

Investigating molecular interactions in helium with control: impulsive alignment in the gas phase versus thermal equilibrium in the bulk

Klaus von Haeften^a, Joshua Szekely^b, Tamara Seideman^b, Luis G. Mendoza Luna^a, Gediminas Galinis^a, Russell S. Minns^c, Andrew M. Ellis^d, Mirjana Mladenović^e, Marius Lewerenz^e, Nelly Bonifaci^f, Frédéric Aitken^f, Nagham Shiltagh^a, Mark Watkins^a, Emma Springate^g, Cephise Cacho^g, Richard T. Chapman^g, I. C. Edmond Turcu^g, Lev Kazak^h, Robert Irsig^h, Slawomir Skruszewicz^h, Sebastian Gode^h, Josef Tiggesbaumker^h, Karl-Heinz Meiwes-Broer^h, Arnaud Rouzéeⁱ, Jonathan G. Underwood^j,

^a University of Leicester, Department of Physics & Astronomy, Leicester, LE1 7RH, United Kingdom,

^b Department of Chemistry, Northwestern University Evanston, IL 60208-3113

^c University of Southampton, Chemistry, Southampton, SO17 1BJ, United Kingdom

^d University of Leicester, Department of Chemistry, Leicester, LE1 7RH, United Kingdom

^e Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR8208 CNRS, 5 bd Descartes, 77454 Marne-la-Vallée, France

^f G2ELab-GreEn-ER, Equipe MDE, 21 avenue des Martyrs, CS 90624, 38031 Grenoble Cedex 1, France

^g Central Laser Facility, STFC Rutherford Appleton Laboratory, United Kingdom

^h Institute for Physics, University of Rostock, Germany

ⁱ Max Born Institute, Max Born Strasse 2A, 12489 Berlin, Germany

^j Department of Physics & Astronomy, University College London, London WC1E 6BT

Synopsis Rotational wavepackets of C₂H₂-He complexes produced in a beam were excited using impulsive laser alignment. The time dependence of alignment was measured via Coulomb explosion of the C₂H₂ molecules. The rotational spectrum of the complex was obtained by Fourier transformation. In bulk helium fluorescence spectra of helium excimers showed that these had cooled at a rate of at least 10¹⁰-10¹¹ K/s to the lowest rotational quantum state.

We explore molecular interactions in helium while seeking novel ways of achieving control over the molecular rotational states. In the gas phase control of the number of helium atoms in a small cluster is important. We show that, in addition, impulsive laser alignment is well suited to provide control of the population of rotational level. In contrast, in the bulk phase we achieve molecular control by establishing thermal equilibrium.

We have excited a beam of small C₂H₂-He_{*n*} clusters non-resonantly with intense femtosecond laser radiation and probed the state of alignment of the C₂H₂ molecules as a function of time. Using this technique it is possible to generate rotational wavepackets and probe their propagation in the time domain. A Fourier-transform of the time-spectrum yielded the complete *pure* rotational spectrum of C₂H₂-He in excellent agreement with theory [1]. We show that the time-dependence of alignment of pure C₂H₂ which is always present in the beam can be used as a diagnostic tool for the study of molecular complexes.

In another experiment bulk helium was electronically excited using a corona discharge and the fluorescence spectrum was measured as a function of

temperature and pressure. Intense fluorescence in the visible region showed the rotationally resolved $d^3\Sigma_u^+ \rightarrow b^3\Pi_g$ transition of He₂^{*}. With increasing pressure, the rotational lines merged into single features that we attribute to fluorescent emission from the lowest rotational quantum state, indicating that these excimers are in thermal equilibrium.

The observed pressure dependence of linewidths, shapes and lineshifts established that within liquid helium excimers exist in two different environments: they are either solvated, and cold, or they are ‘boiling’ within rotationally hot gas pockets. From the electronic lifetime we can deduce an lower limit of the rotational cooling time for which we found 10¹⁰-10¹¹ K/s [2].

Both experimental methods hold great promise for the exploration of superfluidity using molecular probes.

References

- [1] G. Galinis *et al.* 2014 *Faraday Discuss.* **171** 195 – 218; G. Galinis *et al.*, 2014 *Phys. Rev. Lett.* **113** 043004
- [2] L. G. Mendoza Luna *et al.* 2016 *J. Phys. Chem. Lett.* **7** 4666