

Direct Measurement of the Isomerization Barrier of the Isolated Retinal Chromophore

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Synopsis Energy barrier Heights for isomerization of the isolated retinal chromophore were measured using two stages of ion mobility spectroscopy (IMS-IMS).

Ion mobility spectroscopy (IMS) allows one to differentiate between different isomers of a given molecular ion according to their collisional cross-section. Using two stages of IMS (IMS-IMS) one can select a specific isomer, collisionally heat it and follow its isomerization pathways (See Fig. 1). Recently it has been shown that this technique allows one to determine internal energy barrier for isomerization [1].

Here we apply the technique to the important case of the retinal protonated Schiff base (RPSB) [2]. Photoisomerization of the RPSB is the primary in animal vision. We find that the energy barrier for a single *cis-trans* isomerization is 0.64 ± 0.05 eV, which is significantly lower than that observed for the reaction within opsin proteins. Thus the protein has a significant role in increasing the barrier energy for thermal isomerization relative to the gas phase which lacks interaction with the RPSB counterion and steric constraints. High barrier energy is mandatory for efficient vision processes, otherwise thermal noise would overwhelm the signal originating from the photochemical isomerization.

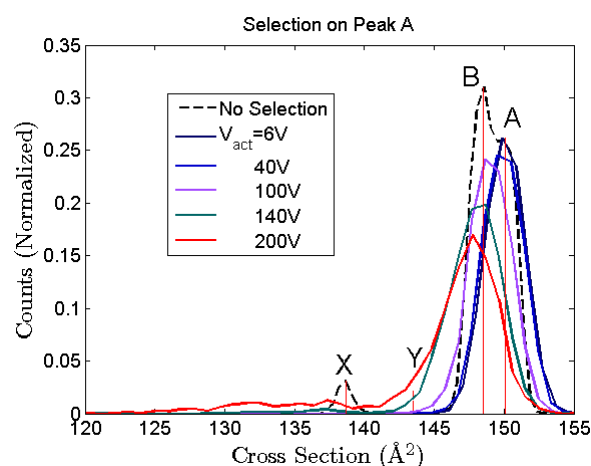


Figure 1. Results of selection and activation when the selection is applied to peak A (the *all-trans* isomer), and activation is performed for different activation voltages, V_{act} . The dashed line corresponds to the IMS of the RPSB with no selection.

References

- [1] N. A. Pierson, S. J. Valentine, D. Clemmer 2015 Int. J. Mass. Spectrom, **377**, 646-654.
- [2] J. Dilger, Y. Toker *et al.* 2015 Ang. Chemie Int. Ed. **127**, 4830-4834.

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