

# Source Function applied to experimental densities reveals subtle electron-delocalization effects and appraises their transferability properties in crystals



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□ The Source Function (SF) [1] enables the electron density (ED) to be seen at a point as determined by source contributions from the atoms of a system, and it is therefore well linked to the chemist's awareness that any local property and chemical behaviour is to some degree influenced by all the remaining parts of a system [1-3].

□ The key feature of the SF is that its evaluation requires only knowledge of the ED of a system, enabling a comparison of *ab initio* and X-ray diffraction derived ED properties on a common, rigorous basis.

□ We here apply the SF descriptor to X-ray derived EDs as a mean to reveal electron-delocalization effects (EDEs) in crystals. Use of the SF to detect them has been firmly assessed for isolated molecules and for theoretically-derived EDs [2,4-5], but extending to crystals and experimental EDs, although being reported at two conferences [6-7] and in two papers discussing heteroaromaticity in a benzothiazol-substituted phosphane [8] or antiaromaticity in cyclopentadienone derivatives [9] needs to be fully demonstrated.

□ Still unanswered questions are whether the EDs from X-ray data may be accurate enough to reveal subtle features caused by electron pairing and whether these are not only detectable, but also reproducible and transferable, whenever appropriate.

## The Source Function

Views the ED at any point  $\mathbf{r}$  as determined, in a cause-effect relationship, by a local source,  $LS(\mathbf{r},\mathbf{r}')$ , which operates at all other points of the space,

$$\rho(\mathbf{r}) = \int LS(\mathbf{r},\mathbf{r}') \cdot d\mathbf{r}'$$

The local source is given by

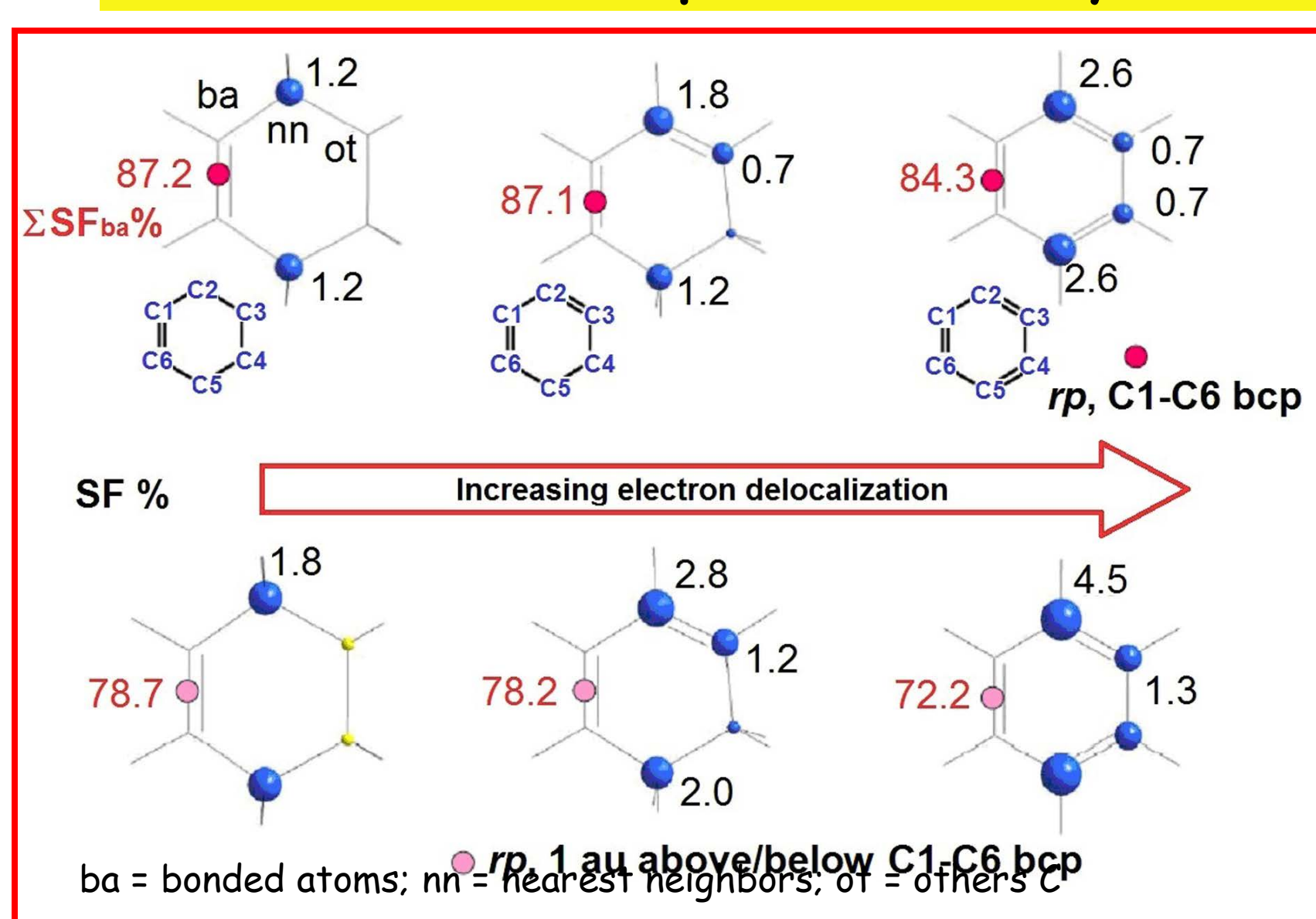
$$LS(\mathbf{r},\mathbf{r}') = -(4\pi \cdot |\mathbf{r} - \mathbf{r}'|)^{-1} \cdot \nabla^2 \rho(\mathbf{r}')$$

where  $(4\pi \cdot |\mathbf{r} - \mathbf{r}'|)^{-1}$  is a Green's function or an influence function representing the effectiveness of how the cause, the Laplacian of the density at  $\mathbf{r}'$ ,  $\nabla^2 \rho(\mathbf{r}')$ , gives rise to the effect, the electron density at  $\mathbf{r}$ ,  $\rho(\mathbf{r})$ .

The operation of the local source over the whole space may then be replaced by separate LS integrations over the atomic basins  $\Omega$  defined by the Quantum Theory of Atoms in Molecules (QTAIM) and the ED at  $\mathbf{r}$ , called the **reference point**  $\mathbf{rp}$ , is so equated to a sum of contributions  $S(\mathbf{r};\Omega)$ , each of which called the *Source Function* (SF) from the atom  $\Omega$  to  $\rho(\mathbf{r})$

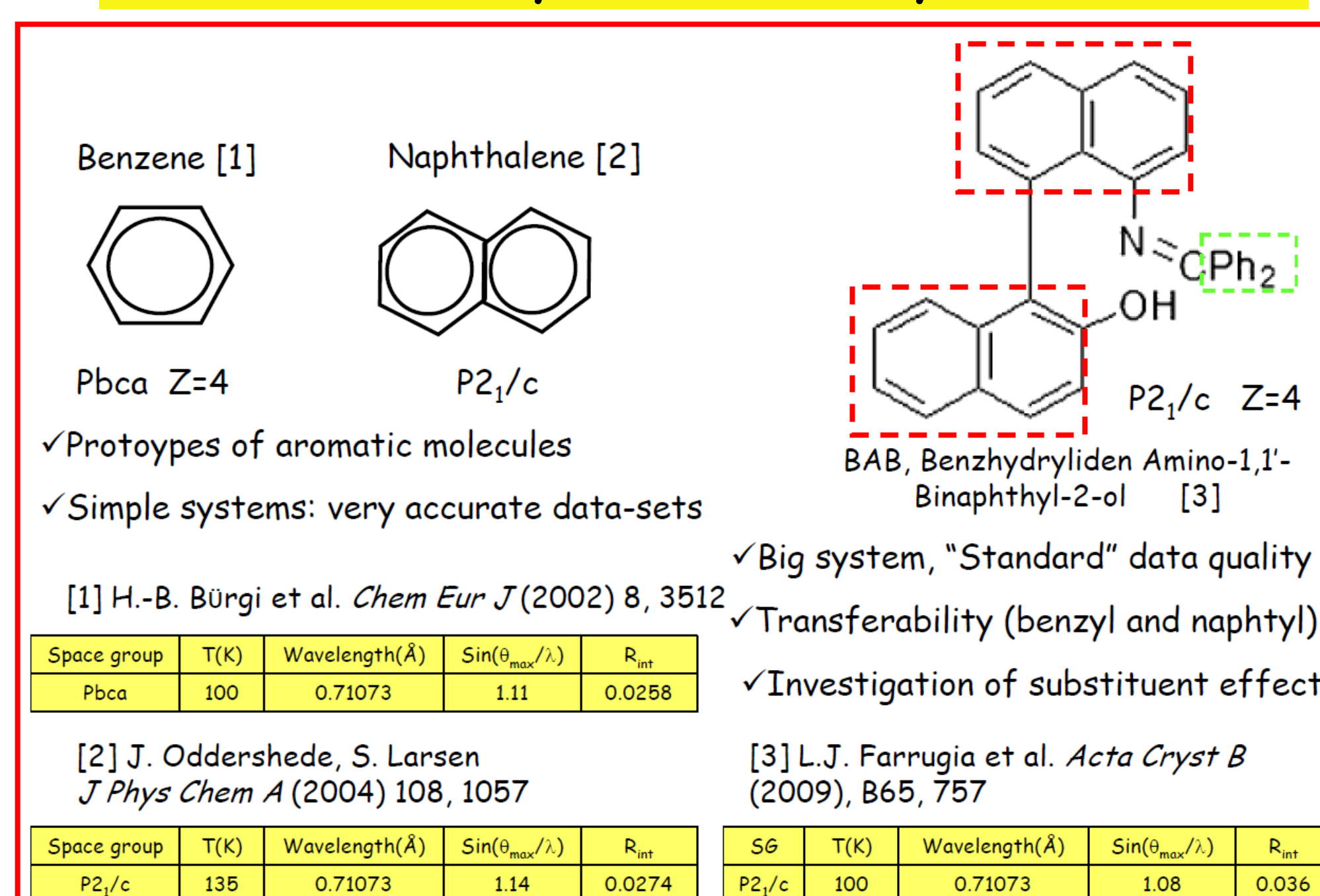
$$\rho(\mathbf{r}) = \int LS(\mathbf{r},\mathbf{r}') d\mathbf{r}' = \sum_{\Omega} \int_{\Omega} LS(\mathbf{r},\mathbf{r}') d\mathbf{r}' = \sum_{\Omega} SF(\mathbf{r},\Omega)$$

### Proof of the concept : in vacuo systems

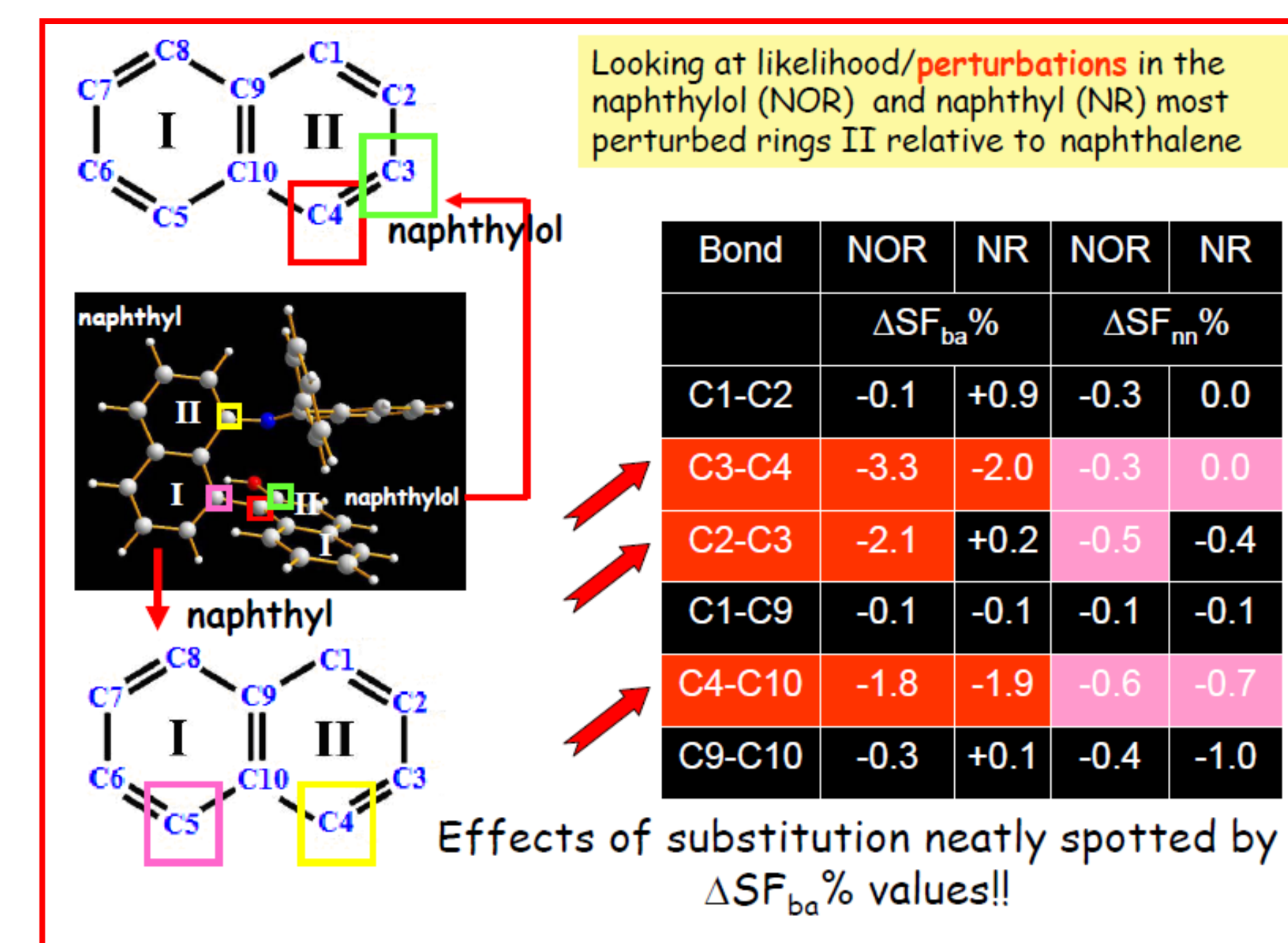
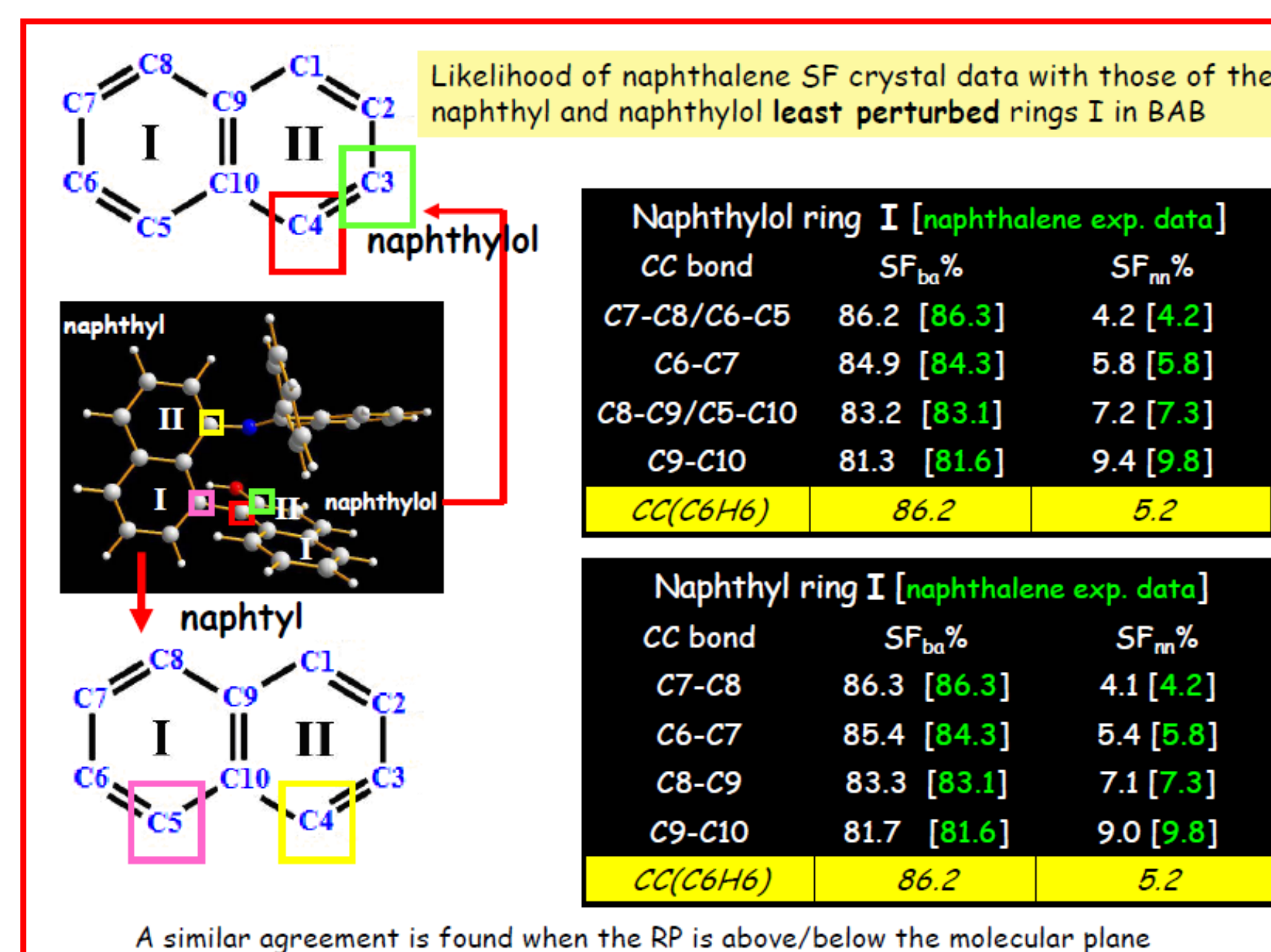
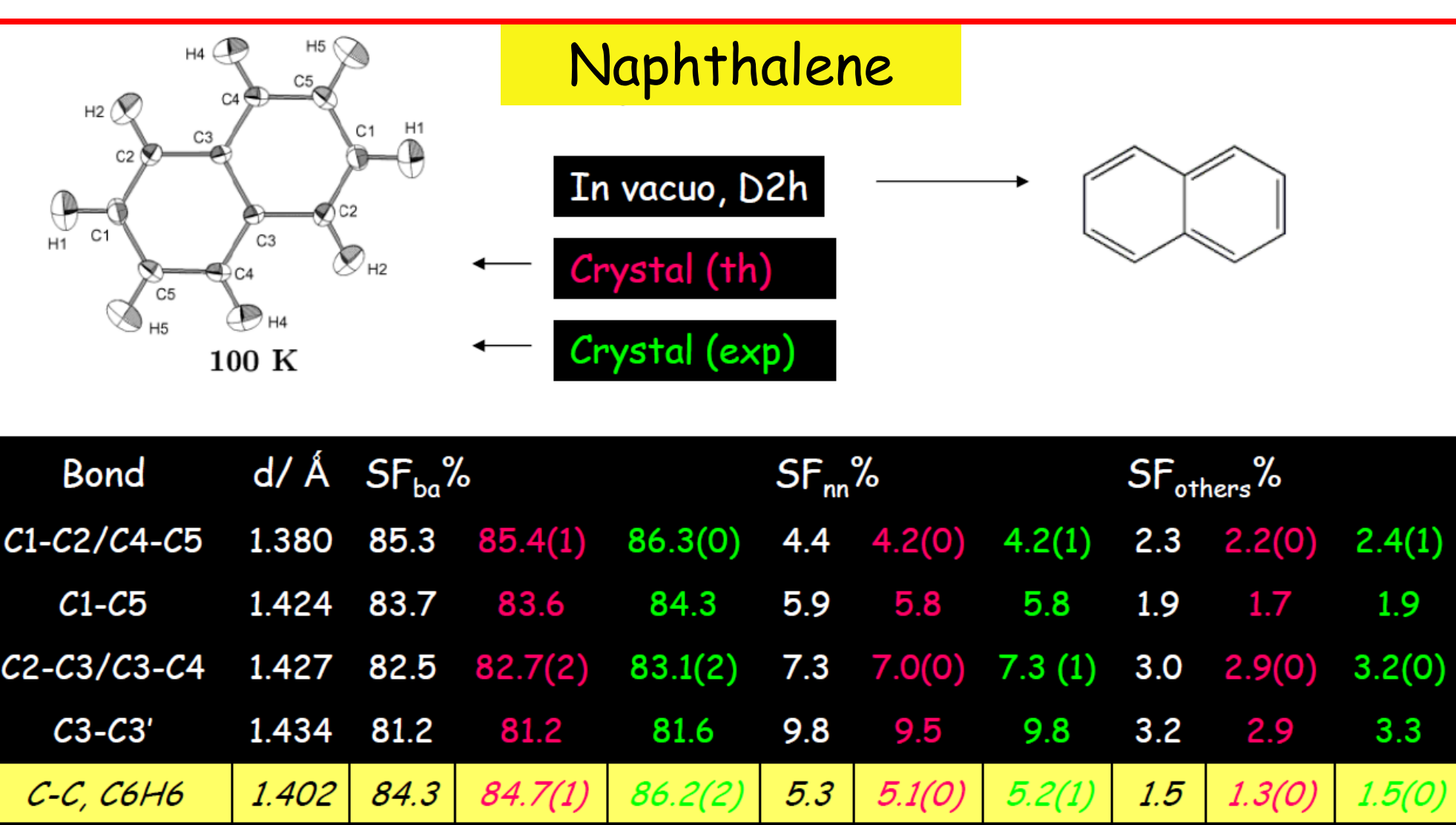
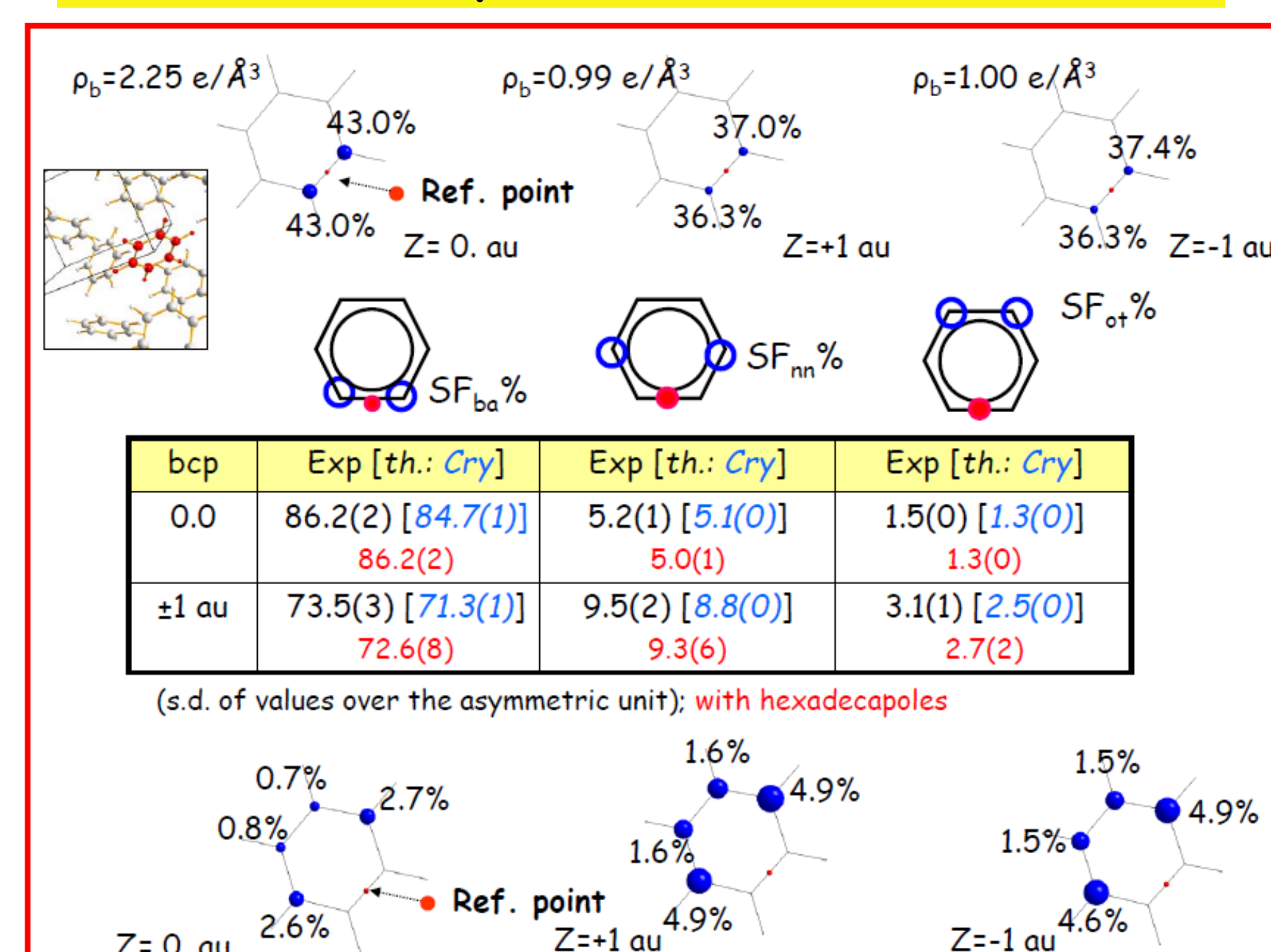


SF<sub>ba</sub>% decreases with increasing e delocalization  
SF<sub>nn</sub>% & SF<sub>ot</sub>% increase with increasing electron delocalization

### Extension to crystals and X-ray derived EDs



### Benzene (X-ray vs ab-initio Periodic DFT)



## Conclusions [10]

□ The SF tool recovers the characteristic SF% patterns caused by  $\pi$ -electron conjugation in benzene and naphthalene in almost perfect quantitative accord with those from *ab initio* periodic calculations

□ The effect of chemical substitution on the transferability of such patterns to the benzyl, naphthyl and naphthylol moieties of BAB is neatly spotted by the observed systematic deviations, relative to benzene and naphthalene of only those SF contributions from the substituted C atoms

□ The capability of the SF to reveal EDEs by using a promolecule ED (PED), rather than the "true" ED has been tested [10]. The PED is unable to reproduce the SF trends anticipated by the increase of electron delocalization

□ The SF has wider applications than those related to the nature of chemical bonds in more or less conventional situations [2-3]. Detection of EDEs is one such new direction, another being the extension of the SF machinery to retrieve the atomic sources of the spin ED [5,11]

