

Exploring and Controlling Chemistry Using Quantum Logic

Prerna Paliwal*, Mikhail Popov, Nanditha Sunil Kumar, and Stefan Willitsch*

Abstract: Over the past years, the development of experimental techniques for the coherent manipulation and control of isolated quantum systems has made impressive progress. Such ‘quantum-logic’ methods are also highly attractive in a chemical context in view of unravelling and controlling the quantum dynamics of molecular collisions and chemical reactions. Quantum technologies have the potential to transform the way chemical dynamics are investigated – by providing highly sensitive methods for state readout and spectroscopy, by opening up new pathways for the quantum-state preparation of molecules and by enabling an improved control of their microscopic behavior on the single-particle level. However, for complex quantum systems like molecules, these techniques are still in their infancy and their considerable potential remains to be unlocked. The aim of the present research program supported by an Advanced Grant of the Swiss National Science Foundation is to merge the fields of quantum science and chemical dynamics by advancing quantum technologies to polyatomic molecular ions and by applying them to the study of ion-molecule collisions and chemical reactions. In this article, we review the salient experimental methods as well as prospects and challenges in the development of molecular quantum technologies and their applications to chemistry.

Keywords: Cold polyatomic molecular ions · Ion-molecule reactions · Molecular quantum technologies · Non-demolition state detection · Quantum logic spectroscopy



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1. Introduction

Quantum technologies employ fundamental quantum principles like energy quantization, tunneling, superposition and entanglement to manipulate the components of a physical system.^[1] Over the years, these technologies have been instrumental in controlling single isolated quantum systems such as single atoms, atomic ions, superconducting circuits, and quantum dots, leading to significant advancements in quantum metrology, sensing, and computing.^[2–4] Recently, there has been a growing interest

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within the quantum-physics community in extending quantum technologies to molecules.^[5] The complex energy-level structure of molecules – consisting of electronic, vibrational, rotational, fine structure, hyperfine, and Zeeman levels – offers numerous opportunities in physics, chemistry, and quantum technologies. However, this complexity poses challenges in controlling both the internal and external degrees of freedom of molecules. One key approach is to cool and trap the molecules. Under these conditions it becomes possible to control them precisely on the quantum level.^[6] Nevertheless, the lack of closed optical-cycling transitions renders the application of laser cooling, the workhorse of atomic physics,^[7] difficult for most molecules. By contrast, sympathetic cooling of molecular ions by the interaction with laser-cooled atomic ions in a trap is a near-universal technique for the generation of translationally cold molecules in the microkelvin temperature range.^[5] In the present article, we discuss how the easily manipulated atomic ions can additionally be used for the precise measurement of the quantum state of the simultaneously trapped molecular ions using, ‘quantum-logic spectroscopy’ (QLS).

The idea of QLS, which originates from the realm of trapped-ions quantum computing and optical clocks,^[8] has unlocked new doors in molecular physics by enabling a precise quantum control over molecules. In this approach, a single target molecular ion for spectroscopy (referred to as the ‘spectroscopy ion’) is co-trapped with an easily manipulated atomic ion (termed the ‘logic ion’), and information exchange occurs through their correlated harmonic motion.^[8] Variations of this approach have so far been applied to both polar,^[9,10] and nonpolar^[11] molecular ions. These pioneering studies offered promising prospects in various fields, including radiation sensing,^[12] measurements of molecular properties,^[13] spectroscopy,^[14] quantum control,^[15] and state-controlled collisions.^[16,17] While these techniques possess broad applicability and could theoretically be extended to a diverse range of molecules, their implementation has thus far been limited to a few diatomic systems. Polyatomic molecules, on the other hand, play crucial roles in the chemical and biological sciences and also exhibit numerous features advantageous for applications in physics.^[18,19] For instance, they are of interest for improved searches for the electric dipole moment of the electron and other beyond-standard-model physics.^[20] Chiral molecular ions offer possibilities for investigating parity violation,^[21,22] while symmetric-top molecules with closely-spaced parity doublets present opportunities in the field of quantum simulation^[23] and quantum information science.^[24]

In the field of chemistry, molecular-ion quantum technologies have the potential to revolutionize the study of molecular interactions. Firstly, they can be used to produce quantum state-purified reactants on the single-particle level by projective state preparation.^[16,25,26] Secondly, they can be employed to map inelastic collisions which change the molecular state with a greatly improved sensitivity compared to established techniques.^[27] While conventional methods have primarily focused on understanding vibrational^[28] and rotational degrees^[29] of freedom, quantum-logic techniques can facilitate the exploration of subtle effects stemming from fine and hyperfine degrees of freedom.^[16] One key advantage of QLS is its ability to perform sensitive measurements on single particles, thus revealing properties that are sometimes averaged out in big ensembles.

2. Quantum-non-demolition State Readout of Single Molecules

In our laboratory, we have recently demonstrated a chemically non-destructive, quantum-non-demolition state-readout method for molecular ions.^[11,16,30] Our approach employs a QLS scheme, using Ca^+ as a logic ion and N_2^+ as an exemplary prototypical spectroscopy ion. Our protocol involves initially preparing the molecular ion in the desired quantum state using state-selective

photoionization, then applying an optical dipole force that depends on the molecular state to map it onto the common motion of both ions in the trap and finally detecting the joint motion through the fluorescence signature of the atomic ion.

Our experiment combines an ion-trapping apparatus with a molecular beam machine^[30] (see schematic in Fig. 1(a)). We use a linear-quadrupole radiofrequency ion trap to generate an effective harmonic potential for confining the ions. Ca^+ ions are loaded into the trap and Doppler laser cooled using laser beams at wavelengths of 397 and 866 nm to form ‘Coulomb crystals’, *i.e.*, ordered structures of cold localized ions in the trap (inset of Fig. 1 (a)). Single N_2^+ molecular ions in their rovibronic ground state are loaded into the trap by threshold photoionization of neutral N_2 molecules from the molecular beam passing through the trap center.^[31] The molecular ion is sympathetically cooled by the Ca^+ ions after which the size of the crystal is reduced to a $\text{Ca}^+ - \text{N}_2^+$ two-ion string (inset in Fig. 1(a)). The two-ion crystal is subsequently further cooled to the quantum-mechanical ground state of one of its motional modes in the harmonic trap using resolved-sideband cooling on the Ca^+ ion ‘clock’ transition at 729 nm (see ref. [30] for the technical details).

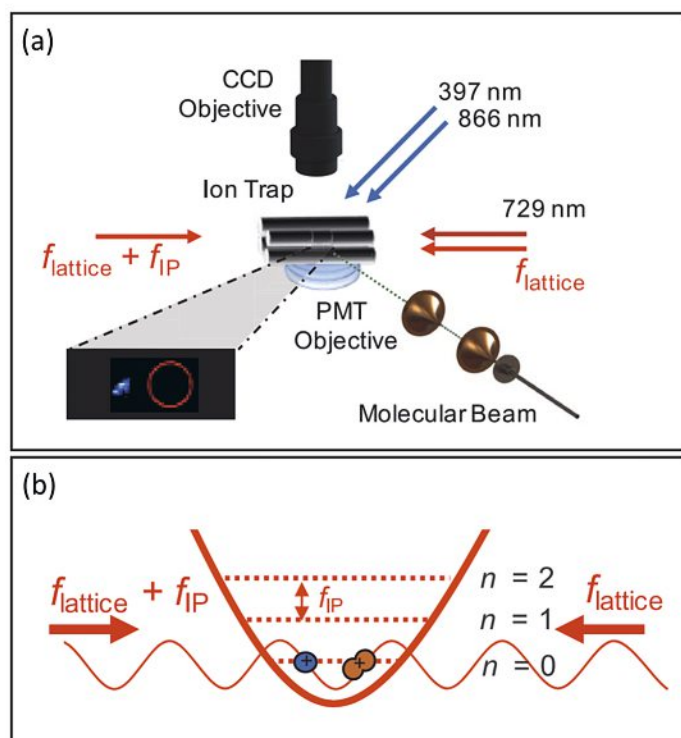


Fig. 1. **Quantum-non-demolition detection of molecular states** (a) Schematic of the experimental setup consisting of a linear radiofrequency ion trap coupled to a molecular-beam machine. See text for details. Inset: false-color fluorescence image of a single laser-cooled Ca^+ ion (blue) sympathetically cooling a single N_2^+ molecular ion (invisible, position indicated by red circle). (b) Illustration of a one-dimensional optical lattice interacting with a $\text{Ca}^+ - \text{N}_2^+$ two-ion crystal with one of its modes of motion cooled to the quantum mechanical ground state $n=0$ of the harmonic ion trap. The optical lattice generates an optical dipole force (ODF) on the molecular ion. Depending on the molecular state, the ODF induces a motional excitation of the two ions in the trap which is detected from the fluorescence signature of the atomic ion. See text for details. Figures reproduced from ref. [11].

We then apply an optical lattice formed by two counter-propagating laser beams across the two-ion crystal (Fig. 1 (b)). The frequency of the lasers is chosen to be close (but not identical) to a spectroscopic resonance from a particular quantum state in the

molecular ion thus generating a strong optical dipole force (ODF), similar as in an optical tweezer. The laser beams are amplitude-modulated at the frequency of the originally cooled motional mode of the ions. When the molecule is in the targeted quantum state, the state-dependent ODF leads to a coherent excitation of the motion of the ions in the trap, which is detected through the fluorescence of the atomic ion.^[30] Note that due to the dispersive nature of the coupling to the optical lattice, no transition is excited in the molecular ion, thus preserving its internal state for further experiments. By repeatedly measuring the molecular state, we have achieved state-detection fidelities > 99% and non-destructive spectroscopy on the single ion using this methodology.^[11]

Extensions of this scheme have been demonstrated to be particularly useful for identifying the molecular state in a dense reservoir of possible states.^[16] Moreover, one can also probabilistically prepare a single molecular ion in a specific quantum state by measuring its state non-destructively. Our method is also capable of tracking the state in inelastic and reactive collisions thus offering valuable insights into state-dependent reaction dynamics.^[16]

3. Applications in Chemistry

The objective of the present SNSF Advanced Grant project is to harness quantum technologies for highly precise studies of molecular collisions and chemical reactions, as demonstrated in first proof-of-principle experiments in refs. [16,17]. As discussed, quantum-logic techniques can detect quantum states of single molecules with great sensitivity enabling studies of molecular energy transfer and chemical reactions by monitoring changes in energy levels during molecular collisions. This capability paves the way for investigations of reaction mechanisms, the determination of reaction rate constants, and the optimization of reaction conditions with a high degree of control.

In our experiments, we use QLS for the projective preparation of polyatomic molecular ions in specific rovibrational-hyperfine-

Zeeman quantum states. Collisions are initiated by introducing neutral particles in a molecular beam. Upon collision between a neutral particle with the molecular ion, three possible outcomes may occur: *elastic*, *inelastic*, or *reactive scattering*. In the case of reactive scattering, the collision will lead to the formation of a different chemical species. The resultant ion may or may not be trappable within the experimental environment. By contrast, elastic and inelastic collisions leave the chemical structure of the collision partners intact. Since the reactants are initially prepared in their minimum energy configuration in the trap, these collisions lead to an increase in the kinetic energy of the reactant pair (Fig. 2). The internal state of the molecular ion remains unperturbed in an elastic collision, whereas it changes in an inelastic collision.

A collision event is detected by monitoring the impartment of kinetic energy to the motion of the ions in the trap, *i.e.* by their heating through the collision. To characterize the outcome of the collision, we first re-cool the ion pair to its motional ground state of the harmonic trap. We then identify the mass of the trapped ion by measuring its mass-dependent oscillation frequency in the trap. This allows us to identify reactive collisions in which the product ion species remained trapped. If the chemical identity of the molecular ion was conserved, a state-dependent optical dipole force is applied to determine whether its quantum state was preserved (elastic collision, Fig. 2 (a)) or changed (inelastic collision, Fig. 2 (b)). In the latter case, we can identify the final molecular state to study state-to-state inelastic molecular collisions with QLS detection. The present scheme is particularly relevant for studying the role of molecular states which are otherwise difficult to prepare using standard methods, *e.g.* hyperfine states.

4. A New Experiment for Quantum Technologies for Polyatomic Molecules

Thus, while the adaptation of quantum-logic techniques to study collisions of larger molecules holds great promise, it is important to highlight the inherent challenges posed by polyatomics.

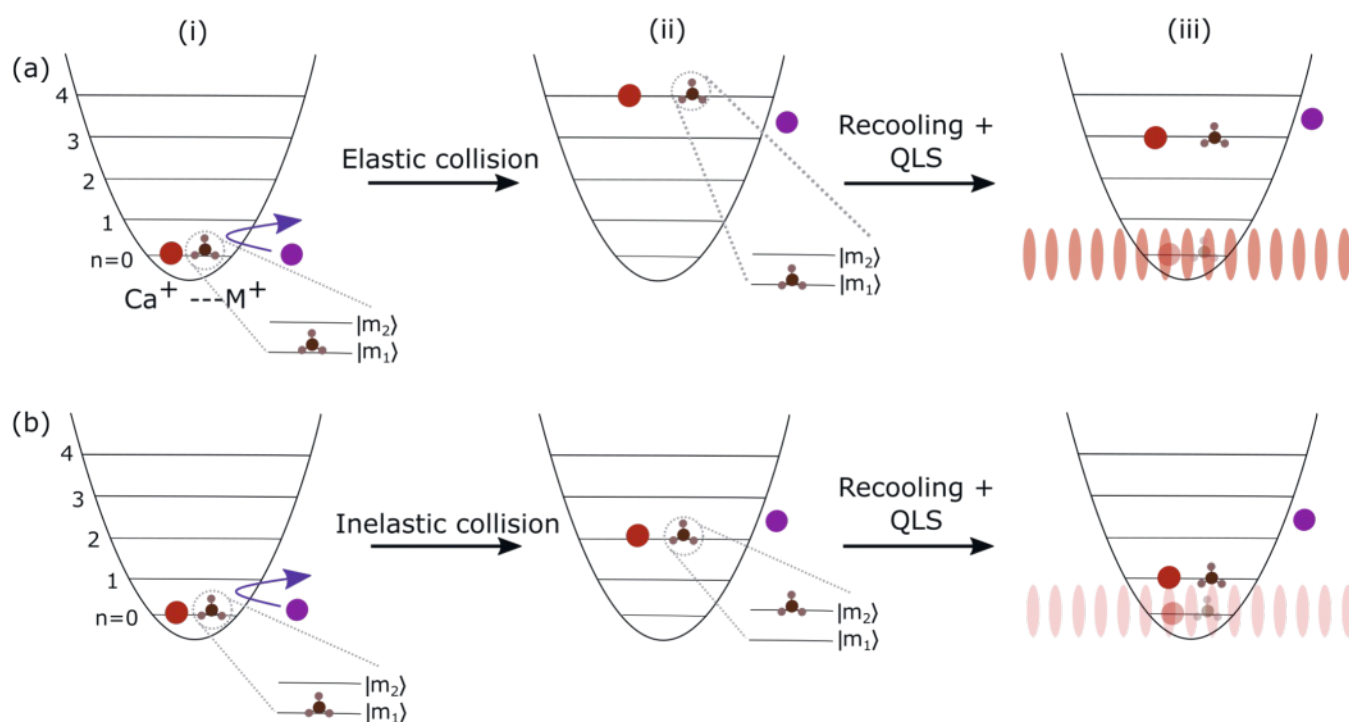


Fig. 2. Quantum-logic-spectroscopic (QLS) detection of (a) elastic and (b) inelastic collisions. (i) A two-ion string consisting of a laser-cooled atomic ion and the molecular ion of interest are prepared in the ground state $n=0$ of their joint motion in the harmonic ion trap. (ii) A collision is heralded by the transfer of kinetic energy to the ions leading to their motional excitation in the trap. (iii) The ions are re-cooled to their motional ground state and a possible change of state ($|m_1\rangle \rightarrow |m_2\rangle$) of the molecule is probed by QLS. The dark (light) shade of the optical lattice implies a strong (weak) optical dipole force when the molecular ion is in the same (different) internal state, leading to a stronger (weaker) motional excitation.

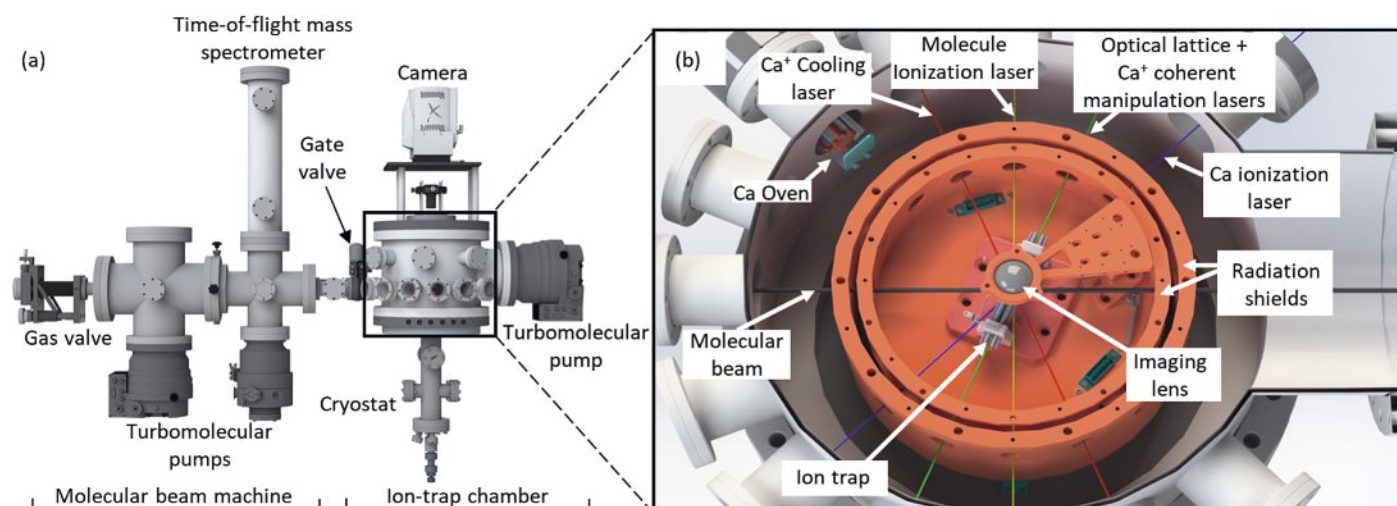


Fig. 3. **New experimental apparatus for QLS of polyatomic ions:** (a) Setup consisting of a cryogenic ion-trap chamber coupled to a molecular beam machine equipped with a time-of-flight mass spectrometer. (b) Cryogenic linear radiofrequency ion trap encased in two nested radiation shields. The optical axis for various lasers passing through the center of the trap are shown by straight lines in different colors.

In particular, polar systems which are trapped for extended periods of time are prone to state loss due to optical pumping by ambient blackbody radiation (BBR).^[9,10,27,28] The uncontrolled loss of the quantum state implies the termination of every quantum protocol. Moreover, polyatomic molecules exhibit a greater number of vibrational degrees of freedom compared to diatomics. This leads to increased possibilities for transitions between quantum states and, in general, shorter inherent state lifetimes. Furthermore, the added complexity introduces numerous inelastic and reactive channels due to collisions with background gases.

To address these issues, we are currently developing a cryogenic experimental setup enabling QLS of polar polyatomic molecular ions. The cryogenic environment at temperatures below 10 K significantly reduces the BBR intensity and suppresses spurious collisions with background gas molecules by improving vacuum through cryogenic pumping. The construction of the new apparatus (Fig. 3 (a)) is currently underway. The core of the setup is a linear RF ion trap cooled by a cryostat. BBR is reduced by two nested radiation shields around the trap maintained at temperatures below 10 K.

As in our previous setup, the experiment features a molecular-beam machine for introducing molecules into the trap. The setup is equipped with a time-of-flight mass spectrometer enabling photoionization spectroscopy of the molecules in the beam. The desired ions are produced by resonance-enhanced threshold photoionization of the molecular beam traversing the ion trap. To maintain an ultra-high vacuum environment in the trapping region, the science chamber and the molecular-beam source chamber are separated using gate valves and skimmers. Laser beams used for the photoionization of calcium and the molecules, for laser cooling and coherent manipulation as well as for generating the optical lattice for state readout are introduced through different viewports (Fig. 3 (b)). The fluorescence of the laser-cooled atomic ions is imaged by a high-numerical-aperture optical system.

4. Conclusions

Novel quantum technologies enable the precise manipulation and control of single molecules at the quantum level. In this article, we have discussed a method for quantum-non-demolition state detection of single trapped molecular ions which offers a considerably higher sensitivity than traditional spectroscopic methods. A significant advantage of this approach is the ability to measure and projectively prepare the quantum state of single molecules, which opens the possibility of elucidating state-to-state collision

dynamics. The present method is general, and with our new apparatus, it will be extended to polar polyatomic molecular ions. The capability to precisely manipulate single molecules holds promise for addressing longstanding questions in chemistry by correlating a single molecule's quantum state with its reactivity.

5. Behind the Scenes

The current project is the culmination of 15-years of research effort in our group to achieve control of single molecules on the quantum level. After having reached important milestones like rovibrational state preparation of trapped molecular ions, highly sensitive spectroscopy and non-destructive quantum-logic-based state detection,^[11,28,32] we are now harnessing these developments to push the quantum control of polyatomic molecules towards a new frontier.

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