1 million structure method for photoelectron spectra: restricted normal mode sampling, and Dyson orbital transitions

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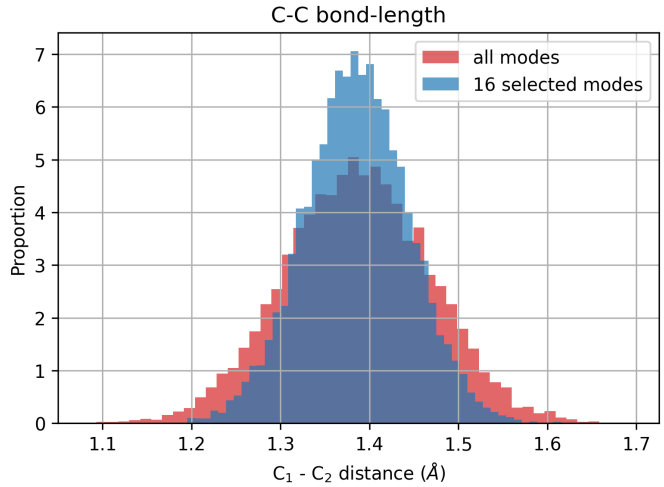
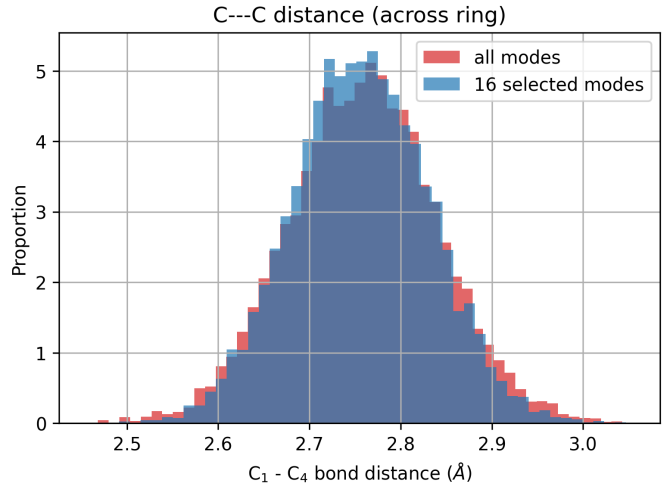
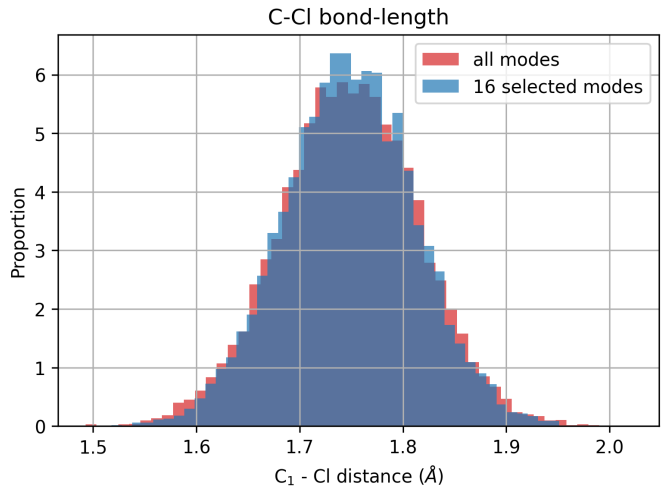
Chlorobenzene normal mode sampling



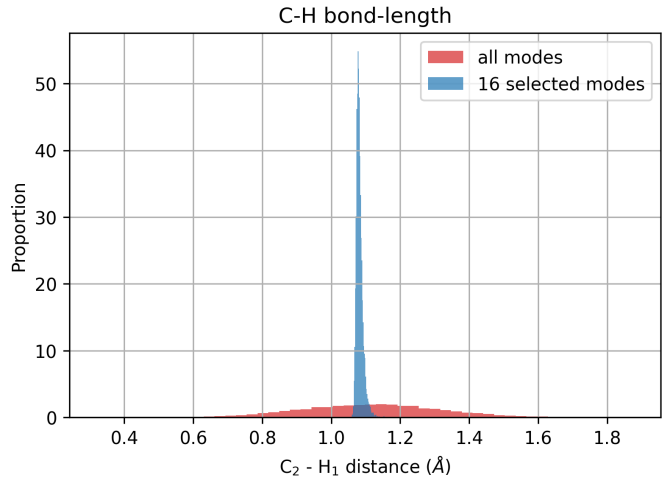
(a) C_1-C_2 distance



(b) C_1-C_4 distance



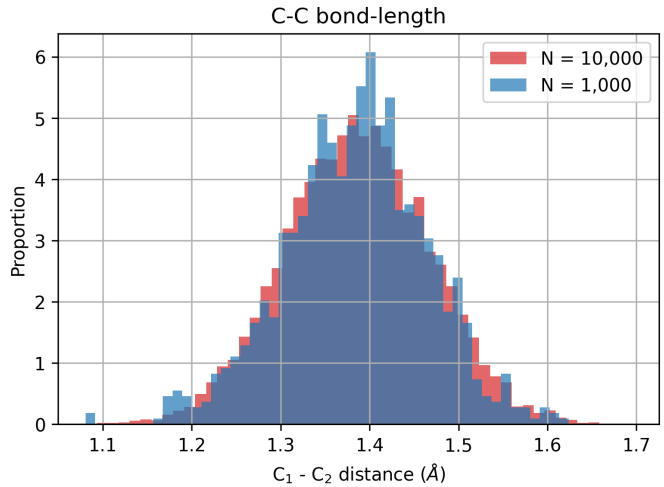
(c) C_1-Cl distance



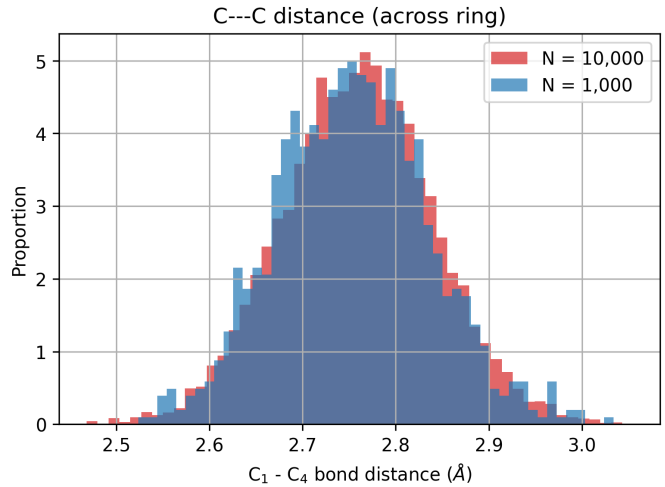
(d) C−H distance

1. Chlorobenzene has 30 normal modes
2. Sampling over a selection of 16 'heavy atom' modes effectively clamps the C−H bonds (fig. 1d) while keeping the other distances similar (above figures)
3. Doing this slightly restrains the C−C bonds (fig. 1a), but only by a difference in fwhm $\simeq$ 0.02 Å.
4. I used a sample size of 10,000 molecular structures for the above figures.

Chlorobenzene normal mode sampling, vary sample size N



(a) C_1-C_2 distance



(b) C_1-C_4 distance

- From bond-distances statistics, it seems that $N = 1000$ and $N = 10000$ agree relatively closely. $N = 10000$ gives a smoother bell curve distribution for inter-atomic distances.
- These samples were generated using all normal modes.

Sampling method

The sampling equation for generating the displaced molecular coordinates is,

$$\mathbf{R} = \mathbf{R}_0 + \sum_{i}^{\text{modes}} a_i \mathbf{d}_i \tag{1}$$

with starting geometry $\mathbf{R}_0$, and displacement unit vectors $\mathbf{d}_i$ for each normal mode are obtained from a frequency calculation. The factors a_i are randomly generated within a bell curve centered at $\mu = 0$, and chosen standard deviation, σ.

Chlorobenzene Dyson transitions

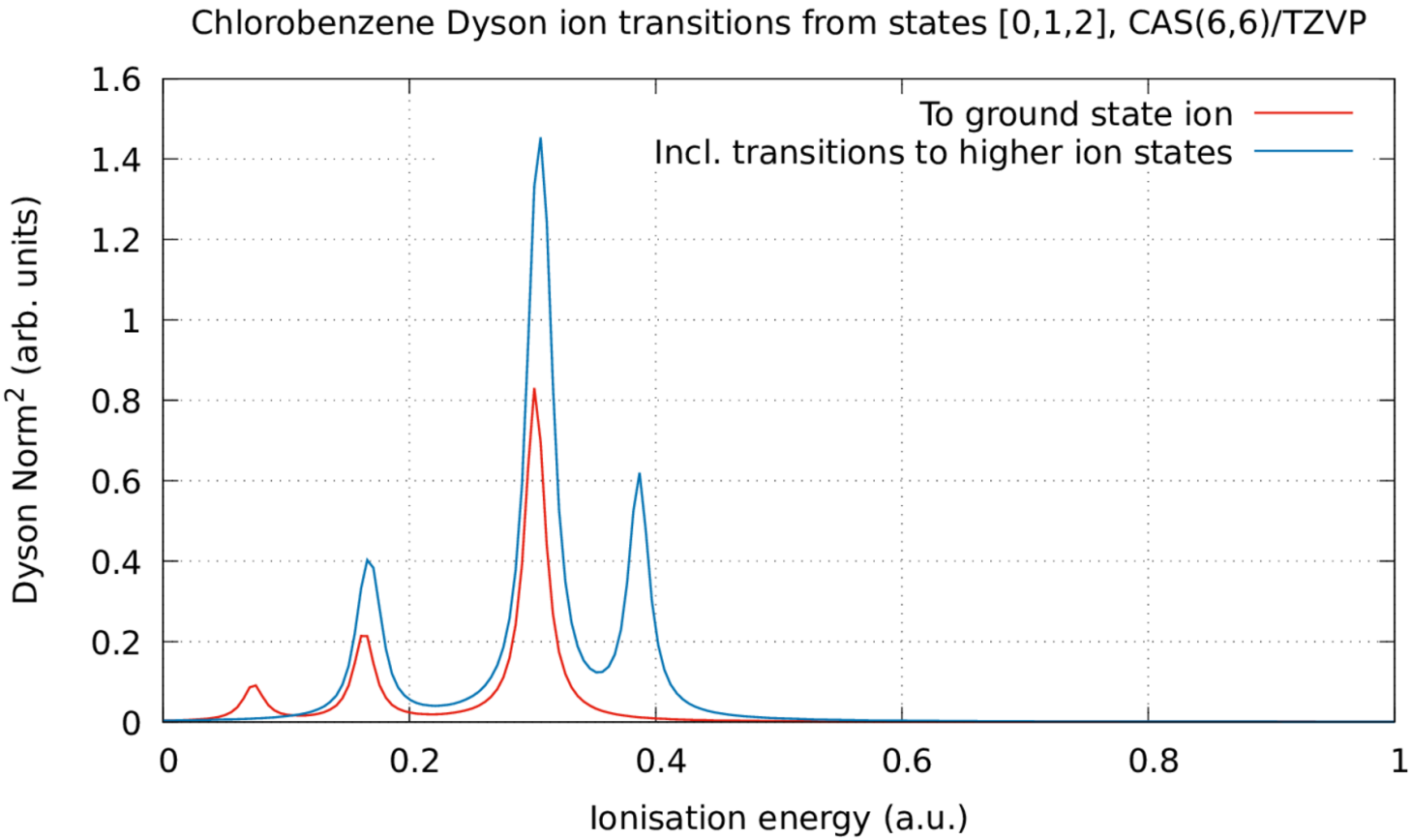


Figure: Chlorobenzene Dyson orbital transitions between the ground state and its ion (chlorobenzene+). The transitions are from states [0, 1, 2], i.e. ground state, S_1, and S_2, to the ion states. The red line is only transitions to the ground state ion, and the blue includes transitions to states [0, 1, 2] of the ion.