Benzene cation summary

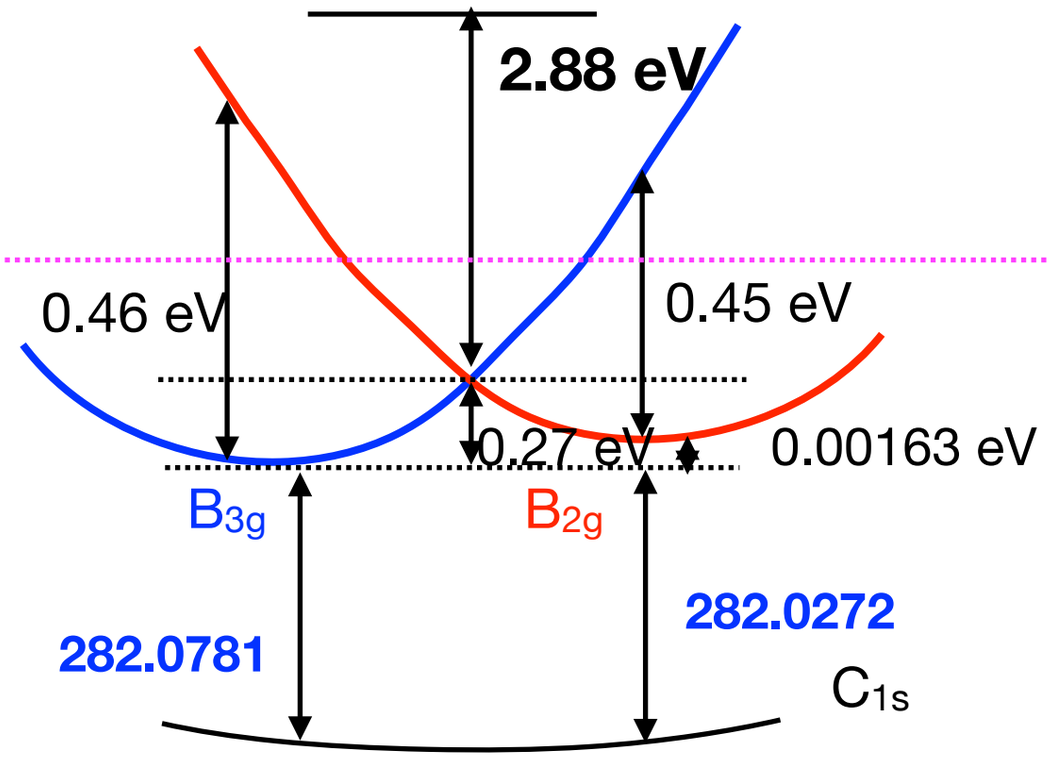
- Adiabatically, the JT states are nearly degenerate. And the JT distortion does not affect energies of the core orbitals. Consequently, the core-pi transitions computed at the two minima are virtually the same.
- As shown long time ago, the B2g and B3g minima are connected by tiny barrier and zero vibrational level is much higher. So Bz+ can be described as exhibiting free pseudorotation
- How can we see 2 peaks in the core spectrum? Only assuming that 2 lowest adiabatic states of the cation are populated. Then XAS probing 2 states will have 2 peaks split by ~ 0.4 eV.
- The question now is what is prepared in the experiment?

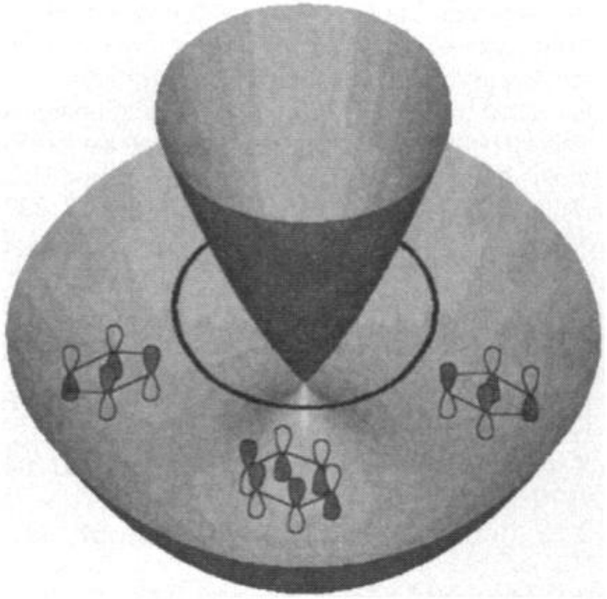
Two photons: 9.29 eV
Three photons: 13.9 eV

2 photons give 0.07 eV above vertical IE
to the X state, which corresponds
to 0.34 eV excess above the cation minimum.
So this is enough to populate
both lowest adiabats.

	$3b_{2u}$	14.802
D	$4b_{2u}/5\mathrm{b}_{3u}$	14.402
C	$1\mathrm{b}_{1u}$	12.547
B	$3\mathrm{b}_{1g}/6a_g$	12.108
X	$1b_{2g}/1b_{3g}$	9.224

2-photon excitation: 0.37 eV above B2g/B2g min





CORE-pi transition splitting: only 0.0509 eV

Note zero level above both minima

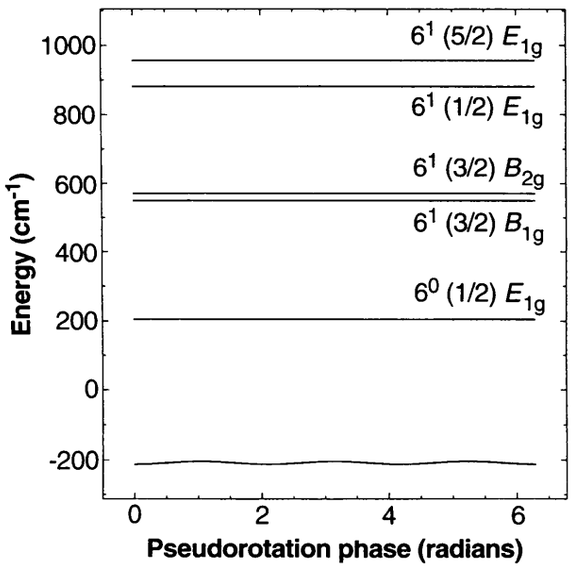


Fig. 4. Diagram showing the energy of the zero point and the first few excited vibrational levels in the ν_6 normal coordinate compared with the modulation of the radial minimum of the potential energy surface as a function of phase angle in the pseudorotation coordinate.

If we can suggest that vibronic levels are strongly mixed and we have enough energy to populate upper adiabat, then we can explain double peak. We need to put sufficient energy into the system to populate both sheets. I think that 0.37 eV is sufficient for that.

Multistate multimode vibronic dynamics: Entanglement of electronic and vibrational degrees of freedom in the benzene radical cation

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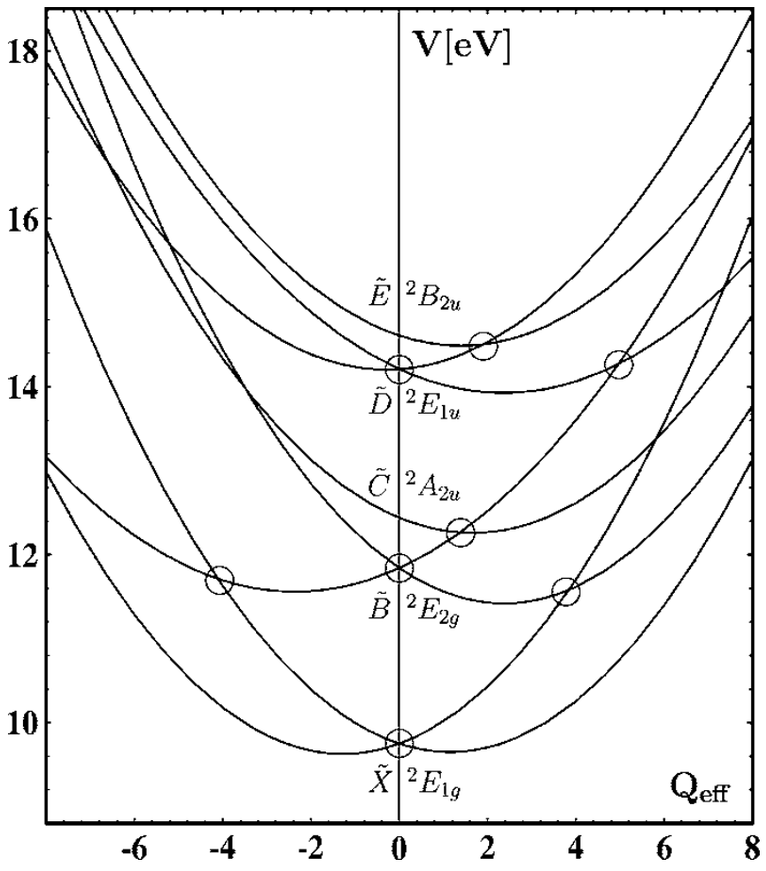
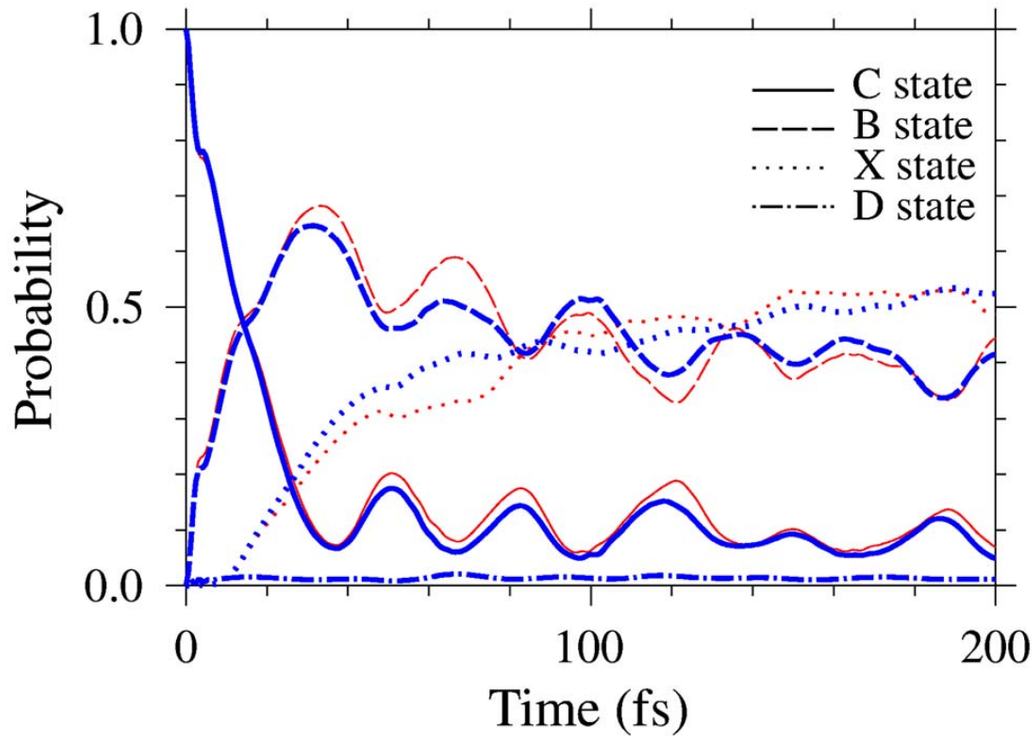


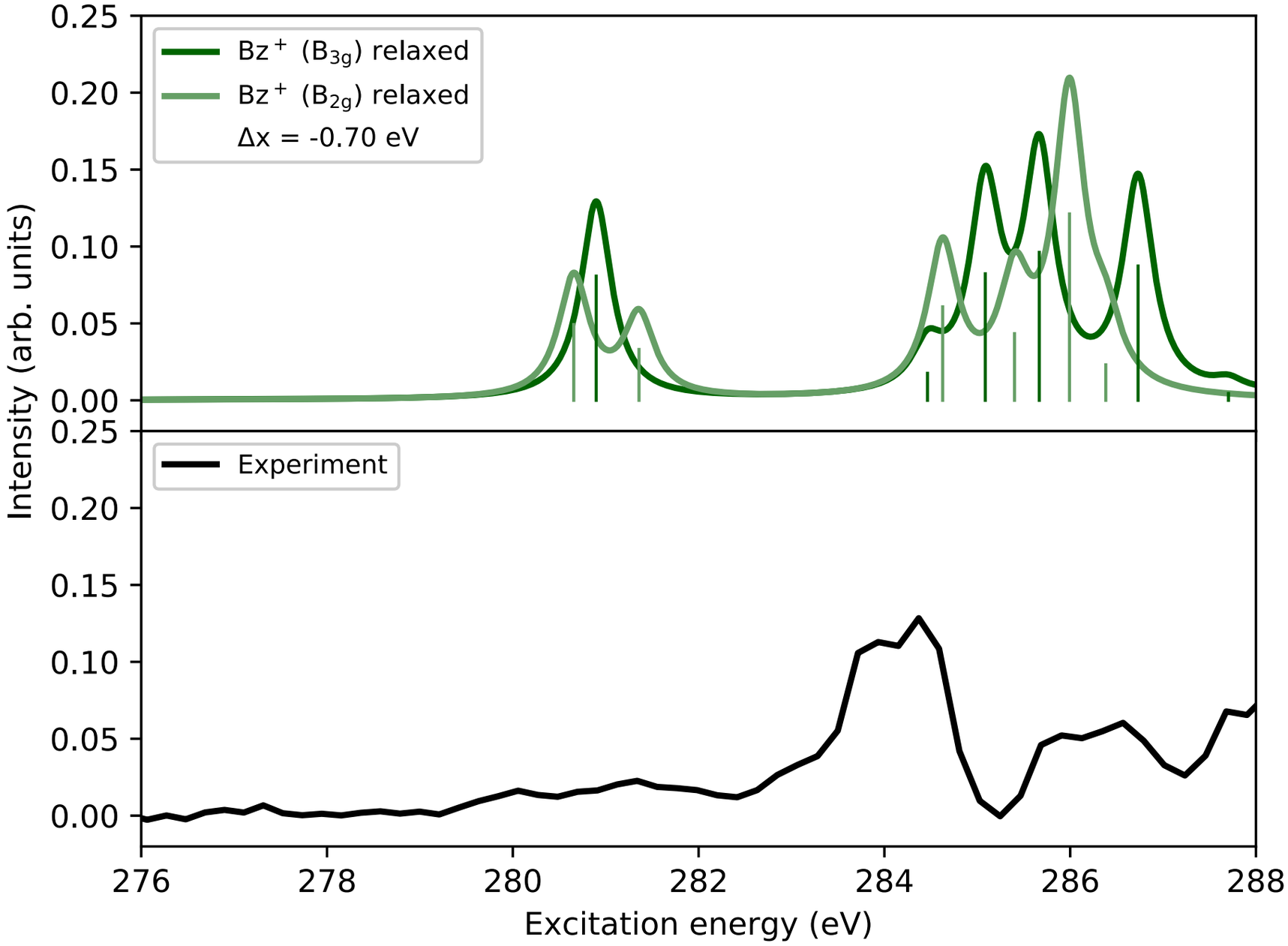
FIG. 1. Schematic representation of the low lying conical intersections in the $\tilde{X}$-$\tilde{B}$-$\tilde{C}$-$\tilde{D}$-$\tilde{E}$ system of Bz^+ (drawn by open circles) resulting from crossings of adiabatic energy curves (cf. Ref. 29).



Dynamics is ultrafast and **is over in 100 fs.**
The population is distributed between X state (2 lowest adiabats) and B state (next degenerate pair)

If we excite with 2 photons, we have 0.37 eV excess energy. Not much, but enough to start to see the effect of the second adiabat (state in the cone).
With 3 eV, we will have plenty of population in the two adiabats, but also should see contributions from B-state (at lower energy).

Correct XAS spectrum: B2g and B3g peaks are on top of each other, which is consistent with energetics derived from core and valence IPs.



The splitting of B2g peak is artifact due to open-shell reference (not supported by XES calculations)