

## UNIMOLECULAR REACTION DYNAMICS FROM KINETIC ENERGY RELEASE DISTRIBUTIONS: EXTENT OF PHASE SPACE SAMPLING

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The statistical theories of mass spectra assume that the internal energy is randomised before the dissociation takes place. The analysis of the kinetic energy released to the fragments during a dissociation gives insight into the reaction mechanism and the extent of energy randomisation.

This communication will focus on the experimental results obtained for the Br and HBr loss reactions from  $C_2H_3Br^+$  ions. We investigated these two reaction channels by dissociative photoionisation with the He(I), Ne(I) and Ar(II) resonance lines. The Kinetic Energy Release Distributions (KERDs) have been obtained from the experimental the retarding field spectra using a method based on ion trajectory calculations (1).

According to the maximum entropy method (2) the experimental kinetic energy release distribution is compared to the *prior*, i.e. most statistical, distribution. The observed discrepancy is related to the degree of non-statisticity of the internal energy redistribution. We have found that as the internal energy increases, the fraction of phase space sampled by the pair of dissociating fragments first decreases and then increases again. Coincidence data (3) and independent metastable dissociation data for the Br loss reaction confirm the observed behaviour. It can therefore be concluded that the investigated dissociations are statistical at both low and high internal energies, while at intermediate internal energies energy randomisation is not complete.

### References

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