

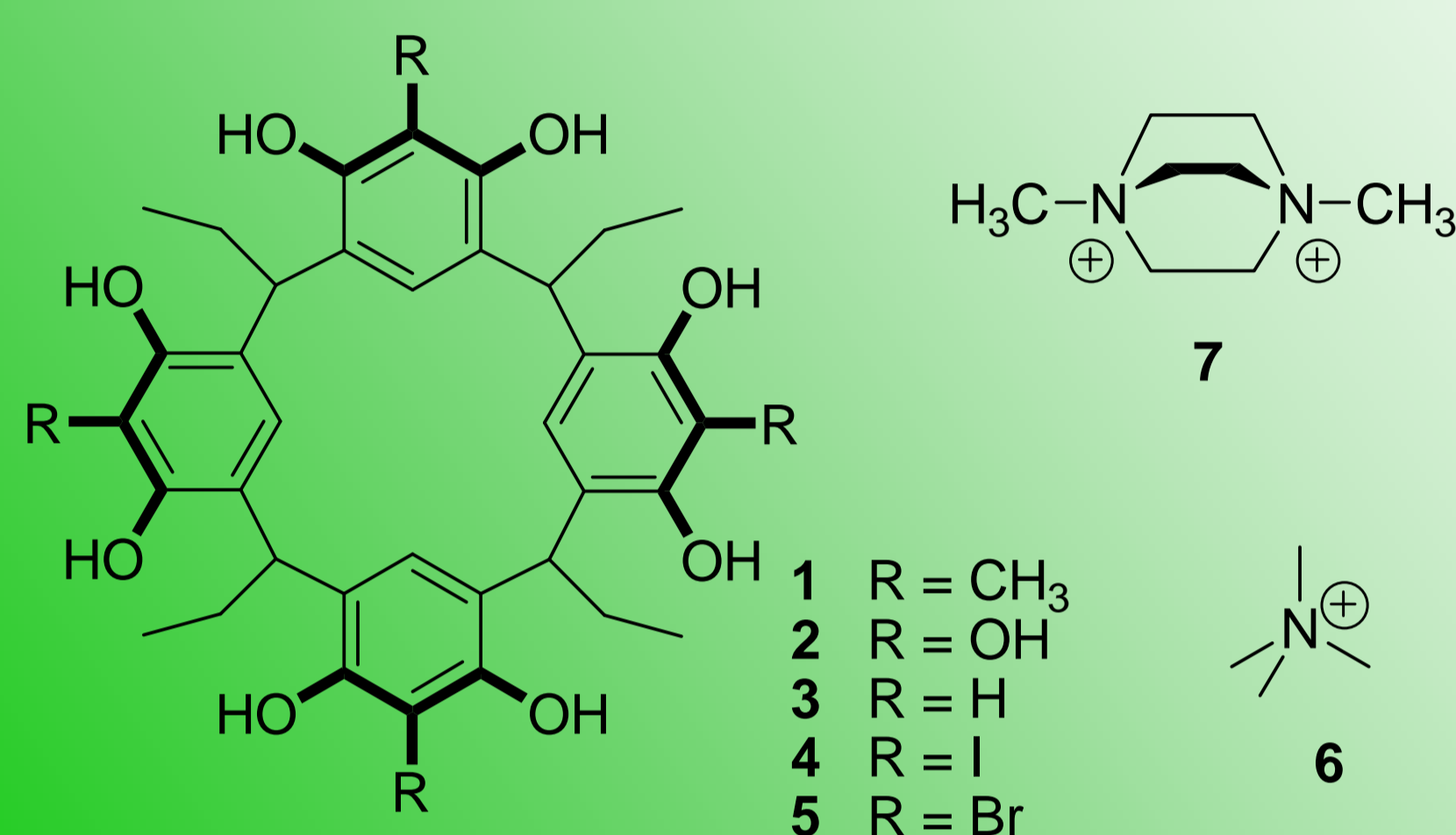


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I. Introduction

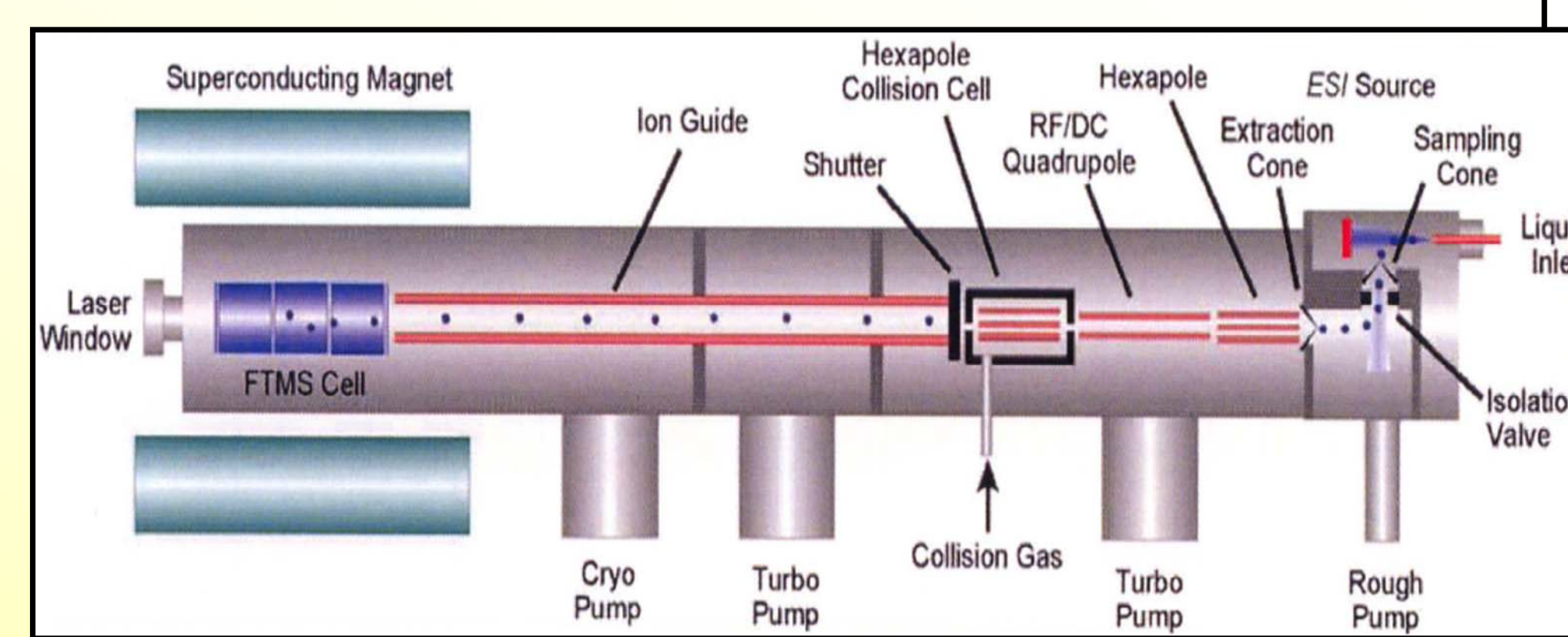
Resorcinarenes are known to form dimeric capsules^[1] including small neutral or positively charged molecules. Here, the binding capabilities of some upper-rim substituted resorcin[4]arenes (**1** - **5**) to singly (**6**) and doubly (**7**) positively charged guests were investigated in solution and in the gas phase. The relative binding strength of these resorcin[4]arenes was analyzed qualitatively using ESI-FTICR mass spectrometry^[2], which is perfectly suited to determine even very small differences in binding energies^[3] and compared to the binding strength in solution obtained from NMR titrations.



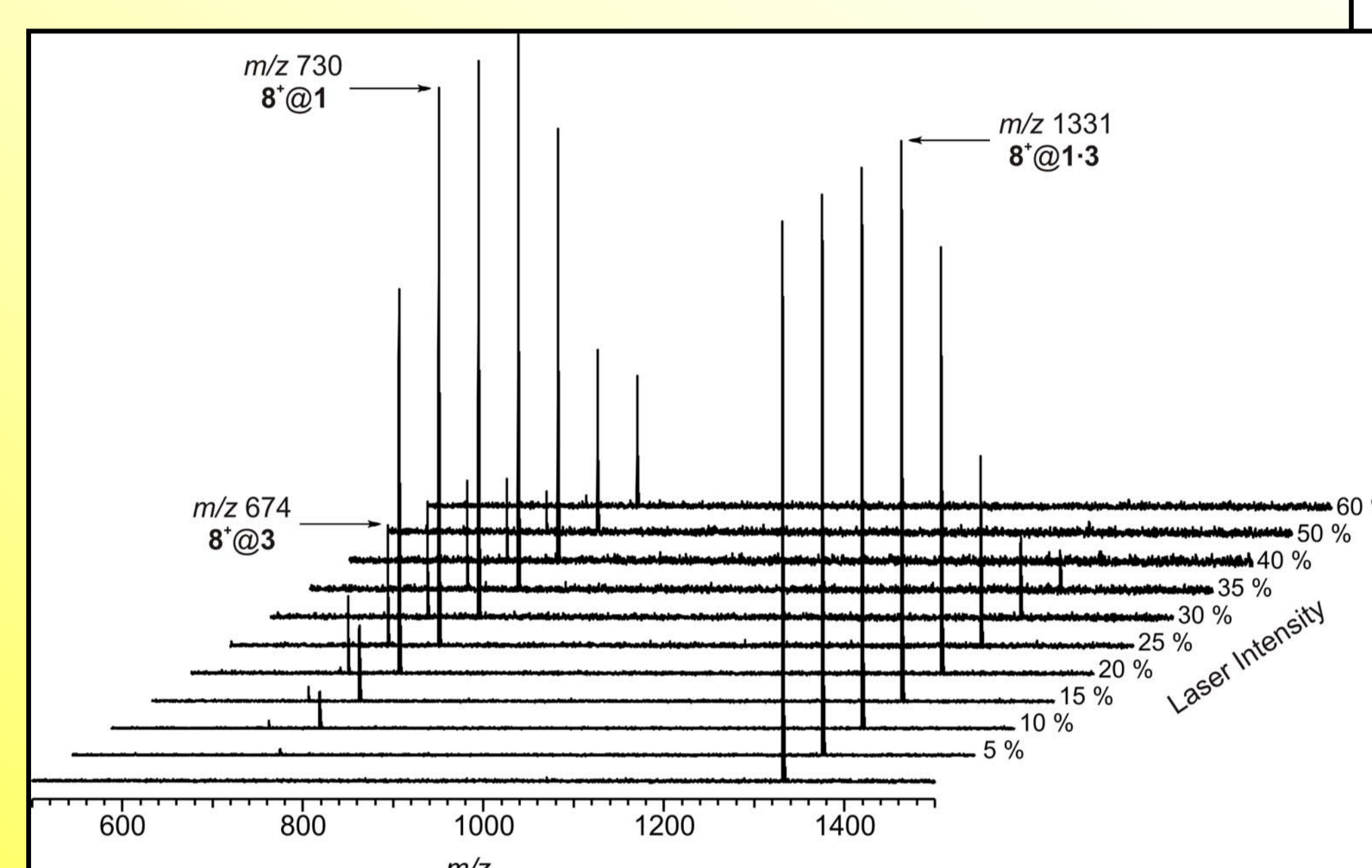
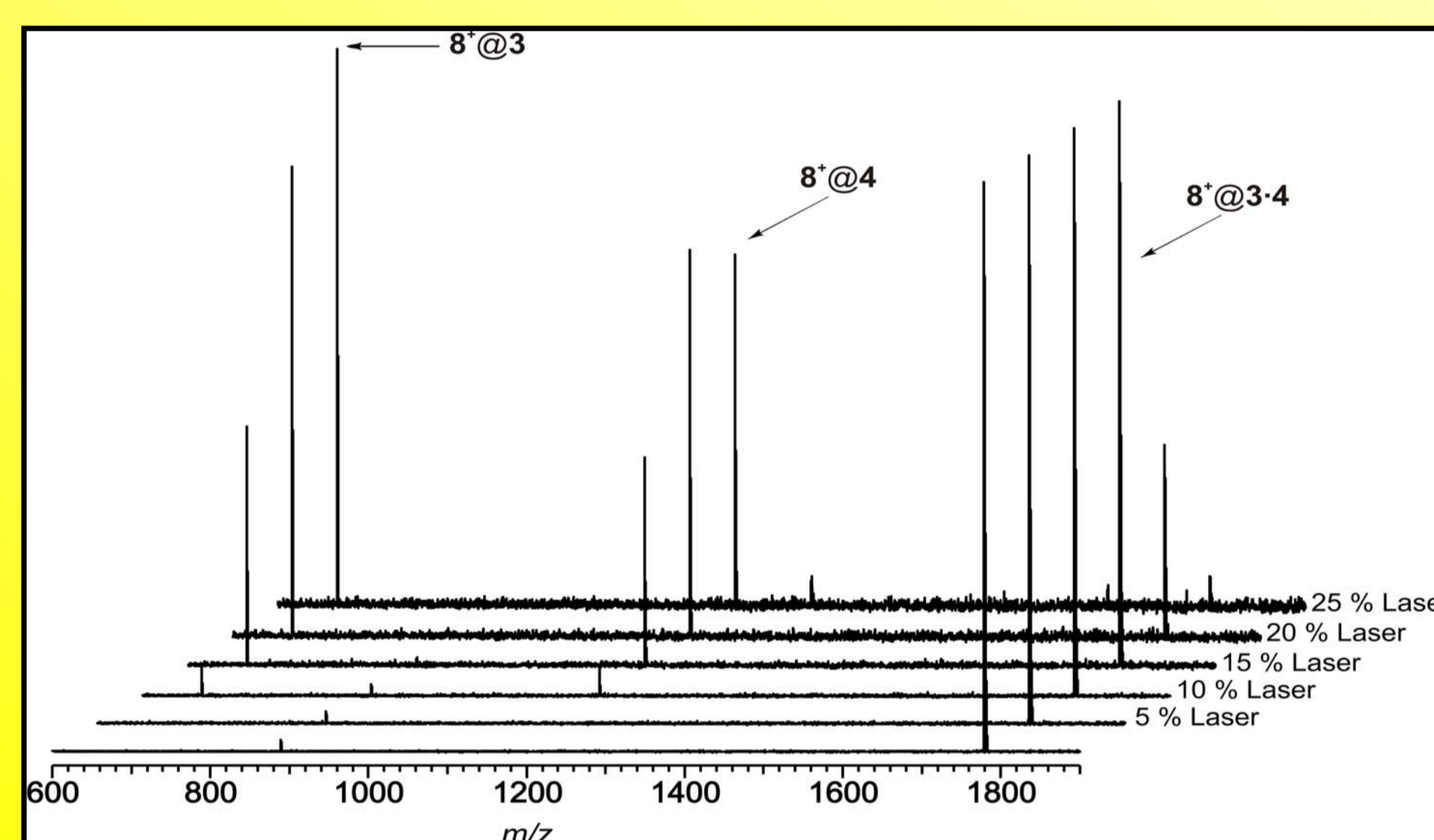
II. Gas Phase Experiments with Tetramethylammonium (6)

To determine the relative binding strength of tetramethylammonium (**6**) to the differently substituted resorcinarenes, an equimolar solution of each two of the resorcinarenes and NMe₄OH in CH₃CN was electrosprayed and the corresponding heterodimeric capsule was isolated.

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.^[3]

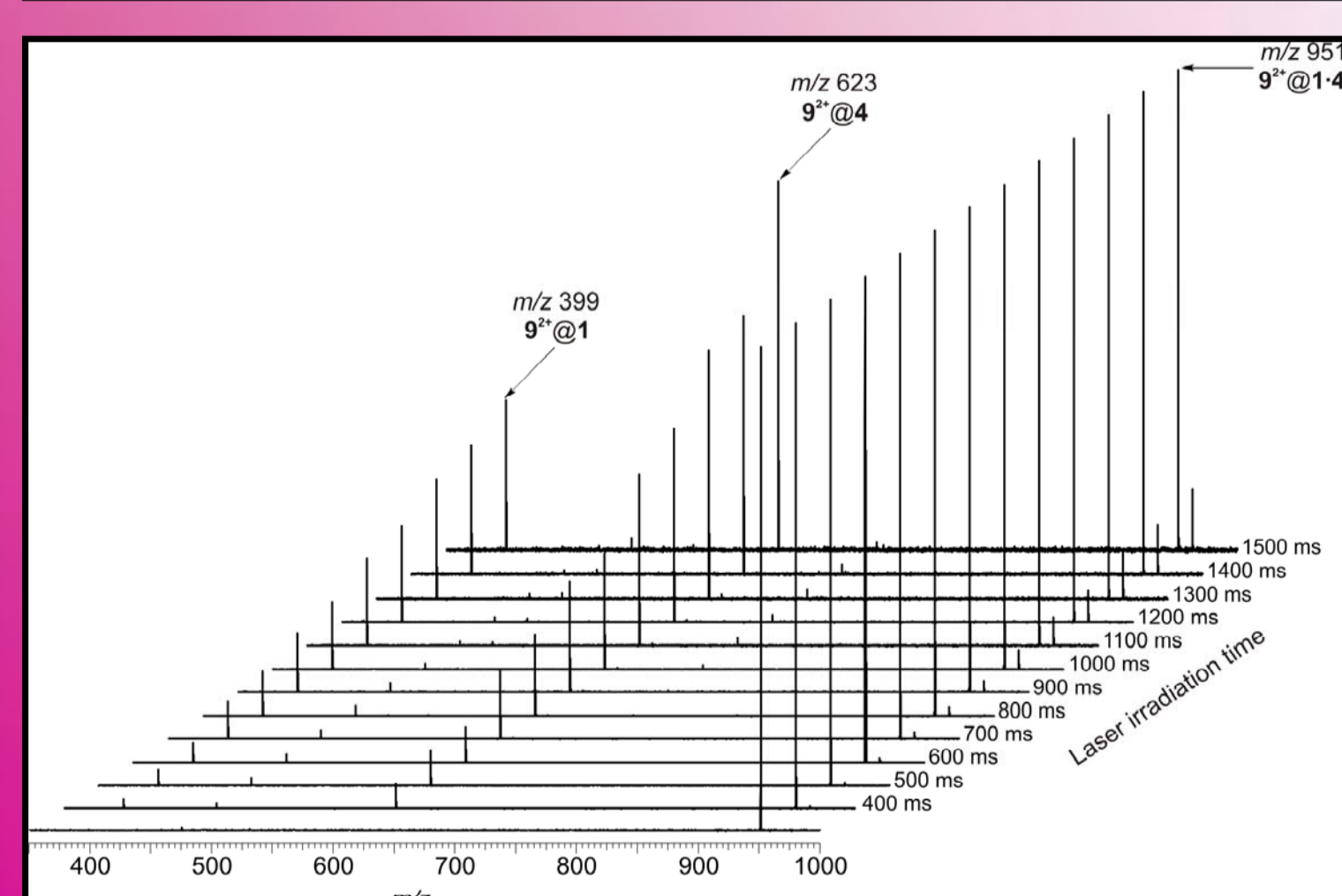
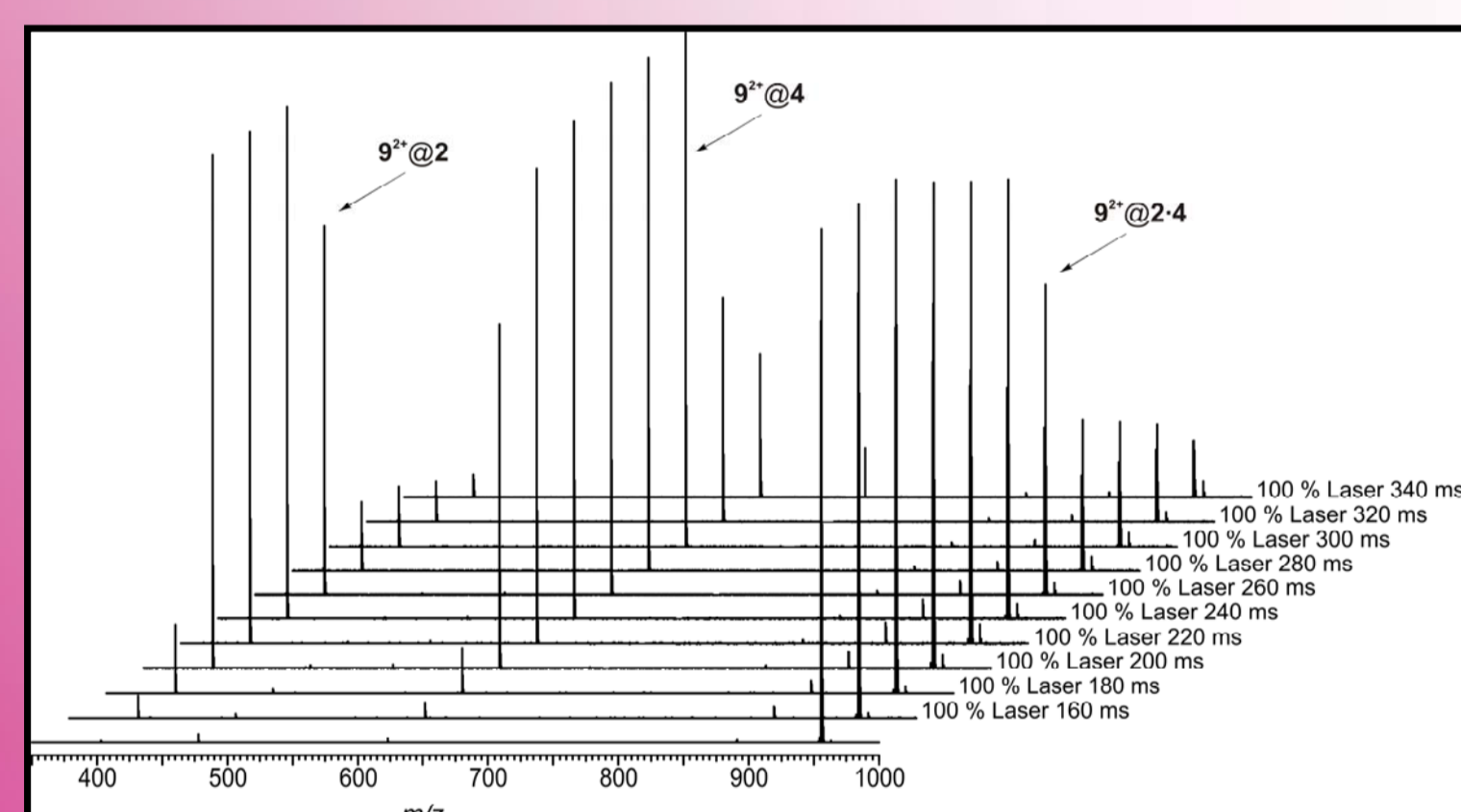


Schematic drawing of the Ionspec QFT 7 FT-ICR mass spectrometer used in this study



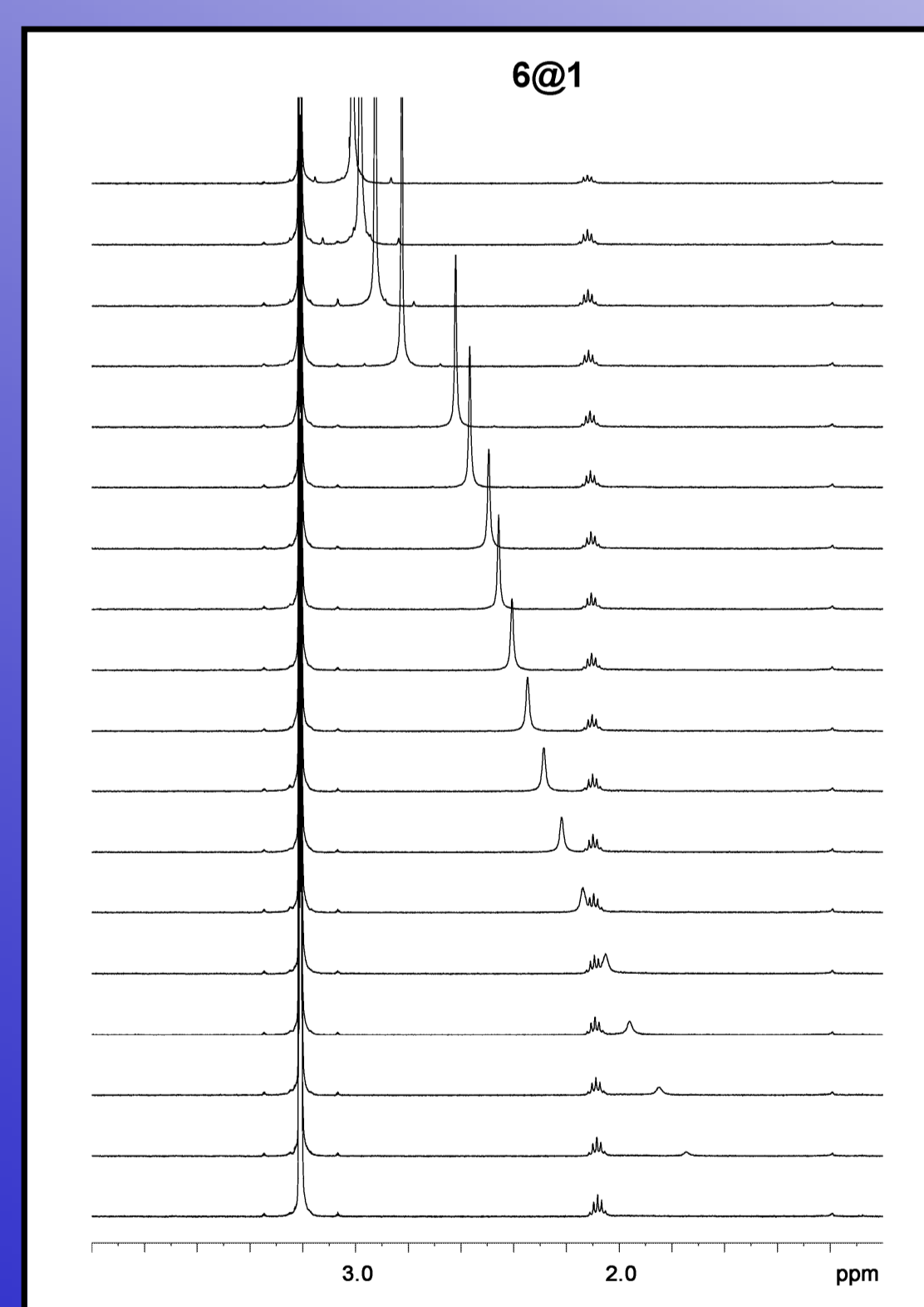
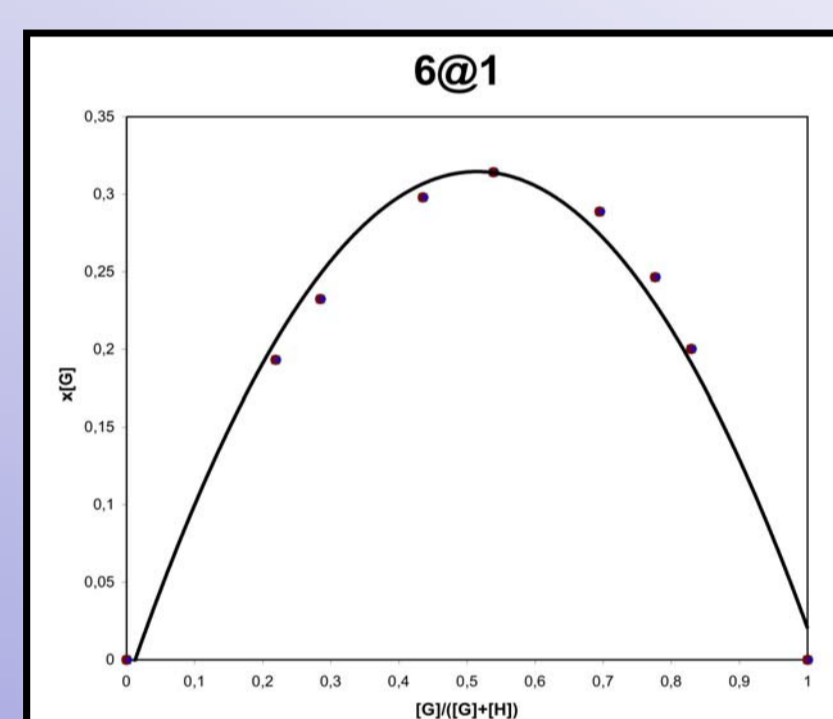
III. Gas Phase Experiments with Me₂DABCO

The gas phase experiments with dimethylated DABCO (**7**) as the guest cation were performed as described above for tetramethylammonium (**6**).



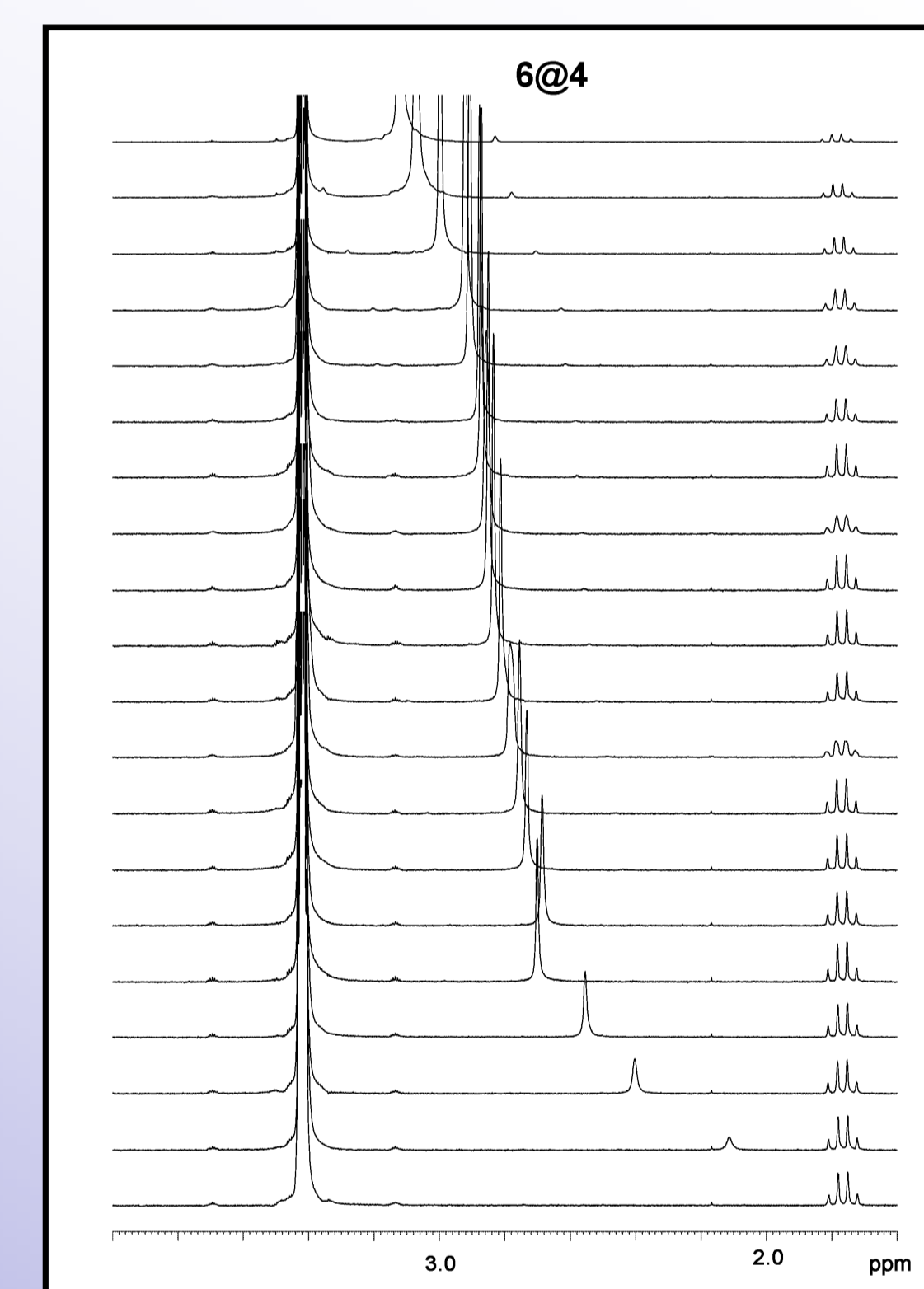
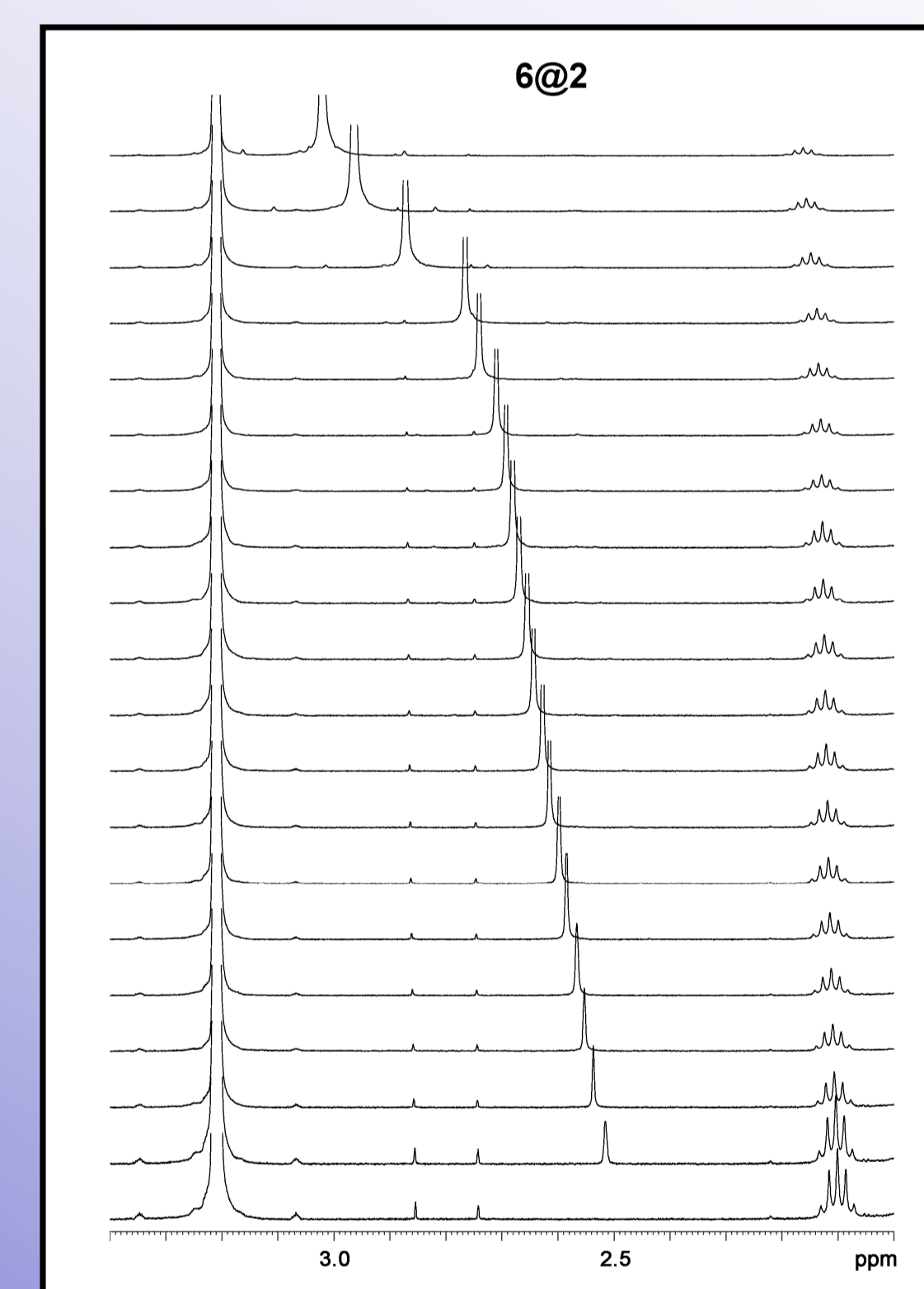
IV. Guest binding in solution monitored by ¹H NMR Spectroscopy

In contrast to gas phase, where 1:1 complexes and dimeric capsules could be observed, resorcinarenes **1** - **5** only form 1:1 complexes with NMe₄ in MeOH solution as indicated by Job plots.



R	k [L·mol ⁻¹]
OH	398
CH ₃	100
H	447
I	7079
Br	646

Scheme 1

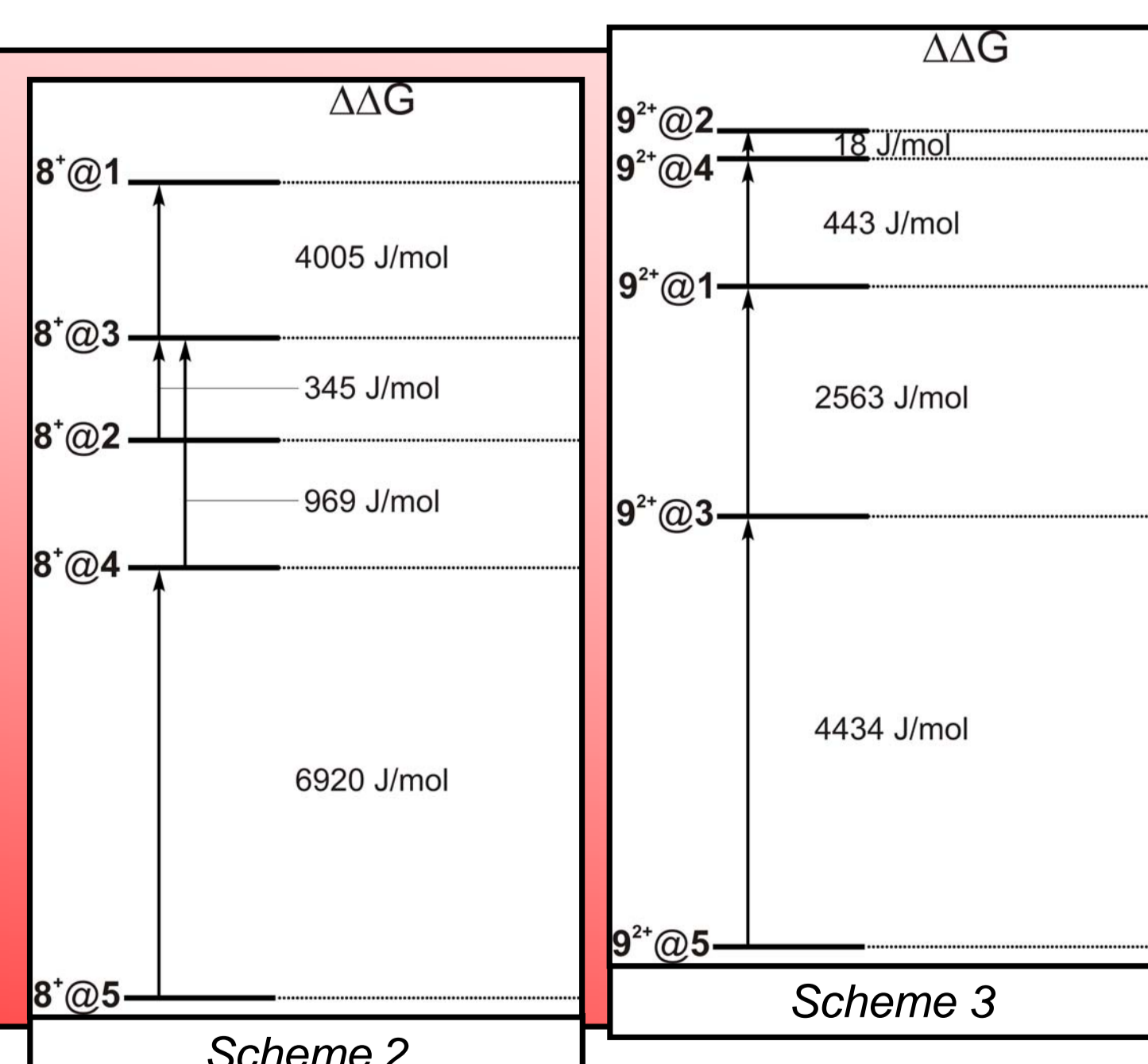


The binding constants of NMe₄⁺ (**6**) to each one of the resorcinarenes **1** - **5** were determined by non-linear fit of the corresponding titration curve using the global analysis software package *Specfit* (Spectrum Software Associates, Chapel Hill, NC, USA). The binding constants are displayed above in *Scheme 1*. Surprisingly, the observed trend does not correspond at all to the one expected from the upper-rim substituents' electronic effects. This unexpected ranking and especially the outstandingly high binding constant to tetra-iodo-substituted resorcinarene rather give a hint, that the binding in solution also involves solvent molecules and/or counter anions.

V. Conclusions

In case of tetramethylammonium (**6**) 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: CH₃ (**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 2*.

In case of dimethylated 1,4-diazabicyclo[2.2.2]octane (**7**) as guest cation, again a clear but completely different ranking of binding strength can be obtained. The capability to complex **9** decreases in the following order of upper-rim substituents: OH (**2**) ≈ I (**4**) > CH₃ (**1**) > H (**3**) >> Br (**5**) (see *Scheme 3*).



Astonishingly, the tetraiodoresorcinarene (**4**) binds **7** nearly as strong as the host with the highest binding capability in this series (pyrogallarene **2**), which might be explained by additional stabilization of the horizontal orientation of **7** inside the cavity of **4**. This assumption is also strengthened by MM2 calculations.

In contrast to the behaviour in the gas phase, both of the halogenated resorcinarenes (in fact the iodinated (**4**) and the brominated one (**5**)) are binding much stronger to NMe₄⁺ in solution than **1** - **3**. This and the trend for all resorcinarenes give a hint that the binding capability in solution is affected by electronic and steric effects of the upper-rim substituents as well as interactions with solvent molecules and counter anions.

[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. Cooks, J. S. Patrick, T. Kotiaho, S. A. McLuckey *Mass Spectrom. Rev.* **1994**, *13*, 287-339.

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