OW7 Measuring the Internal Energy Content of Molecules Liberated from Liquid Surfaces

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Evaporative molecular internal energy distributions are not equilibrated.

Many details concerning the mechanism(s) associated with the liberation of molecules from a liquid surface remain to be elucidated. We use the liquid microjet technique coupled with mass spectrometry and laser spectroscopy to measure the rotational and vibrational energy content of benzene spontaneously evaporating from a water-ethanol solution. These measurements, together with modelling of the gas phase collisional energy transfer efficiencies, provide molecular level insight into the mass and energy transfer processes associated with evaporation. Our results support a model of evaporative molecular energy transfer involving many collisions, resulting in moderate collisional cooling as molecules pass through a narrow liquid–vapour 'interphase' region. We provide key experimental data on the behaviour of the molecular degrees of freedom upon evaporative energy transfer against which predictions from Molecular Dynamics simulations can be rigorously tested. We then present data describing the internal energy content of benzene molecules desorbed from aqueous liquid microjets via pulsed infrared laser irradiation, and discuss mechanistic details of the desorption process in terms of mass spectrometric and laser spectroscopic evidence.