Supplementary material to article

Formation of Heterogeneous Clusters in Superfluid Helium Nanodroplets: Phthalocyanine and Water

J. Fischer and A. Slenczka
Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg, Germany

Reprint of the top and side view of three configurations of the phthalocyanine-water cluster as obtained by quantum chemical calculations discussed in Ref.[25].

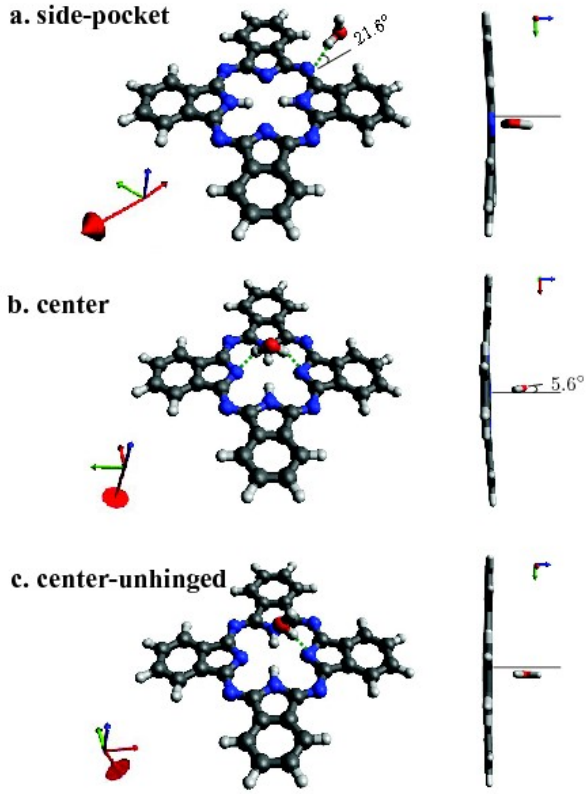


Fig. S1: Three isomeric configurations of the gas-phase Pc-H_2O cluster arranged from top to bottom in an order of decreasing overall relative stabilities. The principal axes of the system, *abc*, are indicated in red, green and blue respectively, in addition to a dipole moment vector. Hydrogen bonds are indicated with green dashed lines. Reprinted from Ref. [25] with permission.

Poisson profiles of the fluorescence intensity of the 1:1 cluster signals and 1:2 cluster signals recorded under variation of the particle density in the pick-up unit for water. Fluorescence intensities were taken from the peak area (instead of peak hight) as given by a Gauß peak fitted to the red tail of each signal. Only for signal (5L) a Lorentzian shape was used.

The experimental observable for the particle density was the signal intensity at mass 18 recorded from a quadrupole mass spectrometer (QMS). In order to eliminate the influence of time drifts in the sensitivity of the QMS the signal of water was normalized to the corresponding signal of helium at mass 4. A global Poisson fit including the 95\% confidence area was added for the 1:1 cluster signal and for the 1:2 clusters. Additional Poisson profiles of Pc-water clusters are found in Ref. [25, 40].

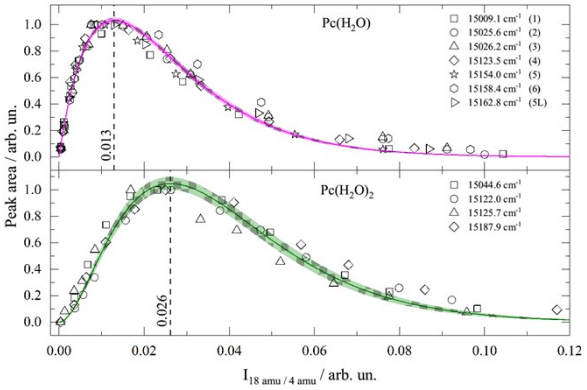


Fig. S2: Poisson plots as function of the particle density in the pick-up unit for water for the 1:1 cluster signals (top panel) and for some 1:2 cluster signals (bottom panel). Corresponding wavenumber and signal ID are added to the legend. The result of a global Poisson fit to the experimental data was added together with a 95\% confidence area for the 1:1 clusters in pink and for the 1:2 clusters in green.

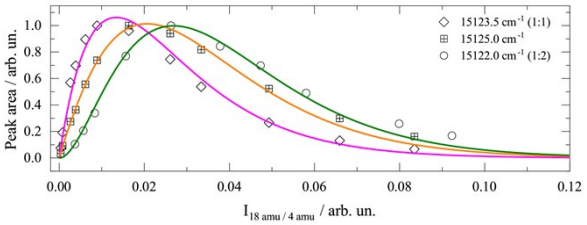
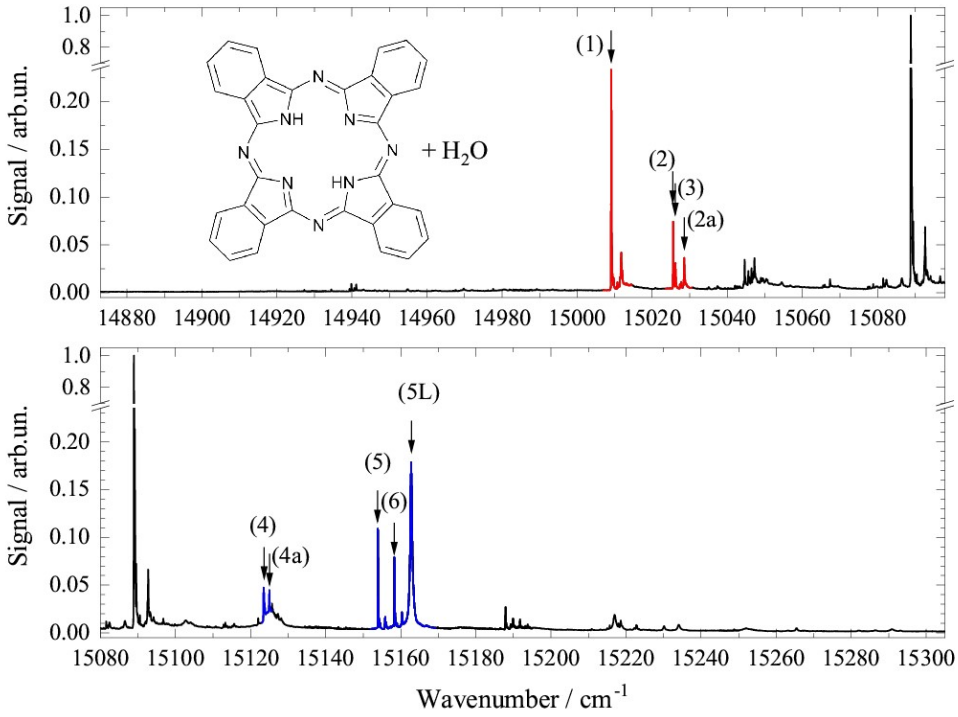


Fig. S3: Poisson plots as function of the particle density in the pick-up unit for water for cluster signals with peak positions at 15125.0 cm^{-1} (square with cross) in comparison to the 1:1 cluster (4) at 15123.5 cm^{-1} (rhomb) and to a 1:2 cluster at 15122.0 cm^{-1} (circle). Solid lines are global Poisson fits considering all three cases, namely, single particle pick-up (magenta), double pick-up (green), and a combined single and double pick-up (orange).

In order to evaluate the doping of water from the background gas of the vacuum machine the fluorescence excitation spectrum recorded upon doping with water (Fig. S5) can be compared with that recorded without water supply to the corresponding pick-up unit (Fig. S4). Both spectra are normalized to the peak intensity of the



electronic band origin of Pc.

Fig. S4: Fluorescence excitation spectrum recorded from helium droplets doped only with phthalocyanine. Doping conditions were optimized for single molecule doping. All six 1:1 clusters listed in Tab. 1 and the Lorentzian peak (5L) marked by arrows can be recognized by doping of water only from the background gas in the vacuum machine.

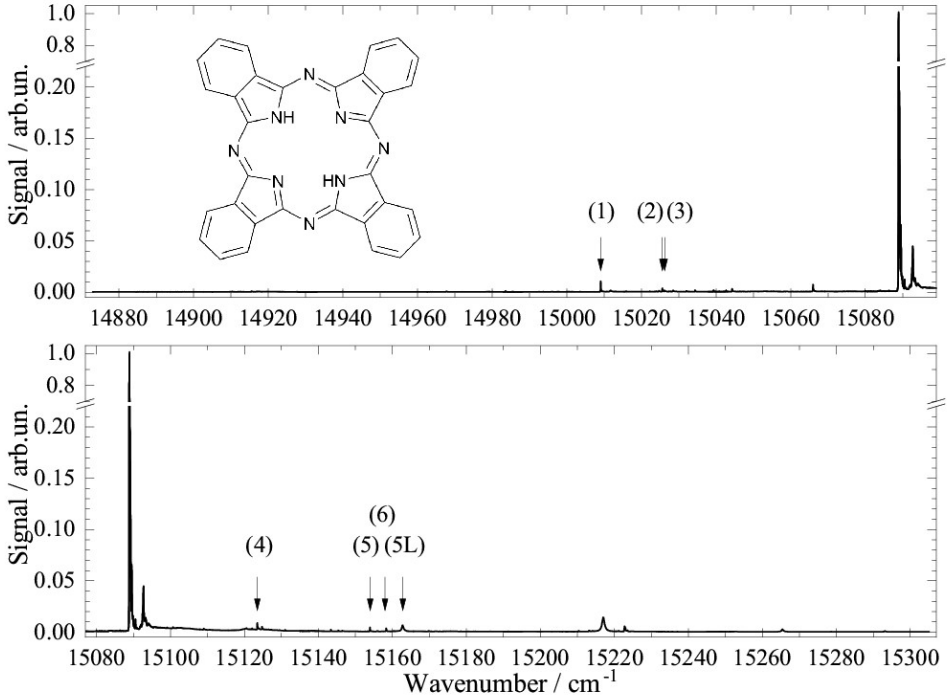


Fig. S5: Fluorescence excitation spectrum recorded from helium droplets doped with phthalocyanine and with water. Doping conditions were optimized for single molecule doping for both pick-up units. In addition to cluster (1) to (6) the peaks of clusters (2a) and (4a) are marked as well as the Lorentzian peak (5L).

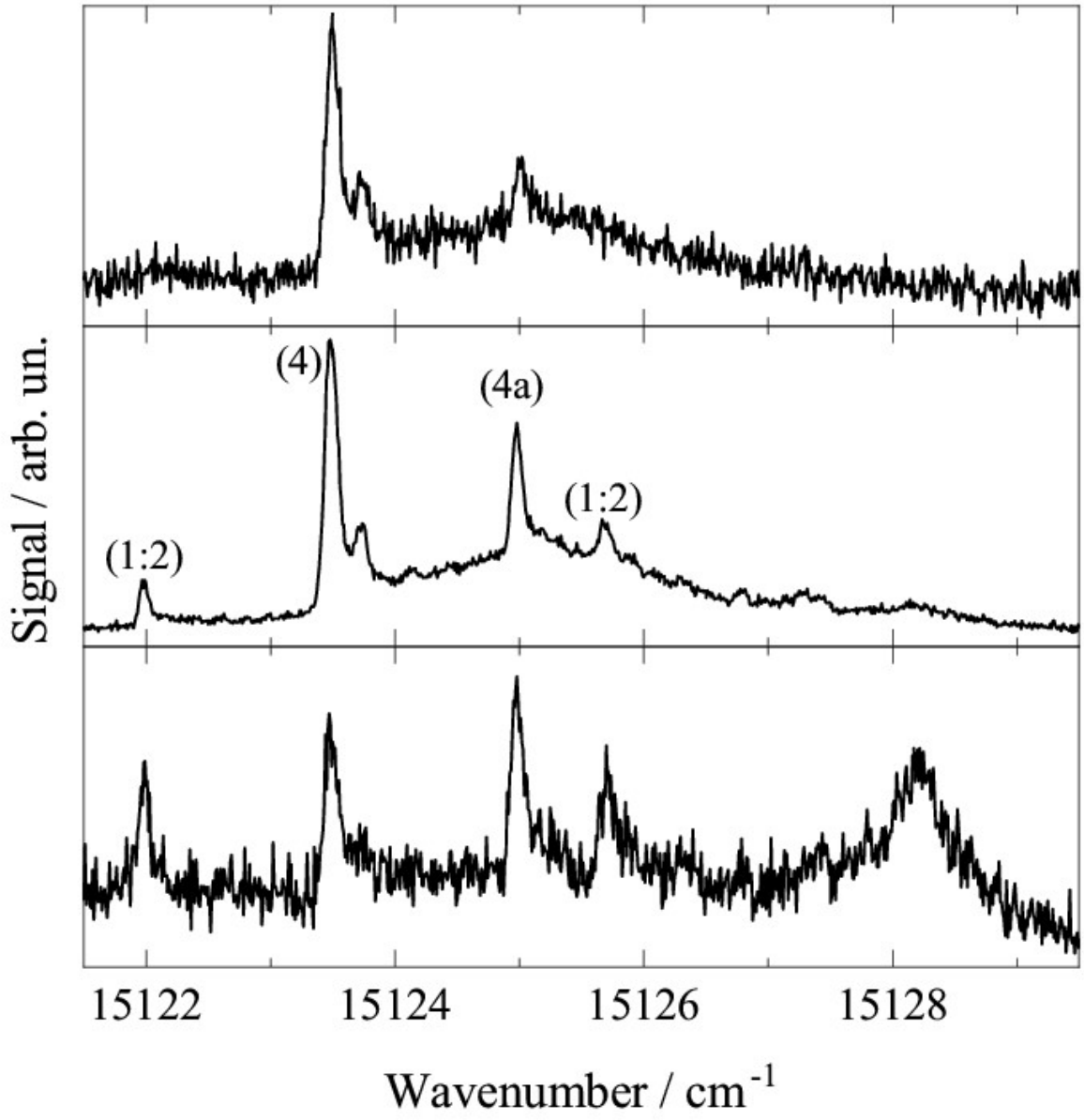


Fig. S6: Fluorescence excitation spectra recorded in the vicinity of the electronic band origin of cluster (4). From top to bottom the supply of water increases from only background (top) to optimized for single molecule doping (center) to optimized for four up to five molecule doping. The intensity of the rather broad background signal follows that of the 1:1 cluster (4) and, therefore, is assigned to the corresponding PW.

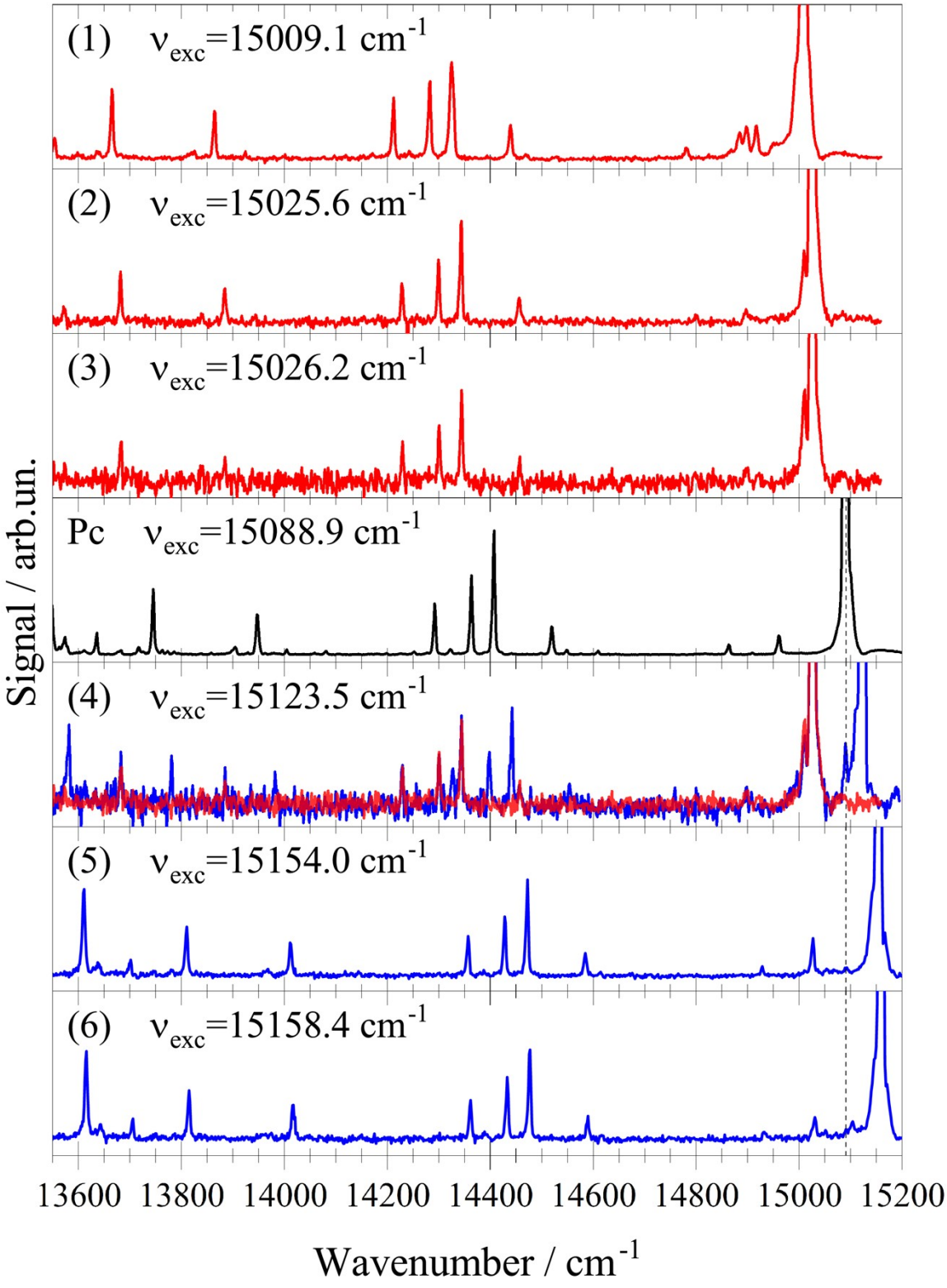


Fig. S7: Dispersed emission spectra upon excitation at the electronic band origin of 1:1 clusters of Pc with water sorted according to the water induced shift to the red (in red), to the blue (in blue). Corresponding spectrum of Pc added for comparison (in black). In panel (4) the spectrum of cluster (3) was added in red. Same spectra as shown in Fig. 3, however, with absolute wavenumber scale. Vertical dashed line marks the electronic band origin of Pc in helium droplets.

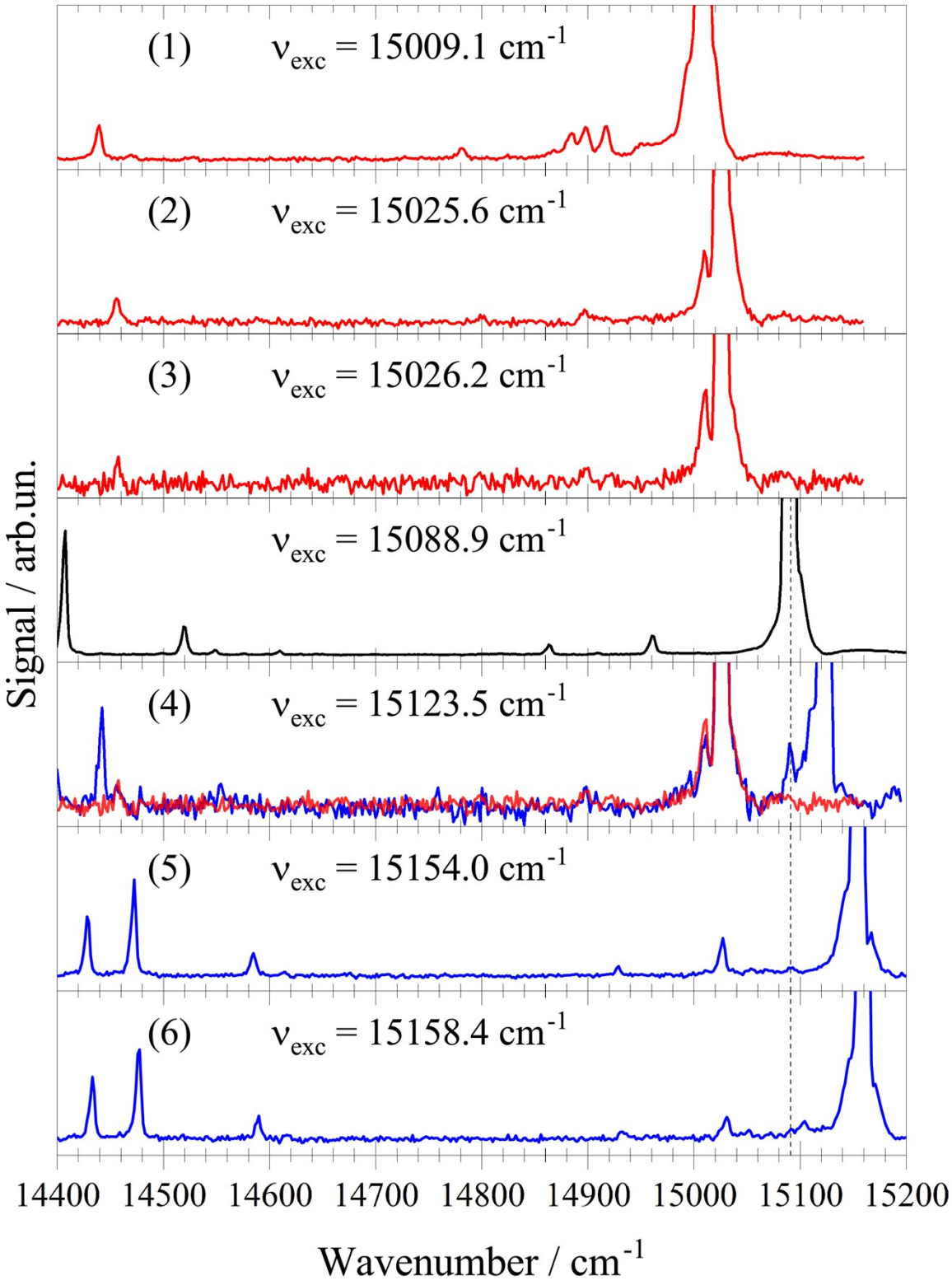


Fig. S8: Dispersed emission spectra upon excitation at the electronic band origin of 1:1 clusters of Pc with water sorted according to the water induced shift to the red (in red), to the blue (in blue). Corresponding spectrum of Pc added for comparison (in black). In panel (4) the spectrum of cluster (3) was added in red. Same spectra as shown in Fig. 4, however, with absolute wavenumber scale. Vertical dashed line marks the electronic band origin of Pc in helium droplets.

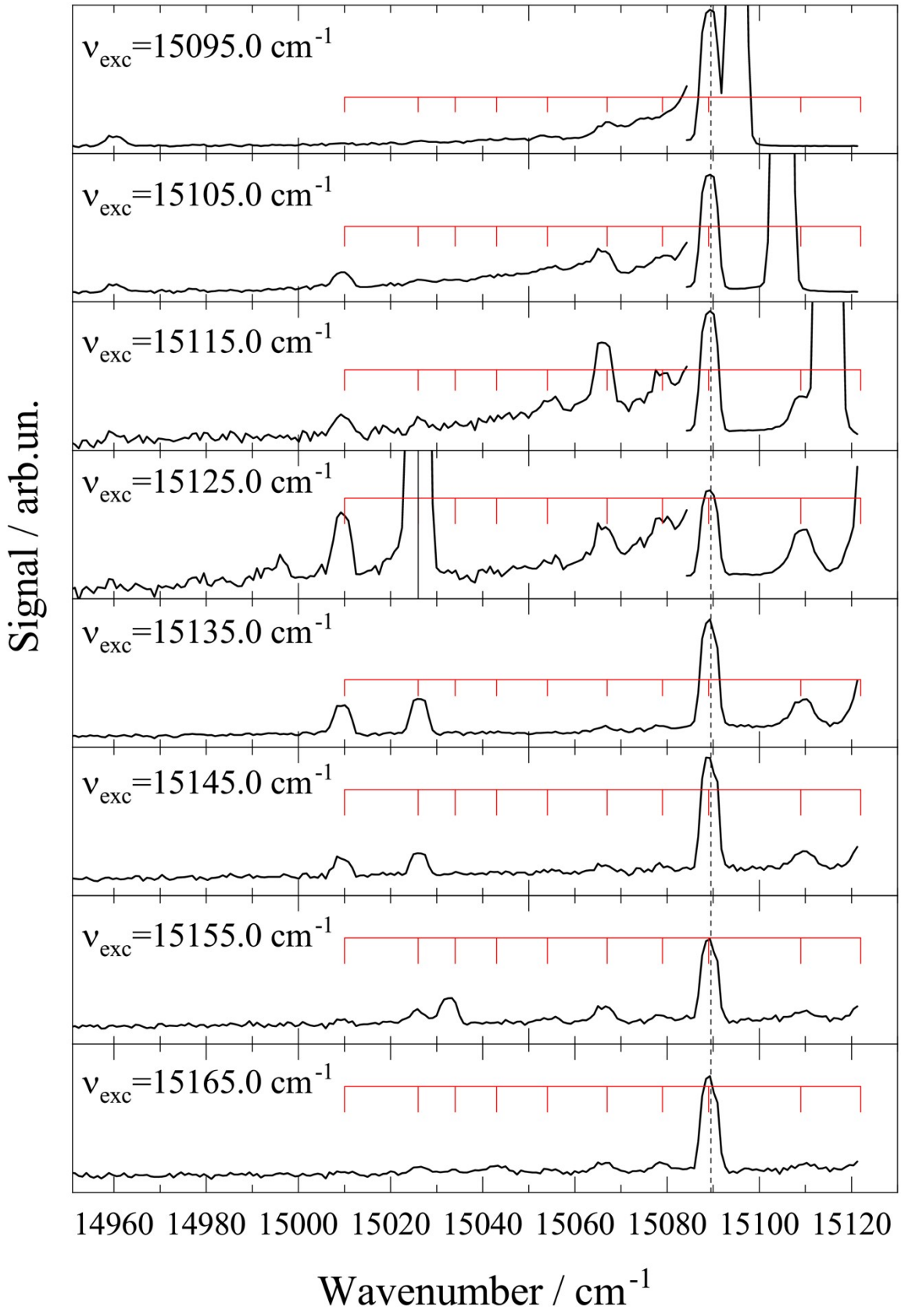


Fig. S9: Dispersed emission spectra upon non-resonant excitation at wavenumbers ν_{exc} as added to each panel. Red combs are identical for all panels and mark peak positions that are independent on the excitation frequency. Vertical dashed line in each panel marks the electronic band origin of bare Pc in helium droplets. In the 4th panel from top the vertical full line marks the electronic band origin of cluster (3) as part of the emission of cluster (4a) resonantly excited with the corresponding ν_{exc}. These spectra were taken from Ref. [56].