2^+ Ion Concentration and the Double Photoionization of Aromatic Organic Molecules

Dave Huber

Physics Department, University of Wisconsin-Madison

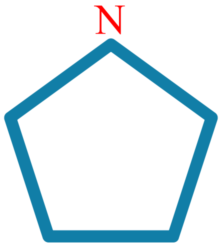
Double Photoionization:

$$M + \nu \rightarrow M^{2+} + 2e^{-} \qquad M = \text{molecule}$$

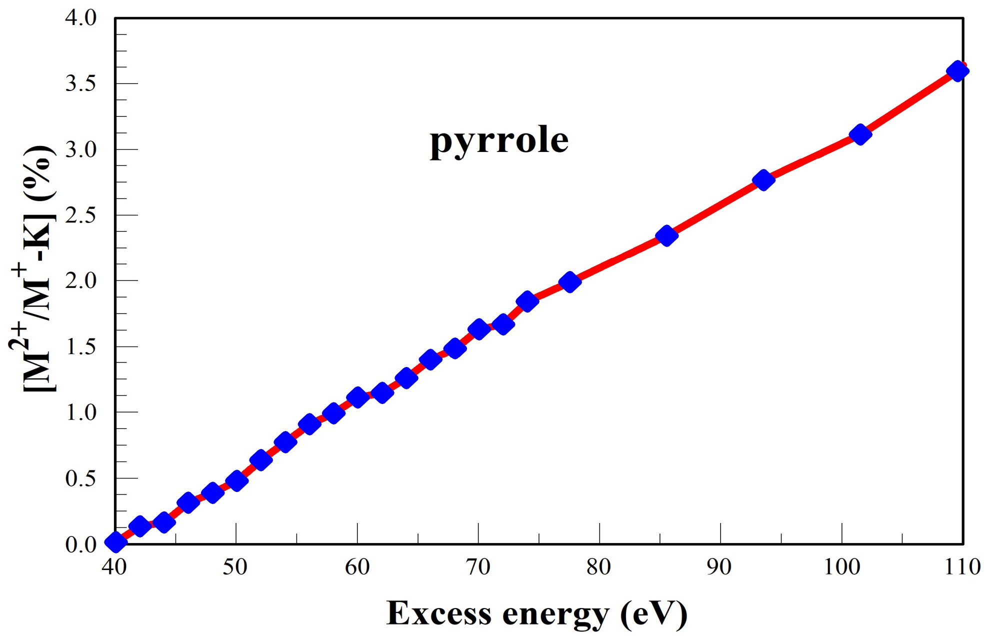
Experiments: R. Wehlitz and colleagues

Analyze M^{2+} and M^{+} data. Subtract 'knock-out' contribution (excited electron knocks out second electron on the way out)

I. Linear behavior in pyrrole: C_4H_4NH



Pyrrole: pentagonal molecule, C replaced by N at one site



K: knock-out contribution

Excess energy: photon energy relative to knock-out threshold

Explanation for linear behavior

A. Transition rate above 40 eV is proportional to the product of the kinetic energy densities of the two free electrons

Rate $\propto (E_{photon} - 40\ \text{eV} - \delta)^{1/2}\delta^{1/2}$ $\quad 0 < \delta < E_{photon} - 40\ \text{eV}$

B. Assuming infinite mass for the pyrrole molecule and neglecting momentum of the incident photon, the momentum conservation equation for the two free electrons takes the form

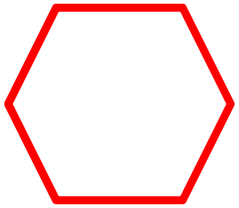
$$0 = p_1 + p_2$$

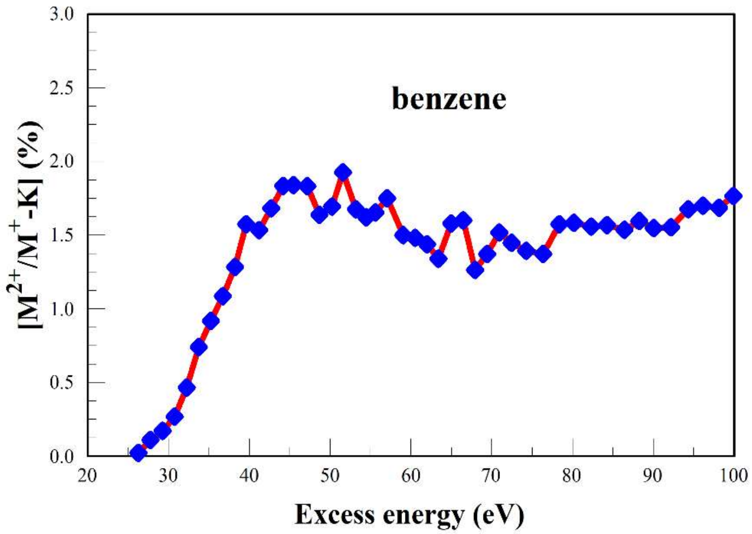
so that the free electrons move in opposite directions with equal kinetic energy

C. The transition rate, and hence the steady-state pyrrole population, are proportional to (1/2) (E_{photon}–40 eV), leading to the linear behavior shown in the preceding panel.

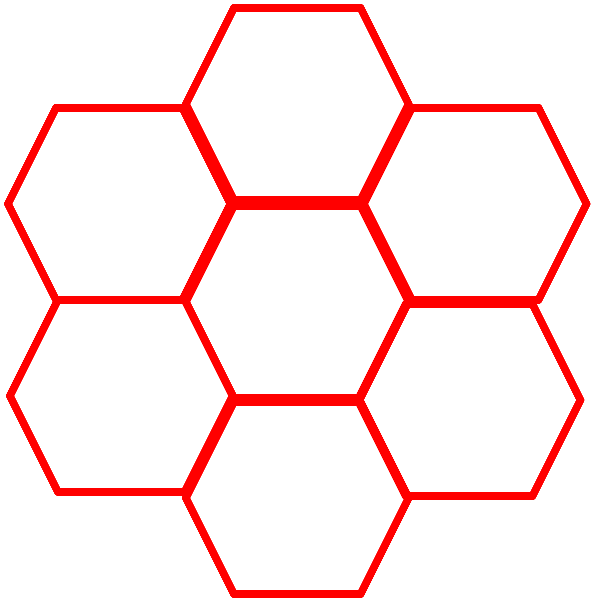
II. Resonances

Benzene: C_6H_6 6 carbon atoms on perimeter

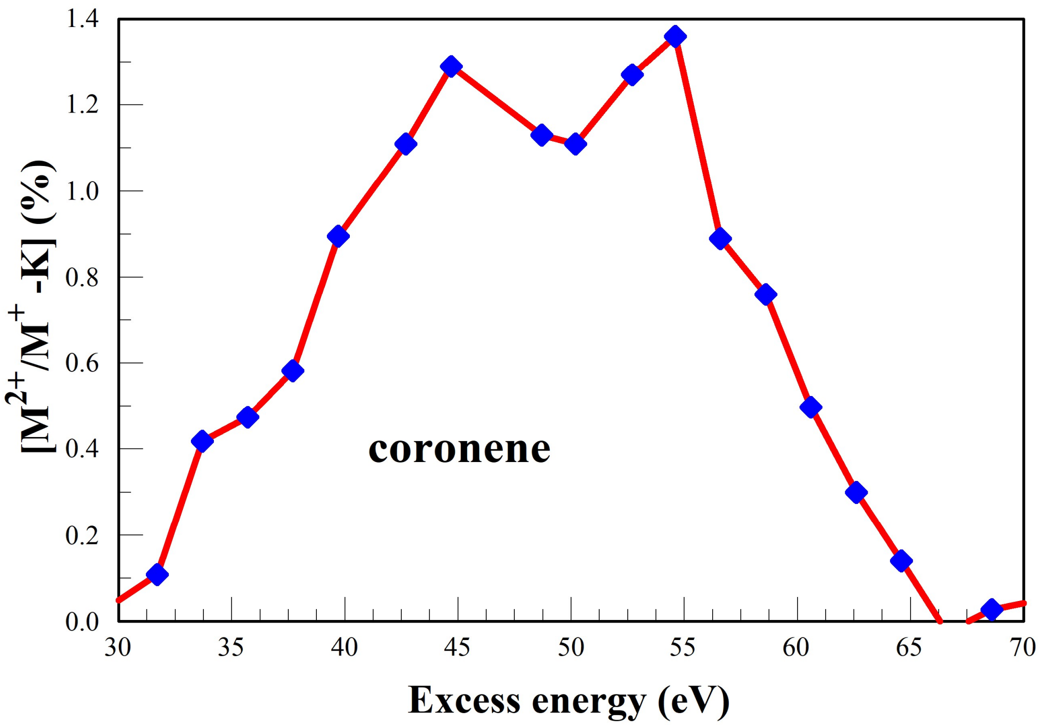




Coronene: $C_{24}H_{12}$



18 carbon atoms on perimeter, 6 in the interior



Peaks at ≈ 45 and 55 eV; maximum overall width ≈ 40 eV

III. Origin of the resonance: ‘Coulomb Pairing’

S. Mahajan and A. Thyagaraja (2006)

“In a periodic external potential, two electrons interacting through a short range repulsive potential [*e.g. screened Coulomb interaction*] can be ‘bound’ to form a spin- zero compound-boson with a spatial extent on the order of a lattice length”

Hypothesis 1: the threshold resonances in the double photoionization of cyclic organic molecules, which occurs when there is closed loop of carbon atoms on the perimeter of the molecule, is associated with the formation of Coulomb pairs.

IV: Origin of the linear behavior in pyrrole and related molecules

Hypothesis 2: The linear behavior in the double photoionization of the five-sided molecules pyrrole, furan, thiophene, and selenophene is associated with the presence of a non-carbon 'impurity'; i.e. instead of C_5H_5 one has C_4H_4I, with I = NH for pyrrole, O for furan, S for thiophene, and Se for selenophene.

The presence of the 'impurity' destroys the periodicity of the hypothetical five-carbon array, eliminating the possibility of Coulomb pairing and allowing the simultaneous back-to-back emission of the electrons reported by K Jänkälä *et al.* (2014).