

# Mass Spectrometric and X-Ray Crystallographic Studies of Guest Binding to Upper-Rim Substituted Resorcin[4]arenes

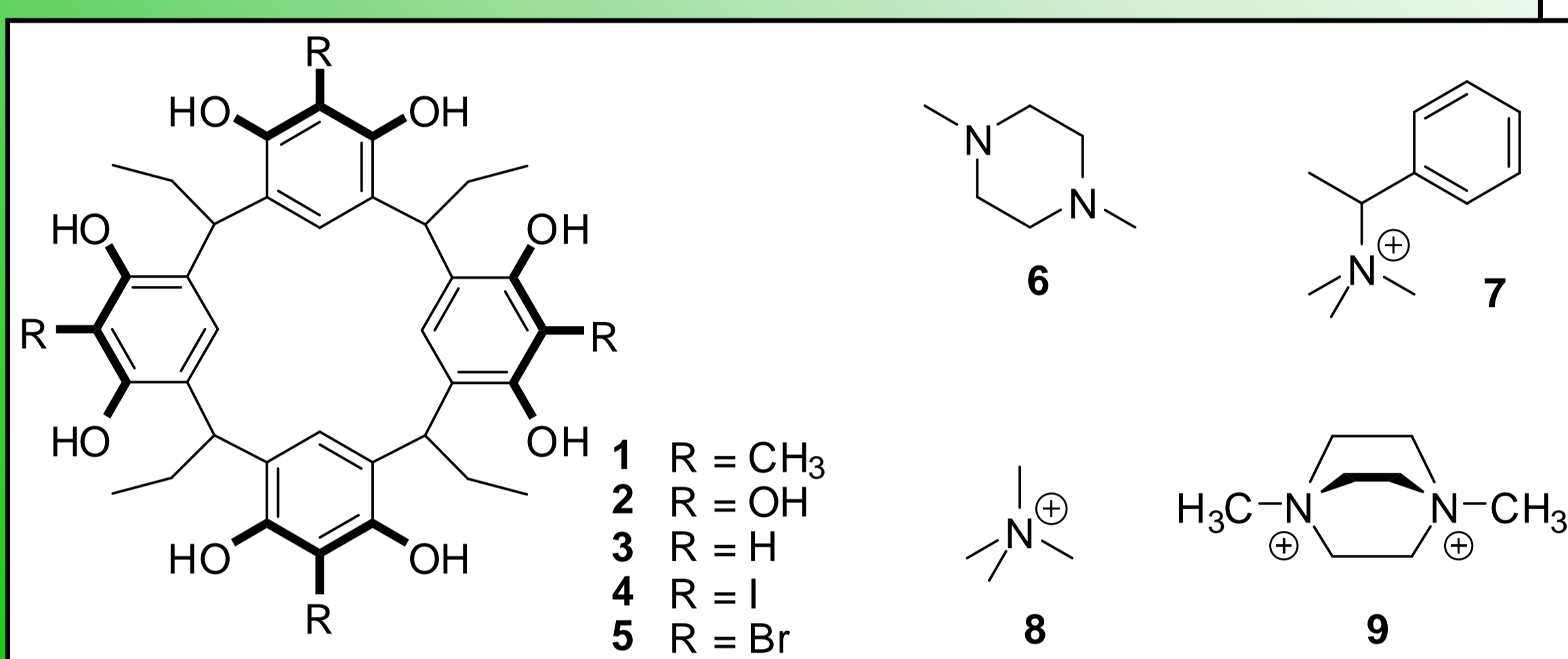
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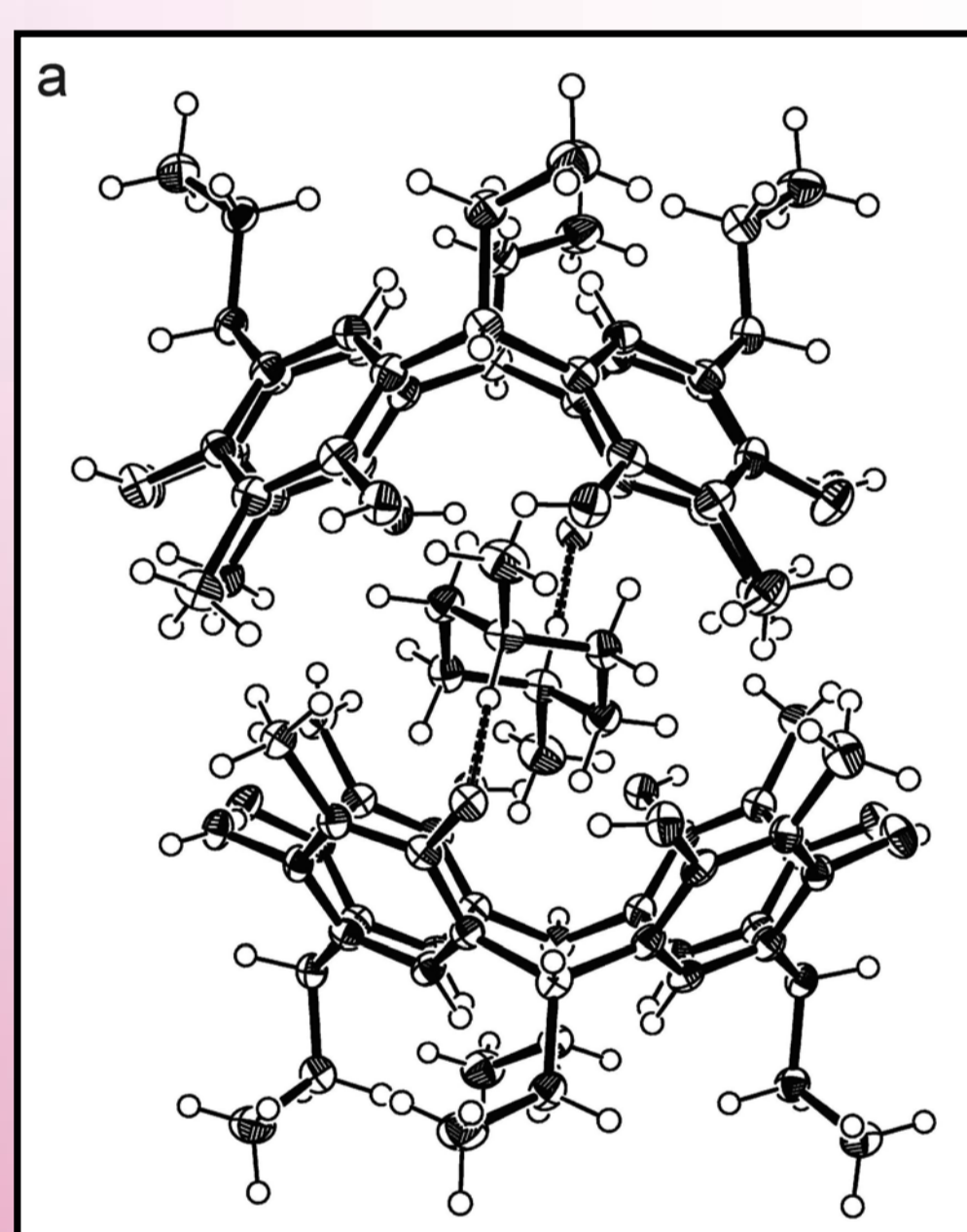
## I. Introduction

Resorcinarenes are known to form dimeric capsules<sup>[1]</sup> including small neutral or positively charged molecules. In this study, the binding capabilities of several upper-rim substituted resorcin[4]arenes (**1**, **4** and **5**) and pyrogall[4]arene **3** to neutral (**6**) as well as to singly (**7** and **8**) and doubly (**9**) positively charged guests were investigated in solid state and in the gas phase. The relative binding strength of these resorcin[4]arenes was analyzed qualitatively and quantitatively using ESI-FT-ICR mass spectrometry, which is perfectly suited to determine even very small differences in binding energy<sup>[2]</sup>, and compared to the unsubstituted "standard" resorcin[4]arene **2**.

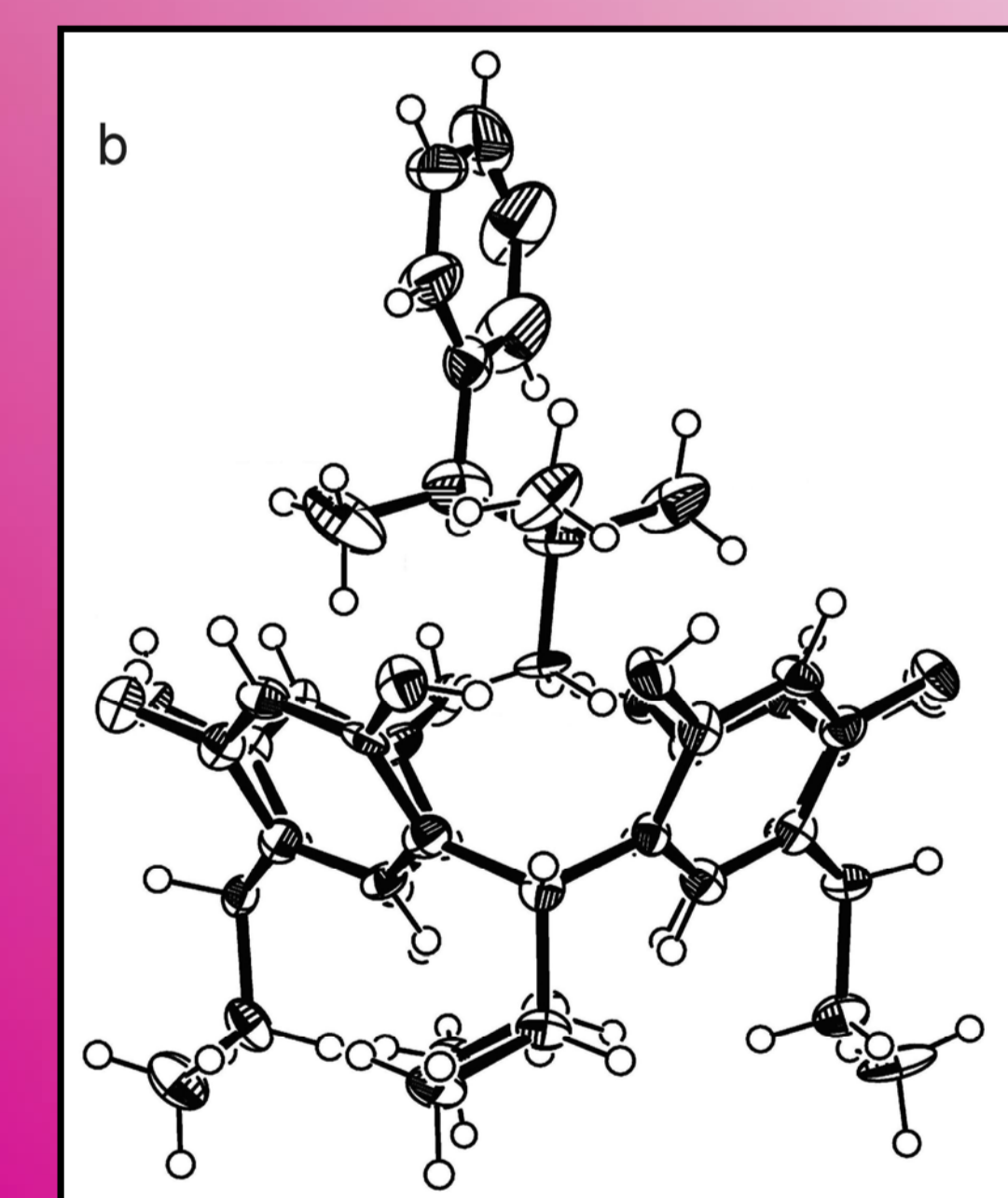


## II. X-Ray Crystallography

The crystal structure of upper-rim methylated resorcinarene **1** with doubly protonated **6** shows, how large approximately a guest molecule can be to be included into the cavity of a dimeric resorcinarene capsule (a) In contrast (*S*)-*N*-2-phenylethyl-*N,N,N*-trimethylammonium (**7**) can be bound by a single molecule of **1** but is too large to be encapsulated by two **1** (b).

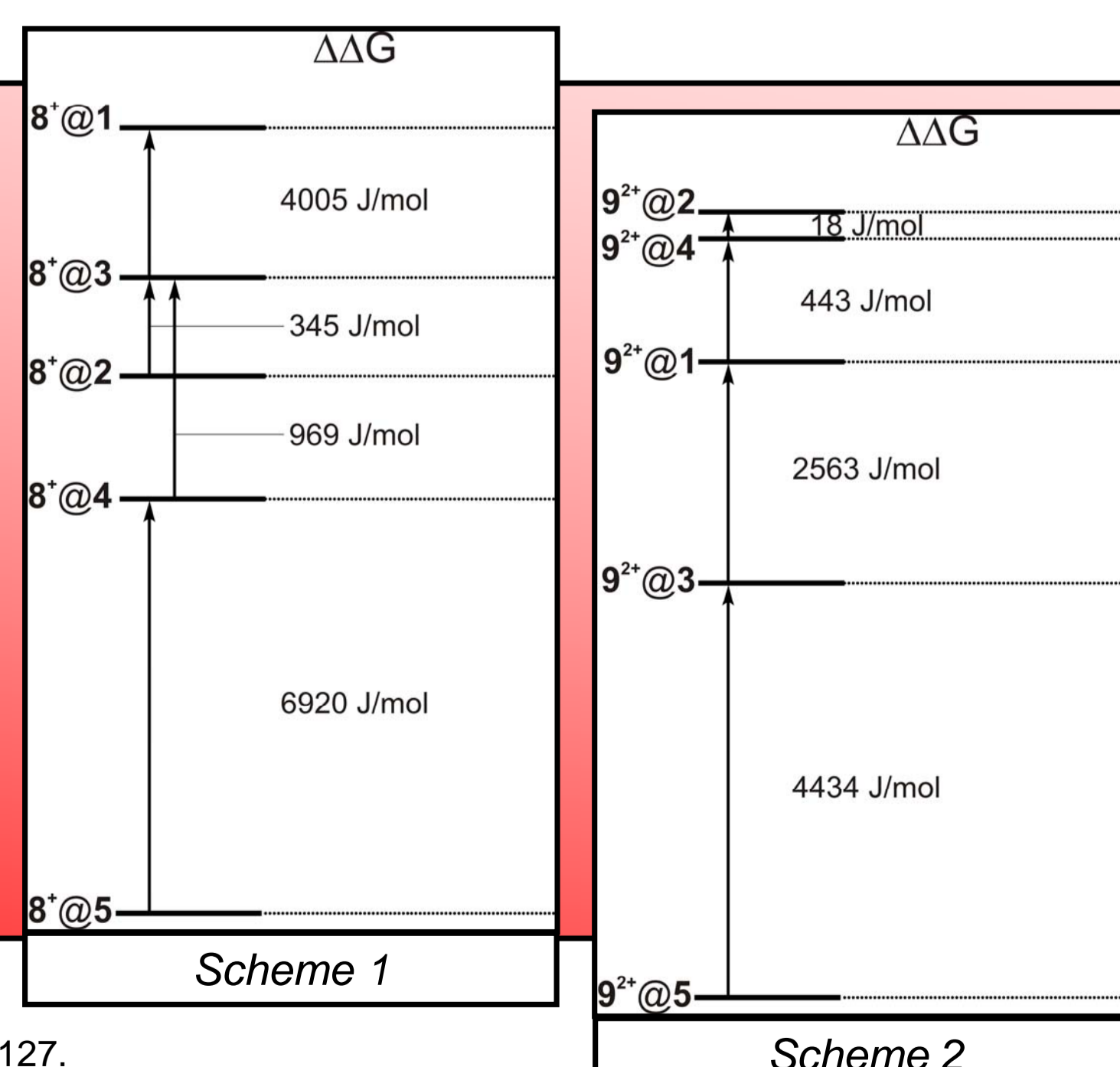


Both structures again confirm the previous results that resorcinarenes are able to bind cationic guests by cation- $\pi$ -interactions and that the formation of a dimeric capsule depends on size and shape of the guest.



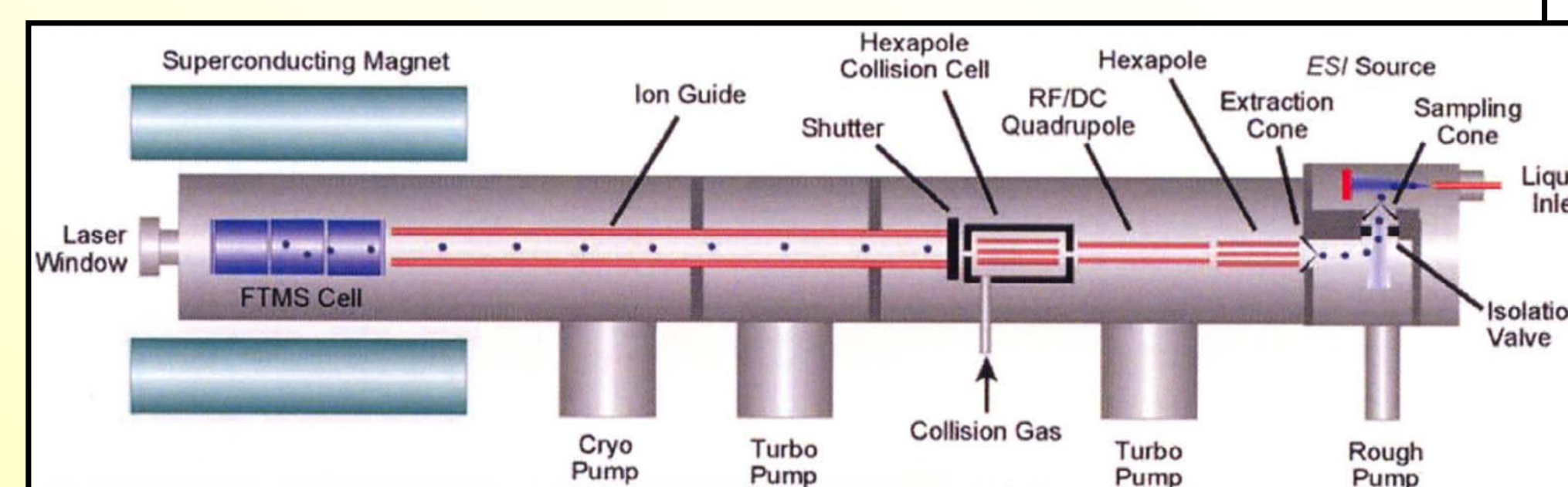
## V. Conclusions

For the case of tetramethylammonium (**8**) as guest cation, the order of binding capability of the resorcinarenes **1-5** is fairly in line with the one expected from the substituents' electronic effects. It decreases in the following order of upper-rim substituents: CH<sub>3</sub> (**1**) > H (**3**) > OH (**2**) > I (**4**) >> Br (**5**). The differences in binding energy calculated according to the kinetic method are schematically shown in Scheme 1.

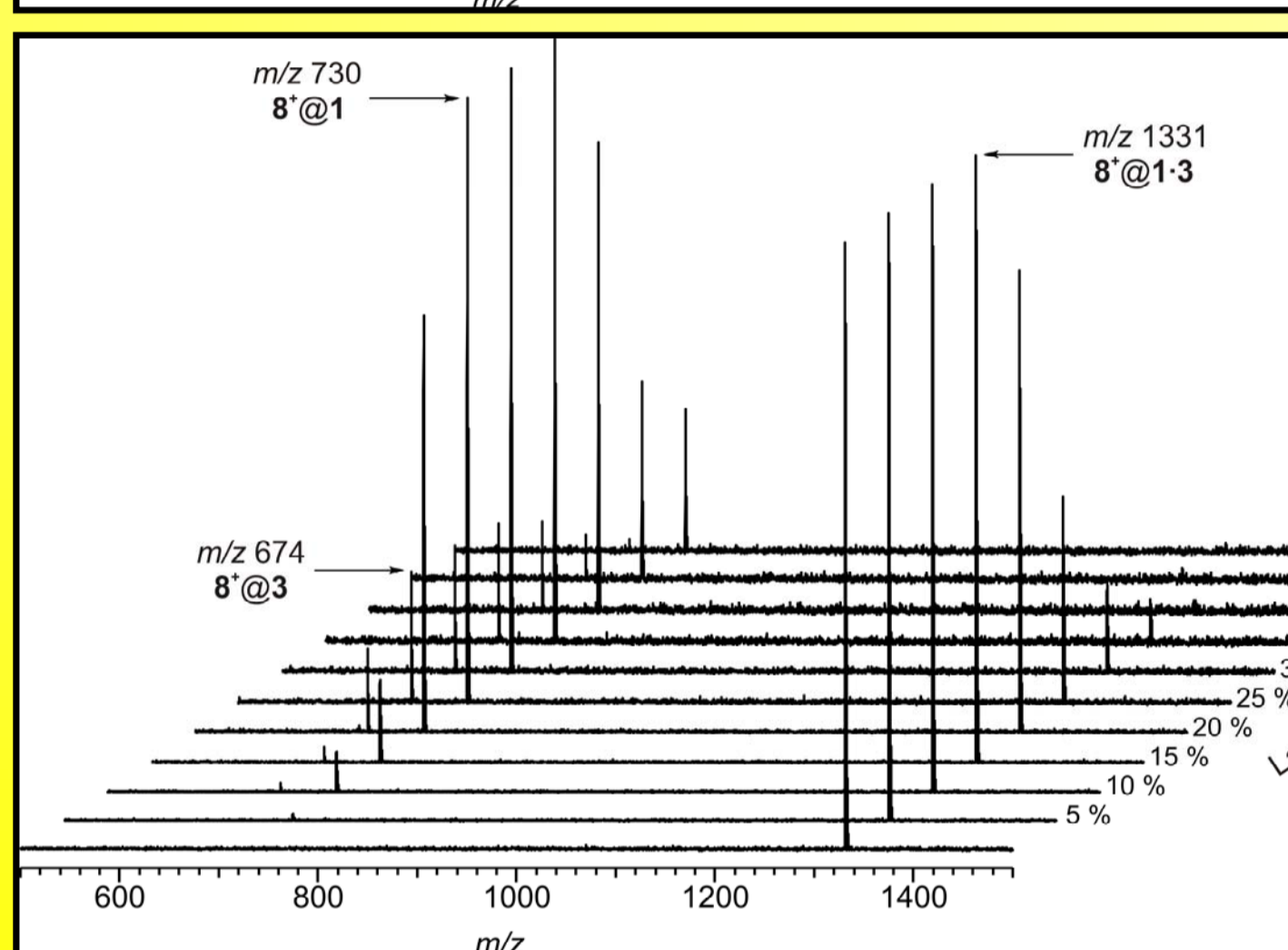
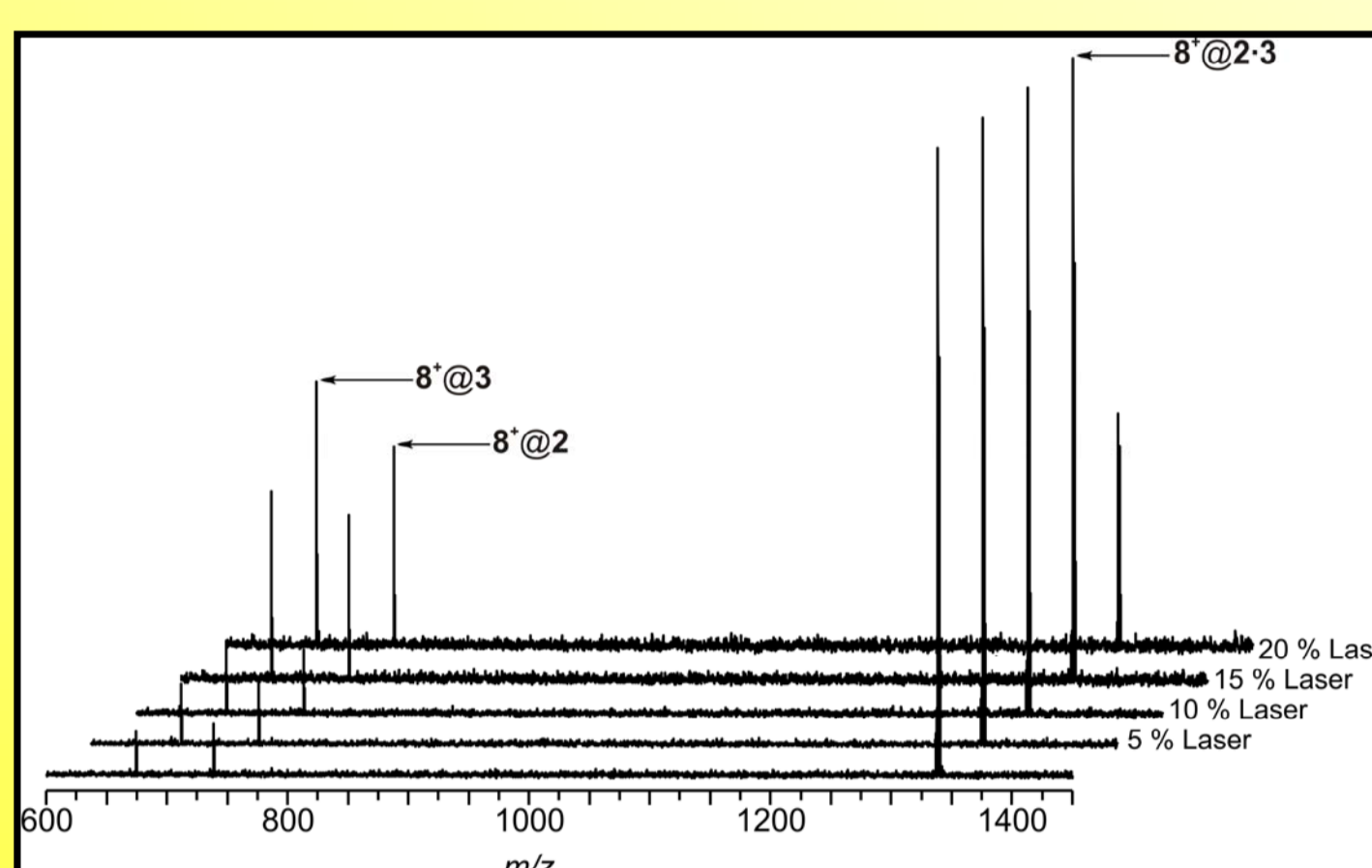


## III. Gas Phase Experiments with Tetramethylammonium (8)

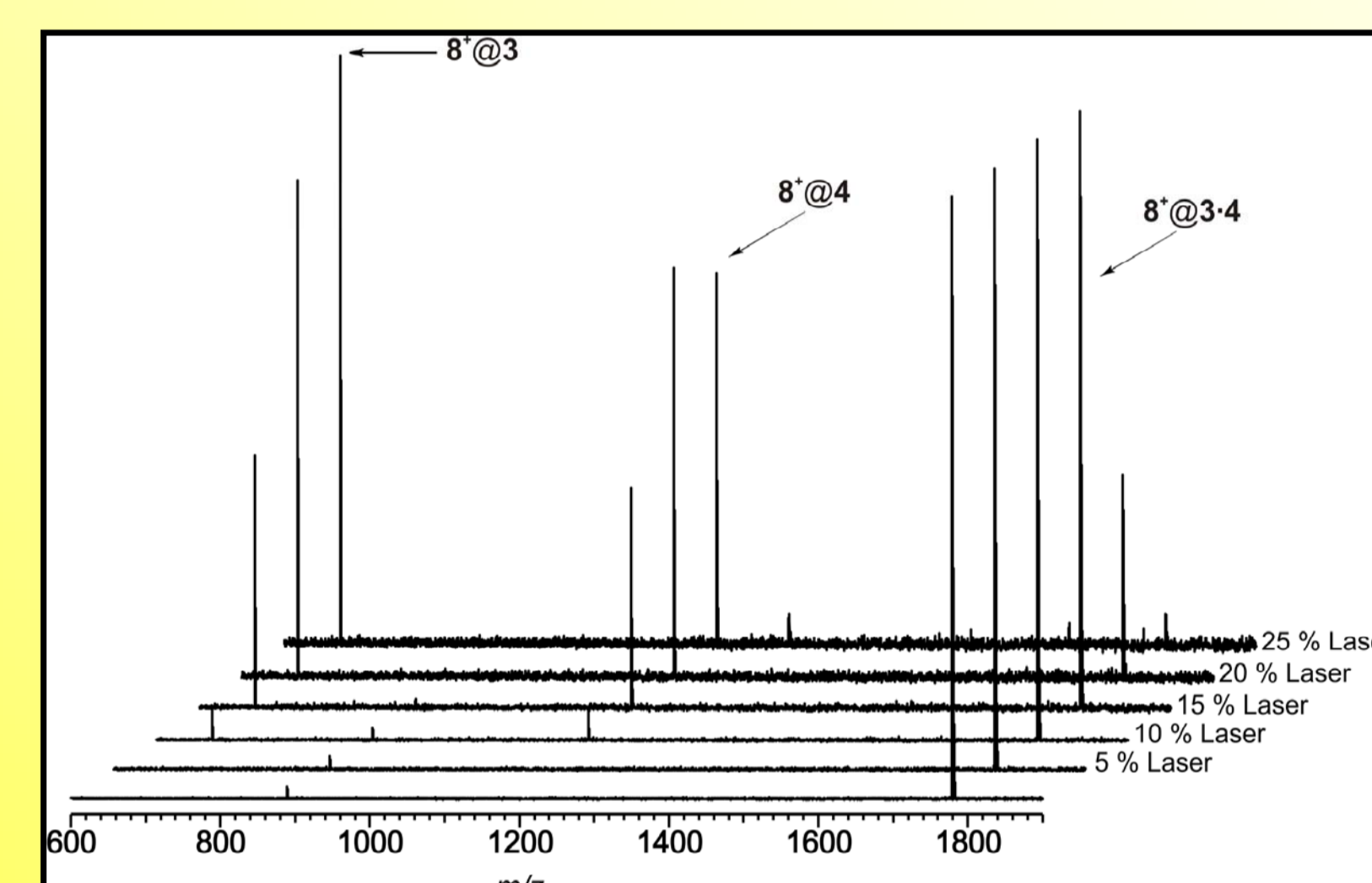
To determine the relative binding strength of tetramethylammonium (**8**) to the differently substituted resorcinarenes, an equimolar solution of each two of the resorcinarenes and NMe<sub>4</sub>OH in CH<sub>3</sub>CN was electrosprayed and the corresponding heterodimeric capsule was isolated.



Schematic drawing of the Lonspec QFT 7 FT-ICR mass spectrometer used in this study

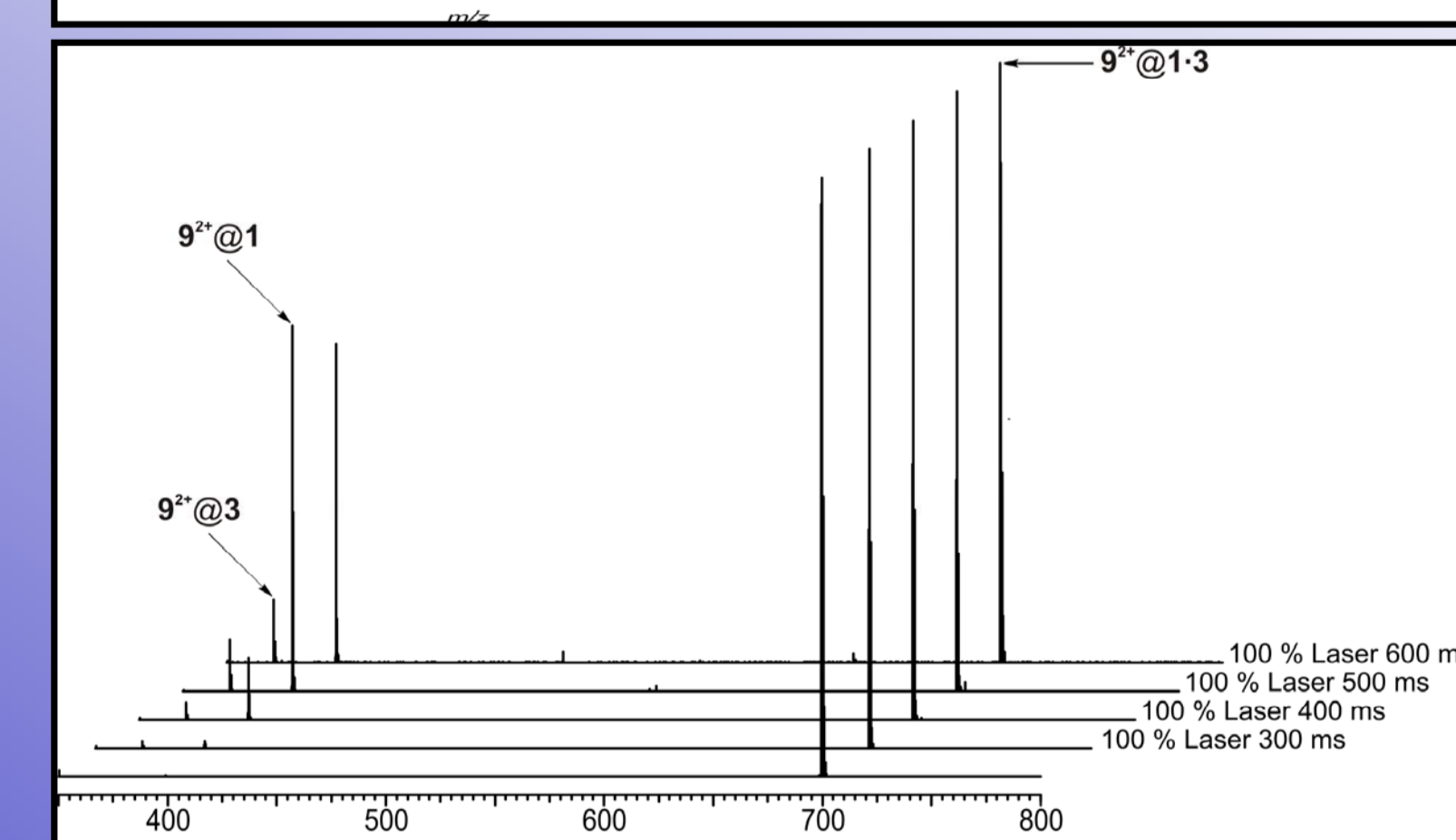
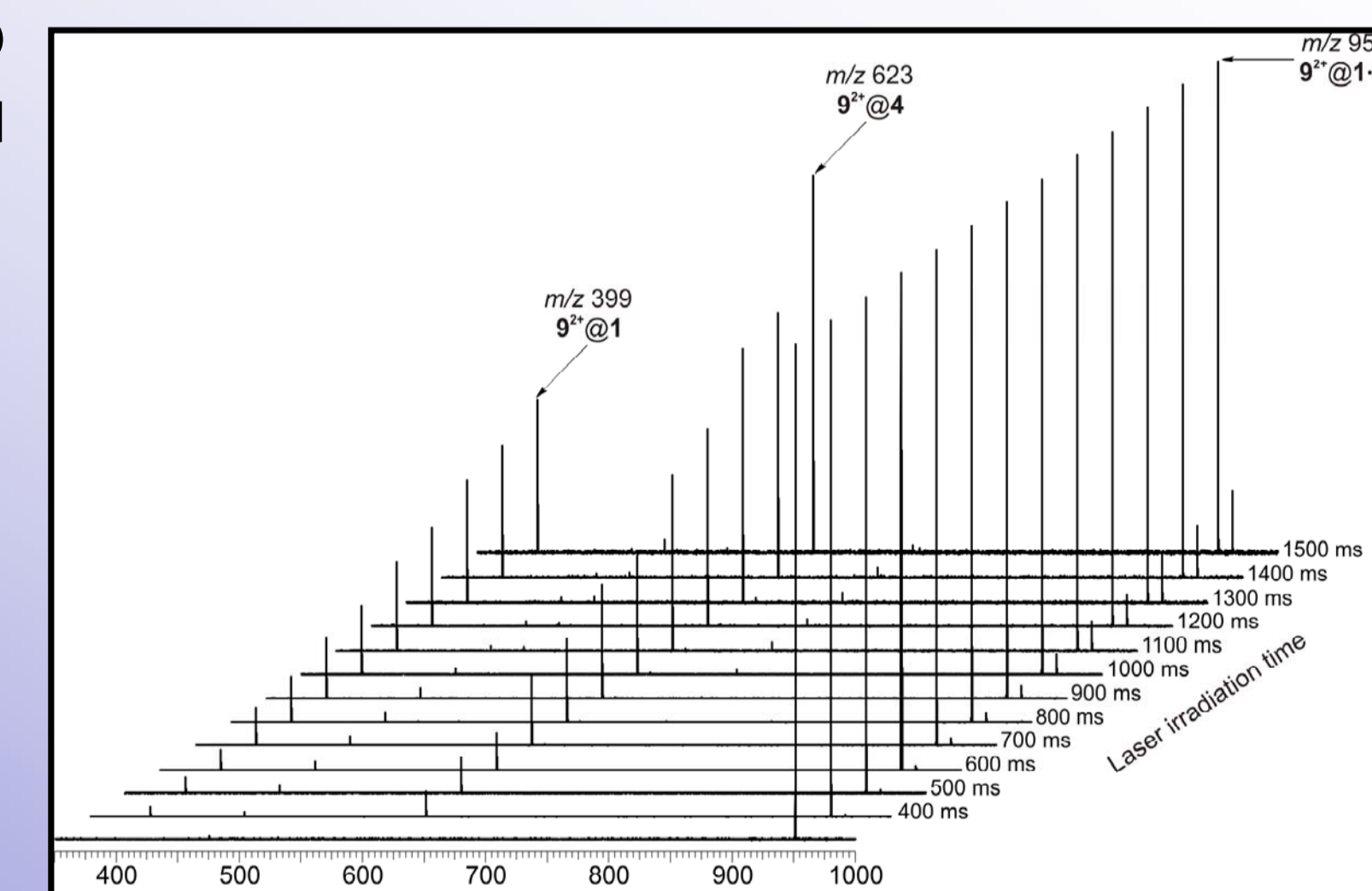
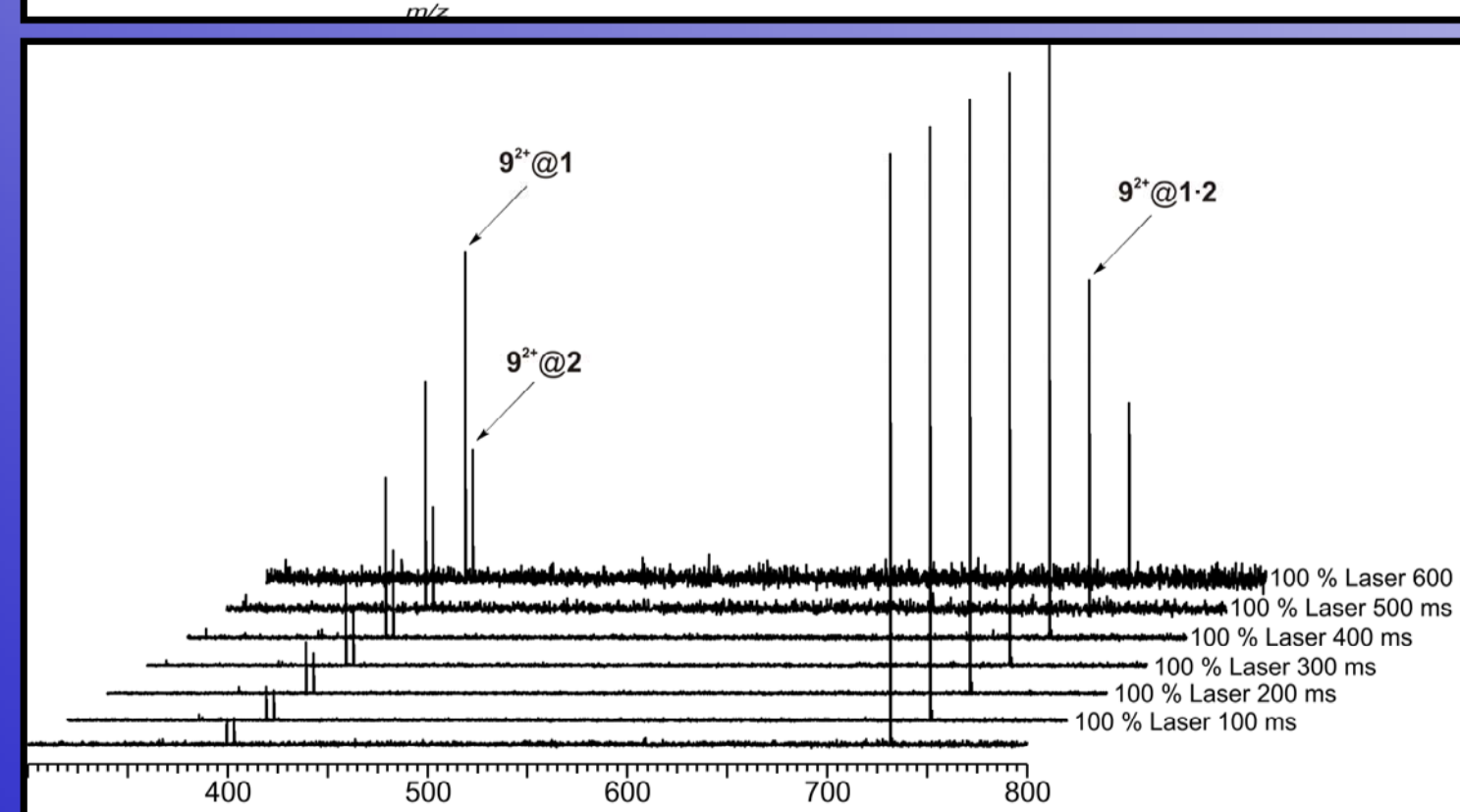
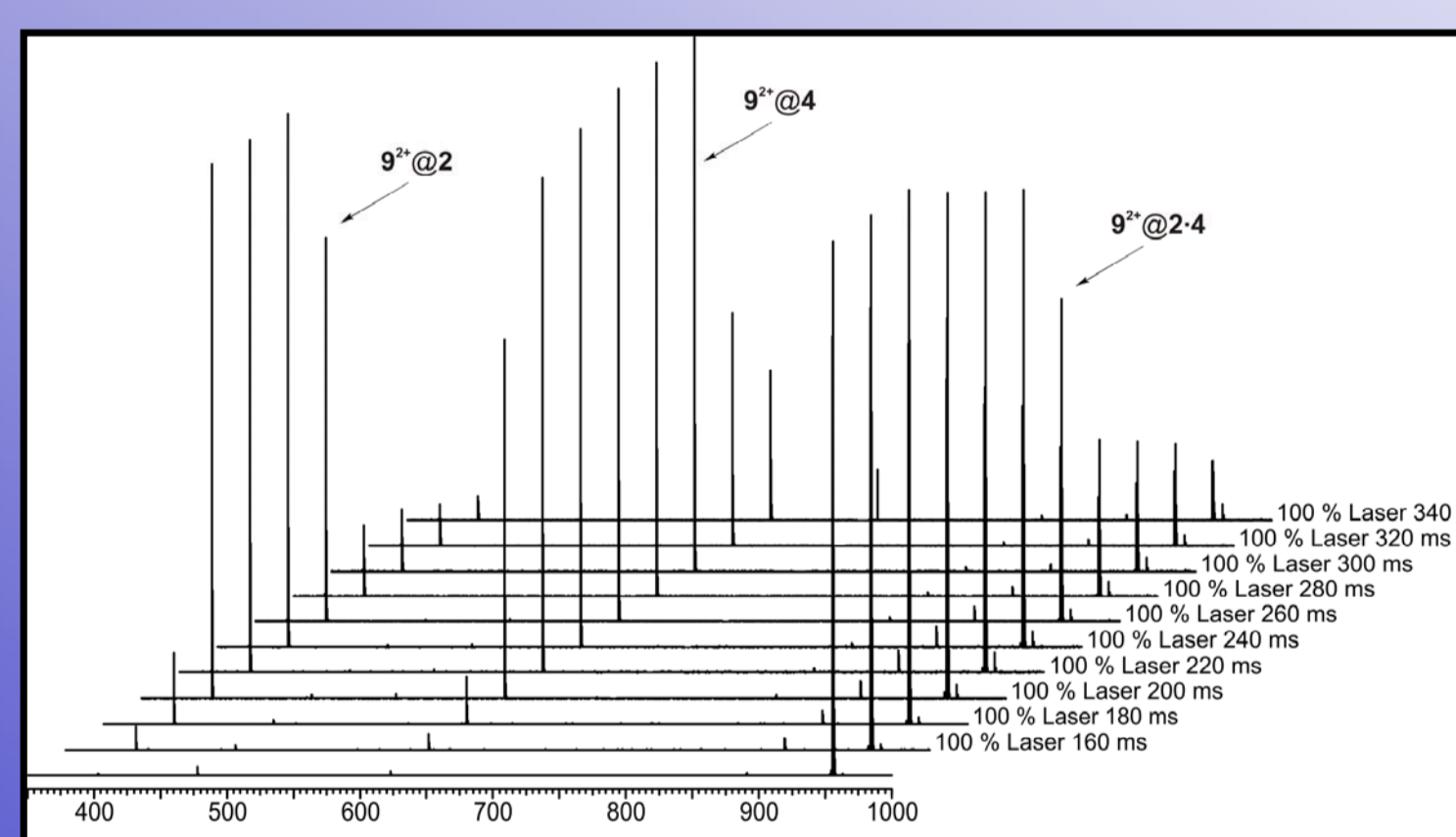


After irradiation with an IRMPD laser, the heterodimeric capsule breaks into two halves and the guest cation preferably sticks to the one with the higher binding capability. The ratio of the two arising peaks for the corresponding monomeric complexes directly corresponds to the difference in binding energy.<sup>[3]</sup>



## IV. Gas Phase Experiments with dimethylated DABCO (9)

The gas phase experiments with dimethylated DABCO (**9**) as the guest cation were performed as described above for tetramethylammonium (**8**).



For the case of dimethylated 1,4-diazabicyclo[2.2.2]octane (**9**) as guest cation, again a clear ranking of binding strength can be obtained. The capability to complex **9** decreases in the following order of upper-rim substituents: OH (**2**)  $\approx$  I (**4**) > CH<sub>3</sub> (**1**) > H (**3**) >> Br (**5**) (see Scheme 2). Astonishingly, the tetraiodoresorcinarene (**4**) binds **9** nearly as strong as the host with the highest binding capability in this experimental series (pyrogallarene **2**), which might be explained by additional stabilization of the horizontal orientation of **9** inside the cavity of **4**. This assumption is also strengthened by MM2 calculations.

[1] H. Mansikkamäki, C. A. Schalley, M. Nissinen, K. Rissanen, *New J. Chem.* **2005**, *29*, 116–127.  
[2] D. P. Weimann, C. A. Schalley, *Supramol. Chem.* **2008**, *20*, 117–128.  
[3] R. G. Cook, J. S. Patrick, T. Kotiaho, S. A. McLuckey *Mass Spectrom. Rev.* **1994**, *13*, 287–339.

**Acknowledgements:**  
We thank the Deutsche Forschungsgemeinschaft (DFG) and the Fond der Chemischen Industrie (FCI) for financial support. CAS thanks the FCI for a Dozentenstipendium.