

Dissociation of Molecular Ions During the DC Field Evaporation of ZnO in Atom Probe Tomography

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In atom probe tomography, a tip-shaped sample is evaporated atom by atom in a high DC field. The atoms are field ionized and accelerated to a two-dimensional detector, and their measured impact position and time-of-flight enable the three-dimensional reconstruction of the evaporated volume [1]. In some materials, a large fraction of the material evaporates as molecular ions, which can dissociate in the high DC electric field [2]. The study of such dissociations can give valuable information in the field of field induced chemistry [3], to better understand the effect of the electric field on molecules stability. In addition, such dissociations can have an effect on the quality of atom probe data and may induce composition artifacts. The understanding of the way such dissociations affect the data are necessary to predict and maybe correct these artifacts.

In this work, we first study experimentally the field evaporation of a ZnO sample. In the figure 1.a, a two-dimensional histogram shows the correlation between the time-of-flight difference and the distance between impacts, for pairs of ZnO^+ ions detected at the same evaporation event. Different regions can be identified. The horizontal line (region I) mostly corresponds to correlated evaporation [4]. The two ions reach the detector at the same time but with a spacing on the detector that reflects their original spacing on the tip surface (Figure 1.b.I). The diagonal line in the histogram, however, evidences the presence of dissociation of $\text{Zn}_2\text{O}_2^{2+}$ ions into ZnO^+ ions, with different molecular orientation with respect to the electric field. Depending on the orientation of the parent ion, the Coulomb repulsion between the dissociation products has an effect either on the time-of-flight difference between the two ions (region II) or on the spacing between their impact on the detector (region III). We show that this correlation plot can be used to extract complex information about the dissociation of molecular ions, like the parent ion lifetime, the molecule orientation when dissociation occurs, and the energy transferred by the dissociation (or kinetic energy release).

Ab initio calculations are also performed to predict the stability of molecular ions in high field. For simplicity's sake, calculations are performed for the dissociation of ZnO^{2+} ions (Figure 2). It is found that different dissociation paths can exist, with different barriers, depending on the molecule initial orientation. In particular, one orientation leads to the dissociation into neutral oxygen, which cannot be detected by atom probe and can cause important artifacts. This confirms the importance of a future study of dissociation phenomena in high field, both experimental and theoretical [5].

References

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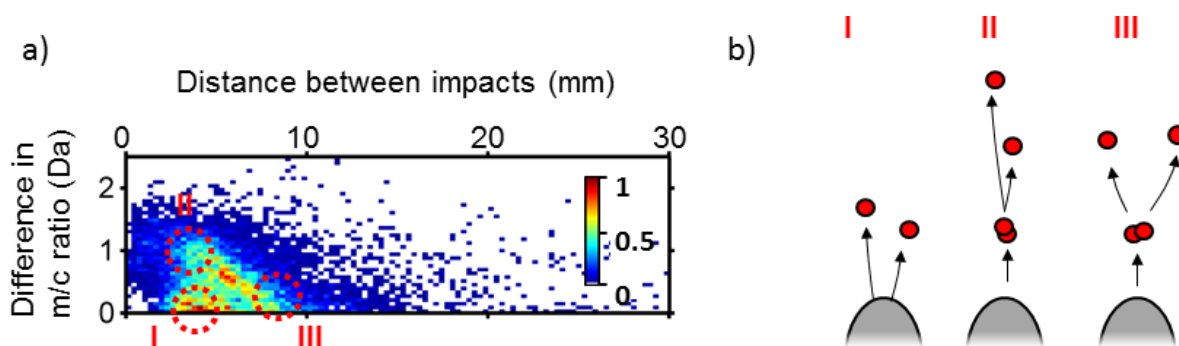


Figure 1 (a) Two dimensional histogram showing the correlation between the difference in mass-to-charge state ratio and the distance between impacts on the detector for pairs of ZnO^+ ions and (b) schematic describing the different mechanisms leading to the detection of the pairs of ions highlighted in (a), with I, correlated evaporation, and II and III dissociation with parallel and perpendicular orientations to the electric field.

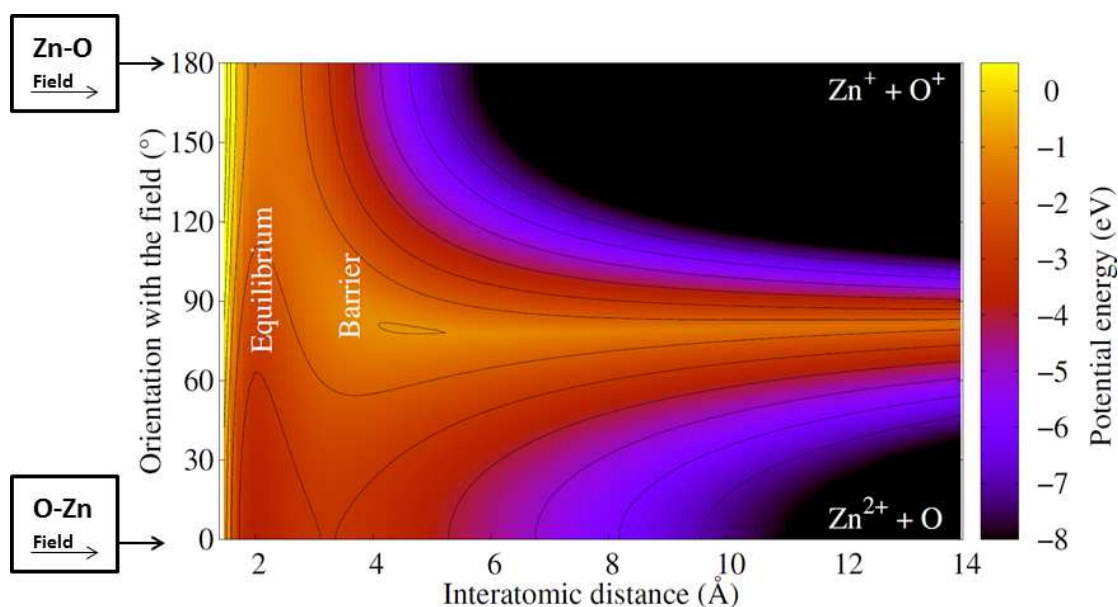


Figure 2 Two-dimensional plot of the potential energy for ZnO^{2+} as a function of the interatomic distance and the molecule orientation with respect to the 1.8 V/Å electric field.