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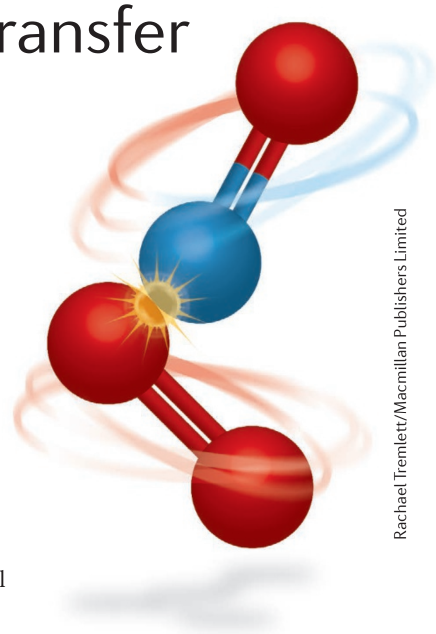
MOLECULAR COLLISIONS

A crash course in energy transfer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We have a good understanding of what happens when a single atom collides with a molecule — only one particle has rotational degrees of freedom and thus can be rotationally excited. It is less clear what happens when two molecules collide, as both partners can become rotationally excited. Collisions are important as they are a means by which elementary (single-step) reactions occur. They are at play in atmospheric chemistry, combustion or in astrochemistry, where molecular collisions enable molecular diversification and the evolution of interstellar clouds. The intricate and counter-intuitive mechanism of energetic exchange in bimolecular collisions has now been identified by a team led by Sebastian van de Meerakker and Gerrit Groenenboom, who report their results in *Nature Chemistry*.

"We were particularly interested in inelastic collisions in which kinetic energy of the molecules is transferred to rotational energy in one or both molecules," explains van de Meerakker. "Our main question became: what is the relation between the excitations in both molecules, and do the rules we know for atom–molecule systems also apply to bimolecular systems?" The lack of information regarding the kinematics of bimolecular collisions is due to our need for stringent experimental conditions (in terms of sample density and purity) and high-resolution analytical techniques to probe excitations in both molecules. The team decided to look at the correlation between the rotational excitation of two molecules by performing a crossed-beam experiment, in which molecular beams of NO and O_2 collide, but the changes in the velocity and energy of only one molecule are detected. "The idea is that the speed of the detected molecule depends on the possible rotational excitation of the other molecule — the one we do not actively detect — simply due to the conservation of energy," explains van de Meerakker. He also clarifies "This idea is not new, but up to now, the experimental resolution was not sufficient to resolve the very subtle speed differences imparted on the molecules."

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Meerakker and co-workers made use of velocity-map imaging to obtain information about the two molecules involved in the collision. These maps comprise several concentric circles, each of which corresponds to a different rotational state. By linking information on the particle's velocity and internal energy, such a map provides a complete picture of the kinematics of the bimolecular collision. The separation of the concentric circles depends on the difference in energy between the rotational states, and we therefore need high experimental resolution when the molecular rotational states are close in energy. The team made use of a Stark decelerator to manipulate the motion of molecules prior to the collision, thereby obtaining molecular beams with extremely narrow velocity spreads, and greatly improving experimental resolution.

Rotational energy transfer in a bimolecular collision does not follow the energy-gap law that holds for energy transfer in atom–molecule collisions. This law states that the probability of a specific collision is inversely proportional to the energy that is transferred during the collision. However, this relationship does not hold for collisions between NO and O_2. If NO is initially highly excited, it is more likely to transfer energy to O_2, which then becomes highly rotationally excited. This likelihood decreases with decreasing excitation of NO. "These findings have been rationalized using quantum calculations, which reveal that the collision mechanism depends on how the molecules strike each other," explains van de Meerakker. The theoretical analysis of Groenenboom and co-workers revealed that inelastic scattering is governed by short-range head-on collisions, while collisions that are nearly elastic typically arise from long-range glances. "We were intrigued to find in our calculations that after the collision the molecules become quantum-entangled, with the degree of entanglement depending on the deflection angle of the collision," explains Groenenboom. He concludes "The present experimental set-up cannot probe the nature of the quantum entanglement, but we believe that this result may provide a fascinating challenge for future work."

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