Quasi-free and hindered rotation of single molecules in liquid helium and helium clusters

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The observation of free rotation of single molecules in superfluid helium droplets has caused considerable interest [1]. To understand the specific role of superfluidity experiments were performed with normal liquid ^{3}He droplets and mixed ^{3}He-^{4}He droplets which, depending on the concentrations, provided a superfluid shell of variable thickness around an embedded molecule. These experiments showed that the width of rotational lines of OCS depended on the thickness of the superfluid ^{4}He layer in the ^{3}He droplets. 60 atoms of ^{4}He were needed to produce sharp lines, indicating free rotation. Droplets with less ^{4}He and pure ^{3}He droplets showed strongly broadened features with little resemblance of a rotational spectrum [2].
In another series of experiment the evolution of the effective moment of inertia with cluster size was investigated. These experiments showed the same trend for many different molecules: with addition of a few ^{4}He atoms the effective moment of inertia increased. Further addition brought this increase to a halt and even further addition reversed the trend, showing molecules whose rotation was largely decoupled from the rest of the cluster. The size range in which this happened was between two and fifteen helium atoms, much less than the 60 atoms needed to establish sharp lines [3, 4].
To resolve this apparent contradiction, to elucidate the nature of the line widths and their relation to the effective moment of inertia we have conducted experiments in bulk helium, using helium excimers as single-molecule probes. The excimers are short-lived and emit fluorescence, allowing the investigation of their rotational states using spectroscopy. To generate excimers in sufficient concentration and over a large pressure and temperature range a corona discharge in point-plane geometry was employed, allowing to control the interaction between molecule and environment by variation of pressure at thermal equilibrium.
Spectra of electronically excited ^{4}He were recorded between 3.8 K and 16 K and 0.3 bar and 5 bar. In the entire temperature range the spectra showed for low pressures well-resolved rotational lines. With increasing pressure the lines broaden and merge into a continuum, resembling the envelope of a rotational spectrum at pressures between 3 and 5 bar. The lines were also found to shift in frequency depending on the pressure and temperature. Changes in the rotational B-constant were not observed within our spectral resolution.
Line shifts and broadening were investigated carefully by fitting the rotational lines to Lorentzian functions. Below the critical temperature of helium the analysis of increase of pressure along isotherms showed distinct line shifts before the gas-liquid phase boundary was crossed, indicating the formation of helium clusters around the excimers and a stronger interaction between excimers and helium than helium and helium. These line shifts were observed for Q-transitions but not for P-transitions, indicating that two different types of environment exist at our experimental conditions.
We attribute the Q-lines to excimers that are caged in 7 *Å*-diameter voids. The sharp lines are attributed to excimers in larger gas bubbles that are not in thermal equilibrium with the environ-

ment and may display higher local temperatures. Reducing the temperature of the helium was found to reduce the concentration of these ’hot excimers’. The implication of our findings for probing the superfluid phase of helium will be discussed.

References

[1] M. Hartmann, R. Miller, J. Toennies, and A. Vilesov, Phys. Rev. Lett. **75**, 1566 (1995).

[2] S. Grebenev, J. Toennies, and A. Vilesov, Science **279**, 2083 (1998).

[3] A. McKellar, Y. Xu, and W. Jäger, Phys. Rev. Lett. **97**, 183401 (2006).

[4] L. Surin *et al.*, Phys. Rev. Lett. **101**, 233401 (2008).