

**When experiment challenges theory:
Scattering of vibrationally excited molecules in the cold
collision energy regime**

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The last decade has seen substantial advances in the exploration of inelastic and reactive collisions at collision energies in the cold (<1 K) and ultracold (< 1 mK) regime [1–13]. These advances ushered in an understanding of cold and ultracold collisions that is impacting research areas ranging from molecular spectroscopy to quantum simulation and computation to quantum control of chemical reaction dynamics. Cold collisions are dominated by resonances, amply manifest in most of the systems studied [1, 14]. Resonances are also present in the thermal (>100 K) and hyperthermal (>1000 K) collision energy regimes [15], but obscured by background (non-resonant) scattering and the presence of many partial waves pertaining to higher angular momenta that blur the waves’ individual contributions. Moreover, the outcome of thermal and hyperthermal collisions is somewhat insensitive to the details of the interaction potential – the potential energy surface (PES) – especially to its attractive long-range region. Only in a handful of cases, such as the F+HD exchange reaction, resonances in the thermal regime have been experimentally detected and theoretically accounted for by quantum mechanical scattering calculations [16, 17]. In contrast, in the cold regime, collisions are dominated by only a few partial waves whose effects on the integral and differential scattering cross-sections can be singled out and linked to particular resonances.

The cold collision energy regime has been attained by making use of crossed molecular beams that were either Stark- or Zeeman-decelerated or whose intersection angle could be reduced all the way down to the merging-beams limit. A beam emerging from a Stark or Zeeman decelerator has a variable, well-defined laboratory velocity. When crossed with a secondary beam at small angles (5° - 10°), collision energies in the 0.3-15 K could be readily achieved, as demonstrated by the group of van de Meerakker [9, 11]. The technique of merged beams makes use of the ability to bend one of the beams by a magnetic or electric field such that the crossing angle becomes zero, thereby affording collision energies in the range 0.1 K–10 K. Merging beams have been used in studies of Penning ionization by the groups of Narevicius [5, 12] and Osterwalder [18] and made it possible to unravel shape and Feshbach resonances arising in this process. The techniques mentioned so far require the reactants to be polar or paramagnetic. For reactants that are neither, collision energies as low as 5 K could be achieved by taking advantage of a favorable combination of low intersection angles and low reduced mass of the reactants. This approach has been demonstrated by Bergeat, Costes, Naulin and coworkers in a series of reactive [3, 19]

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and inelastic collision experiments [8, 20] of H_2 . Yet another approach to achieving low relative collision velocities relies on the co-expansion of the collision partners in a single molecular beam.[21] If their masses are similar, both partners will end up with nearly the same velocities, within a few ms^{-1} . Using this technique, Zare, Mukherjee, and coworkers carried out a series of experiments in which rotational quenching of HD by H_2 , D_2 and He was investigated. Moreover, in these experiments the HD molecule was prepared in $v=1$ and $j=2$ using Stark-field induced adiabatic Raman passage that allowed, in addition, to align the rotational angular momentum of the HD reactant molecule with respect to the initial relative velocity of the $\text{HD} + \text{He}$ reactants [22–24].

Collisional energy transfer between rotation and translation, in which a molecule is excited or relaxed via scattering by an atom or another molecule, has been of particular significance for developing our understanding of inelastic collisions. Most notably, the scattering of NO molecules by rare gas (Rg) atoms has served as a benchmark system for both experimentalists and theorists for decades. In its ground electronic state, NO is a $^2\Pi$ molecule with a single unpaired electron in an antibonding π^* orbital. In this state, the rotational levels are split into two spin-orbit manifolds, defined by the projection $|\Omega|$ ($= \frac{1}{2}$ or $\frac{3}{2}$) of the electronic angular momentum (orbital and spin) on the internuclear axis. The rotational levels with the same j in the two manifolds are separated by approximately 123 cm^{-1} for $v=0$ (117 cm^{-1} for $v=10$). In addition, each rotational level within each manifold is further split into two Λ -doublet states ($\epsilon = \pm 1$, e/f), which are nearly degenerate, but differ in parity, $p = (-1)^{j-\epsilon/2}$. As the Rg atom approaches the NO molecule, the degeneracy of the Λ doublets is lifted, giving rise to two potential energy surfaces, A' and A'' , in which the orbital of the unpaired electron lies, respectively, in the plane of the three atoms or perpendicular to it. In computational practice, it is more convenient to use linear combinations (sums and differences) of the A'' and A' potential energy surfaces. Using hexapole focusing or Stark deceleration combined with detection via velocity ion imaging, fully state-to-state resolved integral and differential cross sections for rotationally elastic and inelastic collisions could be measured with high resolution [9, 11, 25, 26].

More than that, the orientation and alignment of the scattered (outgoing) NO molecules could be measured as a function of the scattering angle [27–30] and, quite recently, the effects of orientation of the reactant (incoming) NO molecules on the differential cross section in collisions with Rg, mostly Ar, could be established

[31–35]. On the theory side, quantum mechanical close coupling (QMCC) scattering calculations on accurate two-dimensional *ab initio* potential energy surfaces using the benchmark coupled-cluster, CCSD(T), method with the NO internuclear distance fixed at its equilibrium value [36] were performed and found to account for all the details revealed by the experiments. Although state-of-the-art, most of these experiments except for those described in Refs. [9, 11] were carried out at thermal energies for NO molecules in their lowest level, $|v = 0, j = \frac{1}{2}, \Omega = \frac{1}{2}, f\rangle$.

Scattering of highly vibrationally excited molecules in the cold energy regime remained an unexplored frontier until the recent work by the groups of Arthur Suits, Ad van der Avoird, Gerrit Groenenboom, and Hua Guo who added spin-orbit and rotational state selection and looked for spin- and rotational-state changing collisions to boot. Published in the current issue of *Natural Sciences* [37], this work is a culmination of a three-year collaboration that included both implementation of new experimental techniques and boosting of theoretical methods. Working with the NO+Ar system, the authors made use of stimulated emission pumping via the electronically excited $A^2\Sigma^+$ state to promote NO($2\Pi_{\frac{1}{2}}$) molecules to the vibrationally excited state with $v = 10$ and a selected spin-orbit state $|\Omega|$ and rotational state j , $|v = 10, j, \Omega, f\rangle$ [38, 39].

Low (cold) collision energies were achieved in a novel experimental setup of two beams (dual-beam arrangement) crossing at 4° and intersected by the pump and dump laser beams of the stimulated-emission pumping scheme. Downstream, the collision products were probed using 1+1' REMPI with the ionization laser tuned just above the ionization threshold. Fully state-resolved angular distributions of the scattered NO molecules were measured by velocity ion slice imaging and detected by a charge-coupled device (CCD). In order to be able to detect the product (outgoing) molecules resulting from the cold NO + Ar collisions, some excess energy had to be made available to the products. This came in the form of the initial spin-orbit and/or rotational state energy. In the study highlighted herein [37], angular distributions leading to the spin-orbit changing transition $|v = 10, \Omega = \frac{3}{2}, j = \frac{3}{2}f\rangle \rightarrow |v' = 10, \Omega' = \frac{1}{2}, j' = \frac{9}{2}, e\rangle$ were measured at energies in the 2 K-5 K range. Although intra-beam scattering could have been used as an alternative as it had been in previous work,[21] the authors demonstrated that a dual-beam setup provides a superior angular and energy resolution.

The highlighted experiment challenged the existing theoretical treatments of the NO+ Rg systems: firstly, the approximation of fixing NO at its equilibrium dis-

tance was bound to fail for NO in $v = 10$ due to the concomitant elongation of the NO bond. Secondly, for such a highly excited vibrational state, both the long- and short-range interactions are affected, triggering non-adiabatic effects involving rotational and spin-orbit degrees of freedom. The above rendered the single-reference coupled-cluster method used in previous treatments of $\text{NO}(^2\Pi_{1/2}, v = 0)$ inadequate. Therefore, the authors of the highlighted paper [37] constructed a new coupled-cluster PES as well as a multi-reference configuration-interaction (MRCI) PES and carried out full-fledged (3D) QMCC calculations on both potential energy surfaces. These tour-de-force calculations reproduced quite well the experimental differential cross sections and defined a new state of the art in scattering calculations. However, some discrepancies remain as at low collision energies, the accuracy of the long-range potential needed is a challenge for any *ab initio* method. Moreover, treating spin-changing collisions that are dominated by the essentially attractive difference potential, $V_{A''} - V_{A'}$, puts additional demands on the accuracy of the A'' and A' PESs. The calculated integral cross section in the 3-4 cm^{-1} energy interval exhibits a bump that may indicate the presence of resonances that show up as backscattering in the measured differential cross section. A partial-wave analysis points to overlapping resonances associated with contributions from several of the highest partial waves involved. In any case, tracing the resonances may require additional improvements of the existing potential energy surfaces.

All in all, the highlighted combined experimental and theoretical study sets a new standard for our understanding of cold collisions.

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- [1] R. V. Krems, W. C. Stwalley, and B. Friedrich, *Cold Molecules: Theory, Experiment, Applications*. (Boca Raton: CRC Press, 2009).
 - [2] O. Dulieu and A. Osterwalder, *Cold Chemistry. Molecular Scattering and Reactivity Near Absolute Zero* (Royal Society of Chemistry, Cambridge, 2018).
 - [3] C. Berteloite, M. Lara, A. Bergeat, S. D. Le Picard, F. Dayou, K. M. Hickson, A. Canosa, C. Naulin, J.-M. Launay, I. R. Sims, and M. Costes, Kinetics and dynamics of the $\text{S}(^1\text{D}) + \text{H}_2 \rightarrow \text{SH} + \text{H}$ reaction at very low temperatures and collision energies, *Phys. Rev. Lett.* **105**, 203201 (2010).
 - [4] A. B. Henson, S. Gersten, Y. Shagam, J. Narevicius, and E. Narevicius, Observation of resonances in Penning ionization reactions at sub-kelvin temperatures in merged

- beams, *Science* **338**, 234 (2012).
- [5] E. Narevicius and M. G. Raizen, *Chem. Rev.* **112**, 4879 (2012).
 - [6] E. Lavert-Ofir, Y. Shagan, A. B. Henson, S. Gersten, J. Klos, P. Zuchowski, J. Narevicius, and E. Narevicius, *Nat. Chem.* **6**, 332 (2014).
 - [7] Y. Segev, M. Pitzer, M. Karpov, N. Akerman, J. Narevicius, and E. Narevicius, Collisions between cold molecules in a superconducting magnetic trap, *Nature* **572**, 189 (2019).
 - [8] A. Bergeat, J. Onvlee, C. Naulin, A. van der Avoird, and M. Costes, Quantum dynamical resonances in low-energy $\text{CO}(j = 0) + \text{He}$ inelastic collisions, *Nat. Chem.* **7**, 349 (2015).
 - [9] S. N. Vogels, J. Onvlee, S. Chefdeville, A. van der Avoird, G. C. Groenenboom, and S. Y. T. van de Meerakker, Imaging resonances in low-energy NO-He inelastic collisions, *Science* **350**, 787 (2015).
 - [10] M. Costes and C. Naulin, Observation of quantum dynamical resonances in near cold inelastic collisions of astrophysical molecules, *Chem. Sci.* **7**, 2462 (2016).
 - [11] T. de Jongh, M. Besemer, Q. Shuai, T. Karman, A. van der Avoird, G. C. Groenenboom, and S. Y. T. van de Meerakker, Imaging the onset of the resonance regime in low-energy NO-He collisions, *Science* **368**, 626 (2020).
 - [12] P. Paliwal, N. Deb, D. M. Reich, A. van der Avoird, C. P. Koch, and E. Narevicius, Determining the nature of quantum resonances by probing elastic and reactive scattering in cold collisions, *Nat. Chem.* **13**, 94 (2021).
 - [13] Y. Liu, M.-G. Hu, M. A. Nichols, D. Yang, D. Xie, H. Guo, and K.-K. Ni, Precision test of statistical dynamics with state-to-state ultracold chemistry, *Nature* **593**, 379 (2021).
 - [14] D. W. Chandler, Cold and ultracold molecules: Spotlight on orbiting resonances, *J. Chem. Phys.* **132**, 110901 (2010).
 - [15] A. Schutte, D. Bassi, F. Tommasini, and G. Scoles, Orbiting resonances in the scattering of H atoms by mercury at thermal energies, *Phys. Rev. Lett.* **29**, 979 (1972).
 - [16] R. T. Skodje, D. Skouteris, D. E. Manolopoulos, F. D. S. H. Lee, and K. Liu, Resonance-Mediated Chemical Reaction: $\text{F} + \text{HD} \rightarrow \text{HF} + \text{D}$, *Phys. Rev. Lett.* **85**, 1206 (2000).
 - [17] R. T. Skodje, D. Skouteris, D. E. Manolopoulos, F. D. S. H. Lee, and K. Liu, Observation of a transition state resonance in the integral cross section of the $\text{F} + \text{HD}$ reaction, *J. Chem. Phys.* **112**, 4536 (2000).
 - [18] S. D. S. Gordon, J. J. Omiste, J. Zou, S. Tanteri, P. Brumer, and A. Osterwalder,

- Quantum-state-controlled channel branching in cold $\text{Ne}(^3\text{P}_2) + \text{Ar}$ chemi-ionization, *Nat. Chem.* **10**, 1190 (2018).
- [19] M. Lara, S. Chefdeville, K. M. Hickson, A. Bergeat, C. Naulin, J.-M. Launay, and M. Costes, Dynamics of the $\text{S}(^1\text{D}) + \text{HD}$ reaction at collision energies approaching the cold regime: A stringent test for theory, *Phys. Rev. Lett.* **109**, 133201 (2012).
 - [20] S. Chefdeville, T. Stoecklin, A. Bergeat, K. M. Hickson, C. Naulin, and M. Costes, Appearance of low energy resonances in CO-para-H_2 inelastic collisions, *Phys. Rev. Lett.* **109**, 023201 (2012).
 - [21] C. Amarasinghe and A. G. Suits, Intrabeam scattering for ultracold collisions, *J. Phys. Chem. Lett.* **8**, 5153 (2017).
 - [22] W. E. Perreault, N. Mukherjee, and R. N. Zare, Quantum control of molecular collisions at 1 Kelvin, *Science* **358**, 356 (2017).
 - [23] W. E. Perreault, N. Mukherjee, and R. N. Zare, Cold quantum-controlled rotationally inelastic scattering of HD with H_2 and D_2 reveals collisional partner reorientation, *Nat. Chem.* **10**, 561 (2018).
 - [24] H. Zhou, W. E. Perreault, N. Mukherjee, and R. N. Zare, Shape resonance determined from angular distribution in $\text{D}_2 (v = 2, j = 2) + \text{He} \rightarrow \text{D}_2 (v = 2, j = 0) + \text{He}$ cold scattering, *J. Chem. Phys.* **154**, 104309 (2021).
 - [25] C. J. Eyles, M. Brouard, C.-H. Yang, J. Klos, F. J. Aoiz, A. Gijsbertsen, A. E. Wiskerke, and S. Stolte, Interference structures in the differential cross-sections for inelastic scattering of NO by Ar, *Nat. Chem.* **3**, 597 (2011).
 - [26] J. Onvlee, S. D. S. Gordon, S. N. Vogels, T. Auth, T. Karman, B. Nichols, A. van der Avoird, G. C. Groenenboom, M. Brouard, and S. Y. T. van de Meerakker, Imaging quantum stereodynamics through fraunhofer scattering of NO radicals with rare-gas atoms, *Nat. Chem.* **9**, 226 (2016).
 - [27] K. T. Lorenz, D. W. Chandler, J. W. Barr, W. Chen, G. L. Barnes, and J. I. Cline, Direct Measurement of the Preferred Sense of NO Rotation After Collision with Argon, *Science* **293**, 2063 (2001).
 - [28] M. Brouard, H. Chadwick, C. J. Eyles, B. Hornung, B. Nichols, F. J. Aoiz, P. G. Jambrina, and S. Stolte, Rotational alignment effects in $\text{no}(x) + \text{Ar}$ inelastic collisions: An experimental study, *J. Chem. Phys.* **138**, 104310 (2013).
 - [29] M. Brouard, H. Chadwick, C. J. Eyles, B. Hornung, B. Nichols, F. J. Aoiz, P. G. Jambrina, S. Stolte, and M. P. de Miranda, Rotational alignment effects in $\text{NO}(X) + \text{Ar}$ inelastic collisions: A theoretical study, *J. Chem. Phys.* **138**, 104309 (2013).

- [30] H. Chadwick, B. Nichols, S. D. S. Gordon, B. Hornung, E. Squires, M. Brouard, J. Klos, M. H. Alexander, F. J. Aoiz, and S. Stolte, Inelastic scattering of NO by Kr: Rotational polarization over a rainbow, *J. Phys. Chem. Lett.* **5**, 3296 (2014).
- [31] B. Nichols, H. Chadwick, S. D. S. Gordon, C. J. Eyles, B. Hornung, M. Brouard, M. H. Alexander, F. J. Aoiz, A. Gijsbertsen, and S. Stolte, Steric effects and quantum interference in the inelastic scattering of NO(X) + Ar, *Chem. Sci.* **6**, 2202 (2015).
- [32] M. Brouard, S. D. S. Gordon, B. Nichols, V. Walpole, F. J. Aoiz, and S. Stolte, Differential steric effects in the inelastic scattering of NO(X) + Ar: spin-orbit changing transitions, *Phys. Chem. Chem. Phys.* **21**, 14173 (2019).
- [33] C. G. Heid, V. Walpole, M. Brouard, F. J. Aoiz, and P. G. Jambrina, Side-impact collisions of Ar with NO, *Nat. Chem.* **11**, 662 (2019).
- [34] V. Walpole, C. G. Heid, P. G. Jambrina, F. J. Aoiz, and M. Brouard, Steric effects in the inelastic scattering of NO(X) + Ar: Side-on orientation, *J. Phys. Chem. A* **123**, 8787 (2019).
- [35] C. G. Heid, I. P. Bentham, R. Gheorghe, P. G. Jambrina, F. J. Aoiz, and M. Brouard, Inelastic collision dynamics of oriented NO molecules with Kr atoms, *Mol. Phys.* e1946607 (2021).
- [36] M. H. Alexander, A new, fully *ab initio* investigation of the NO(X²Π) Ar system. I. Potential energy surfaces and inelastic scattering, *J. Chem. Phys.* **111**, 7426 (1999).
- [37] C. Amarasinghe, H. Li, C. A. Perera, H. Li, J. Zuo, M. Besemer, A. van der Avoird, G. C. Groenenboom, H. Guo, and A. G. Suits, Collision induced 1 spin-orbit relaxation of highly vibrationally excited NO near 1 K, *Nat. Sci. (Olszt.)* **xx**, xxx (2021).
- [38] C. Amarasinghe, H. Li, C. A. Perera, M. Besemer, A. van der Avoird, G. . C. Groenenboom, C. Xie, H. Guo, and A. G. Suits, Differential cross sections for state-to-state collisions of NO(*v* = 10) in near-copropagating beams, *J. Phys. Chem. Lett.* **10**, 2422 (2019).
- [39] C. Amarasinghe, H. Li, C. A. Perera, M. Besemer, J. Zuo, C. Xie, A. van der Avoird, G. C. Groenenboom, H. Guo, J. Klos, and A. G. Suits, State-to-state scattering of highly vibrationally excited NO at broadly tunable energies., *Nat. Chem.* **12**, 528 (2020).