

Heterogeneous vapor uptake by single atom ions of both polarities using a differential mobility analyzer – mass spectrometer (DMS-MS)

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Sorption of vapor molecules on pre-existing ions (heterogeneous vapor uptake) is a driving force for particle formation and growth in the gas phase. The rate of heterogeneous vapor uptake is dependent on the seed particle size, charge, chemical composition and the vapor molecule - ion interaction depending on e.g., the polarizability or permanent dipole moment. To describe heterogeneous vapor uptake, several different models are often applied, namely, the Kelvin model, and Kelvin-Thomson model. While these models agree very well with experimental results in certain conditions they fail to explain dependencies on chemistry and on the structure of the seed ion, as well as to correctly implement electrostatic effects.

Ion	Molecular mass (Da)	Ionic Radii (nm)
K+	39	0.152
Rb+	85	0.166
Cs+	133	0.181
Br-	80	0.182
I-	127	0.206

Table 1. Ion Properties

In this work we experimentally measured butanol vapor uptake on single atom ions of both polarities, listed in Table 1 (K+, Rb+, Cs+, Br-, and I-), and compared the results with modeling approaches. For the measurements we used a differential mobility analyzer (DMA P5, parallel plate, SEADM, Boecillo, Spain) coupled to a QSTAR-XL mass spectrometer (MS). All ions were introduced into the gas phase by electrospray ionization, sprayed from 10 mM solutions diluted in high performance liquid chromatography grade methanol. The DMA was operated using a counter-flow where the ions are introduced in the measurement region electrostatically only, to avoid contaminations by the introduction of an aerosol flow. The resolving power of the DMA was in the range of 60 to 70 for all measurements.

The heterogeneous vapor uptake was measured by exposing the ions to a certain, well-defined vapor concentration of n-butanol, covering a saturation ratio range from 3 to 20%. The fluid was introduced directly into the temperature controlled sheath flow using a custom-made nebulizer system. The measurements were all done at a temperature of 293 K. For each saturation ratio we observed a certain shift of the ion peaks toward lower mobilities (see Fig. 1), as a consequence of uptake of a certain number of vapor molecules by the seed ions.

The experimental results were compared to modeling approaches: 1) the classical Kelvin model, 2) the model for ion induced nucleation (Kelvin-Thomson), and 3) a modified Kelvin-Thomson model that includes two additional terms to describe the interaction between the ion and the neutral vapor molecule (Yu, 2005). These models give a probability for a certain number of vapor molecules up-taken by the ion and thus, can be used to predict the expected shifts, Rawat *et al* (2015).

It has been found that there is an excellent agreement for uptake rates for all positive ions in n-butanol. For negative ions the predicted up-take rates are overestimated compared to the experimental results. Furthermore, the experimental data show little to no uptake of nonane vapor by all ions. While the modeling results for ion induced nucleation predicts up-take of one nonane molecule for all ions and saturation ratios.

The results show that even for single atom ions the initial size of the seed influences the uptake rate. While the Kelvin-Thomson model can predict the expected shifts with satisfactory accuracy for positive ions, the current model fails to correctly predict the dependencies of uptake rates on size, charge and vapor polarity for single atom ions.

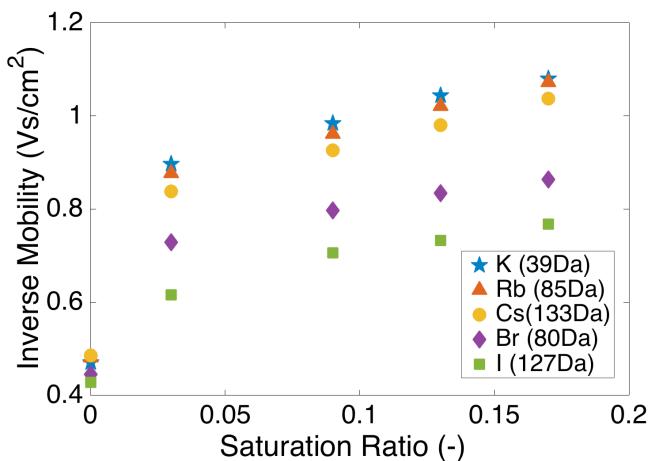


Figure 1. Experimental mobility shifts depending on the saturation ratio for all investigated ions

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Rawat, V.K., Vidal-de-Miguel, G., and Hogan, C.J. (2015) *Analyst*, **140**, 6945-6954.