Open questions on the interaction dynamics of molecules and clusters in the gas phase

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Emerging experimental techniques combined with theoretical advances allow unprecedented studies of the dynamics of gas phase molecules and clusters induced in interactions with photons, electrons, or heavy particles. Here, the authors highlight recent advances, key open questions, and challenges in this field of research with focus on experimental studies of dynamics of ions stored on millisecond timescales and beyond, and its applications in astrochemistry and astronomy.

When gas phase molecules or clusters interact with photons, electrons, or heavy particles, the electronic and structural dynamics set in motion may extend on timescales spanning twenty orders of magnitude—from attoseconds to minutes—while their effects may continue being felt on astronomical timescales (Fig. 1). The timescales of these dynamics span those typical of the electronic motion and its coupling to nuclear motion and molecular rearrangements, to those for ultraslow electron emission, radiative cooling (vibrational and rotational relaxation), and fragmentation. This means that an arsenal of complementary state-of-the-art experimental, computational and theoretical tools is required to fully unravel the dynamics, and to answer open key questions such as:

- How do molecules form and survive in the interstellar medium?
- What are the conditions for the building blocks of life to evolve in extraterrestrial environments?
- What are the mechanisms behind aerosol formation in planetary atmospheres?

A complete description of the intriguing developments being made in this rapidly growing field is unfortunately beyond the scope of this short comment (see, e.g., recent topical roadmaps1–4 and references therein for more details). Here, we focus on the status of some recent advances while sharing our view of a selection of common challenges, as well as more specific ones, and key questions to advance the understanding of the dynamics of ions extending to ultralong timescales.

Status and recent advances

The development of novel light sources such as attosecond lasers and X-ray free electron lasers (XFELs) have opened up completely new research opportunities towards real-time monitoring of electronic dynamics, electron emission, charge transfer, photon emission, and the breaking and making of molecular bonds2,3. In parallel to these advances, studies using ingenious probe and detection schemes at large scale synchrotron facilities or with lab-based table-top lasers have been paramount to further the understanding of ultrafast relaxation processes1,2, as well as slower dynamics extending up to microseconds1,2. The latter often make use of advanced mass...
The experimental advances outlined above provide new opportunities but also new challenges for experiments as well as theory. A common challenge in gas phase studies is to prepare molecules and clusters in well-defined structures and quantum states (electronic- and rotational- and vibrational energy) before the interaction dynamics is ignited. To accomplish this becomes extremely challenging with increasing molecular complexity. Furthermore, it is essential to produce sufficiently large target quantities or ion beams intense enough to study specific processes. The key here is to further refine and combine techniques in novel ways, for instance, soft ionization methods designed to bring fragile molecules into the gas phase, isomer selection schemes, pre-trapping, and cryogenic cooling of ions, as well as state-selective laser probing techniques. It is equally important and challenging to fully characterize the reaction products through, e.g., advanced pump-probe schemes, action spectroscopy, and the development of new techniques and methods to monitor neutral and charged reaction products and the emission of electrons and photons.

Dynamics of stored ions on ultralong timescales. The experimental and theoretical advances in ion beam storage technologies offer unique possibilities towards answering key open fundamental questions, which are largely unknown for interaction dynamics involving internally cooled molecular and cluster ions.
Outlook

The dynamics of gas phase atoms and molecules is a topic of fundamental research largely belonging to chemistry and physics, but the potential applications of the processes being studied are widespread. From characterizing plasmas to understanding how radiation damages organic molecules, and from atmospheric science to astrophysics, gas phase dynamics comes in many flavors. The last example is briefly covered in Fig. 1. The evolution of the interstellar medium (ISM) is driven by the dynamics of atoms and molecules present there. A surprisingly rich inventory of chemical species—from free protons to complex organic molecules—is constantly being processed by intense radiation fields from massive stars and energetic particles from stellar winds and supernovae. The timescales of the excitation mechanisms are the same as in laboratories on earth, but the consequences of these interactions are felt on timescales spanning over many millions of years, the typical lifetime of molecular clouds in the ISM. In addition to improvements in observational techniques, such as the ongoing deployment of the James Webb Space Telescope, many advancements in our understanding of interstellar environments come from experimental and theoretical research on gas phase dynamics. Two recent examples of these are detailed studies of the destruction mechanisms of astrophysically important helium hydride ions $^1$ and PAH molecules $^2$ in cryogenic ion storage rings. Further experimental developments will lead to new insights into the importance of gas phase dynamics in different environments. Types of developments envisioned in the next decade are combining the capabilities of experimental tools highlighted in this communication in novel and ingenious ways, for instance, cryogenic ion beam storage devices with advanced light sources or ion accelerator facilities.

An exciting future lies ahead for those studying the gas phase dynamics of molecules. A key challenge for the community is to seize the transfer of knowledge between different fields whenever possible. Strides to achieve this are constantly being made and are aided by a range of successful international and interdisciplinary networks supported by, e.g., EU framework programs for research and innovation.

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References

1. Zettergren, H. et al. Roadmap on dynamics of molecules and clusters in the gas phase. Eur. Phys. J. D 75, 152 (2021).
2. Ueda, K. et al. Roadmap on photonic, electronic and atomic collision physics: I. Light–matter interaction. J. Phys. B: At., Mol. Opt. Phys. 52, 171001 (2019).
3. Schippers, S. et al. Roadmap on photonic, electronic and atomic collision physics: II. Electron and antimatter interactions. J. Phys. B: At., Mol. Opt. Phys. 52, 171002 (2019).
4. Aumayr, F. et al. Roadmap on photonic, electronic and atomic collision physics: III. Heavy particles: with zero to relativistic speeds. J. Phys. B: At., Mol. Opt. Phys. 52, 171003 (2019).
5. Lindroth, E. et al. Challenges and opportunities in attosecond and XFEL science. Nat. Rev. Phys. 1, 107–111 (2019).
6. Gatchell, M. & Zettergren, H. Knockout driven reactions in complex molecules and their clusters. J. Phys. B: At., Mol. Opt. Phys. 49, 162001 (2016).
7. Hansen, K. Decay dynamics in molecular beams. Mass Spectrometry Rev. 40, 725–740 (2021).
8. Andersen, L. H., Heber, O. & Zajfman, D. Physics with electrostatic rings and traps. J. Phys. B: At., Mol. Opt. Phys. 37, R57–R88 (2004).
9. Schmidt, H. T. Electrostatic storage rings for atomic and molecular physics. Phys. Scr. T166, 014063 (2015).
10. Grumer, J. et al. State-resolved mutual neutralization of Mg$^+$ and D$^+$. Phys. Rev. Lett. 128, 033401 (2022).
11. Novotný, O. et al. Quantum-state-selective electron recombination studies suggest enhanced abundance of primordial HeH$^+$. Science 365, 676–679 (2019).
12. Ball, P. The coolest molecular ion beams. Physics 10, 93 (2017).
13. Shahi, A. et al. Hybrid electrostatic ion beam trap (HEIBT): Design and simulation of ion–ion, ion–neutral, and ion–laser interactions. Rev. Sci. Instrum. 90, 113308 (2019).
14. Schotsch, F. et al. TrapREMI: A reaction microscope inside an electrostatic ion beam trap. Rev. Sci. Instrum. 92, 123201 (2021).
15. Gatchell, M. et al. Survival of polycyclic aromatic hydrocarbon knockout fragments in the interstellar medium. Nat. Commun. 12, 6646 (2021).

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Competing interests
The authors declare no competing interests.

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