Evidence of a Cage Effect in Superfluid Helium Droplets

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Dedicated to Prof. Dr. Dr. h. c. mult. Jürgen Troe on the occasion of his 60th birthday

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**He Droplets / Cage Effect / SF$_6$**

The cage effect is a well known phenomenon e.g. in solid matrix systems where molecular complexes cannot dissociate upon excitation due to the surrounding matrix acting as a cage. Also high density gases or liquids can produce a cage effect as has e.g. been investigated by Troe and his (former) collaborators [1−3].

In the last years a very interesting and extraordinary matrix has stepped into the limelight: the superfluid He droplet [4]. Molecules and atoms trapped in these droplets are surrounded by an ultracold ($T < 0.4$ K), homogeneous and inert environment. Since the droplets are liquid, even superfluid, it could have been expected that molecular complexes can dissociate after excitation. In the following we present our findings on the excitation of a SF$_6$ dimer trapped in a He droplet by a powerful CO$_2$ laser (maximum power output approximately about 60 W); evidence of the cage effect has been obtained also for this case.

The experimental set up will be described in detail elsewhere. Here, only a summary is presented. The He droplets are produced in a supersonic beam expansion, where a source pressure of 25 bar is applied; the nozzle is cooled to temperatures between 14 and 19 K and has a diameter of 5 μm. The He droplets pass through a skimmer and a pick-up cell which is filled with the gas of interest at $10^{-4}−10^{-5}$ mbar. On their way through the cell,

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the He droplets collect one or more molecules, which migrate to the center of the droplet and are excited by a line tunable laser, transversing the molecular beam at a right angle. The vibrationally excited molecule (molecular complex) relaxes back to the ground state, thereby releasing the absorbed energy into the droplet. The droplet regains its original temperature by boiling off several hundred He atoms. This results in a decrease of mass and consequently of kinetic energy, which is detected by a cryogenic bolometer upon which the beam finally impinges. The laser-induced bolometer signal thus is proportional to the number of boiled off He atoms and hence to the number of IR photons consecutively absorbed by the droplet.

When more than one molecule is picked up during the passage through the pick-up cell, molecular complexes are formed due to Van der Waals forces. The \( \nu_3 \) mode of the SF\(_6\) dimer has a quartet structure; two of the four levels can be excited by IR-radiation with their transition dipole moments aligned either parallel or perpendicular to the intermolecular axis. The resonant dipole interaction is responsible for the extraordinary large splitting of about 21 wavenumbers between the two IR-accessible levels [5]. This doublet structure was also found in superfluid He droplets, first by Goyal \textit{et al.} who excited the \( \nu_3 \) transition with a line-tunable CO\(_2\) and N\(_2\)O laser, and then by Hartmann \textit{et al.} who observed a continuous spectrum by applying a diode laser [6, 7].

In our experiment we excited the doublet component with the dipoles perpendicular to the intermolecular axis, at 954.55 cm\(^{-1}\), and observed the dependence of the optothermal signal on the applied laser power. In Fig. 1a, this dependence is shown for He droplets containing an estimated 7000 He atoms. The bolometer signal grows continuously as the laser power is increased up to 40 W. Remarkably, no permanent dissociation was found, which would have led to a constant optothermal signal after absorption of the first photon. The monomer absorption lies at about 946.5 cm\(^{-1}\) and thus cannot be observed, for our chosen laser frequency. Contrastingly, due to the fast relaxation in the droplet several photons are absorbed consecutively by the intact dimer, each time resulting in a decrease of the He droplet size and yielding the continuously growing signal of Fig. 1a.

This consecutive absorption of photons comes to an end when the molecular complexes are embedded in He droplets of small size, as in Fig. 1b.

\textbf{Fig. 1.} Bolometer signal as function of incident laser power. In (a), the nozzle temperature was 14 K, corresponding to an estimated average number \( N \approx 7000 \) He atoms forming the droplets. The slight curvature is attributed to the presence of small droplets in the beam, stripped almost completely by the photoabsorption. In (b), the nozzle temperature was 19 K, corresponding to \( N \approx 1400 \). Here the stripping leads to a complete levelling off of the signal. The laser is focused down to a diameter of approximately 0.2 mm, therefore, 10 W corresponds to an average intensity of \( 25 \cdot 10^7 \) W/m\(^2\).
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Fig. 1

(a) bolometer signal (a.u.) vs. laser power (W)

(b) bolometer signal (a.u.) vs. laser power (W)
where the He droplets contain about 300 He atoms after the pick-up of two 
SF$_6$ molecules. A plateau is reached for large laser powers. The stripping 
of the embedded dimer due to evaporation of practically all He atoms upon 
laser absorption yields the key for this observation. For each 10 µm photon 
absorbed, about 200 He atoms boil off which leads to evaporation of the 
droplet for high laser intensities after absorption of 1–2 photons. The 
almost completely stripped SF$_6$ dimer may still absorb a final photon and 
dissociate but this is the end of its contribution to the bolometer signal.

References
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