mirror image, both CO molecules rotate in the same sense, and when the intermolecular interaction during the collision couples with this rotational motion, the recoil direction will rotate toward the forward direction.

than the initial \(b_i = 3.2\) Å, which was a simple result of conservation of energy and angular momentum when starting with two \(j = 0\) molecules. As \(R\) expanded by 0.8 Å during the collision, it also rotated, causing the final recoil direction to turn from sideways toward forward, as illustrated in Fig. 3.
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Science 369 (6501), 307-309.
DOI: 10.1126/science.aan2729

Molecule-molecule forward scattering
The classical picture of nonreactive inelastic scattering implies that a considerable transfer of translational to rotational energy should be accompanied by backward scattering. Using cross–molecular beam scattering combined with velocity map imaging, Sun et al. provide evidence of an unusual pair-correlated channel in the collision of carbon monoxide (CO) molecules, specifically $^{12}$CO with $^{13}$CO, both initially in the ground rotational state. These two molecules were scattered into the forward direction, both finally in the high rotational states. The experimental work is supported by quasiclassical trajectory simulations that exhibit unexpected molecular dance moves and suggest that similar effects could be expected for other molecule-molecule scattering systems.

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