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Precursor anion states in dissociative electron attachment to chlorophenol isomers

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ABSTRACT

We report a theoretical study on low-energy (<10 eV) elastic electron scattering from chlorophenol isomers, namely, *para*-chlorophenol (pCP), *meta*-chlorophenol (mCP), and *ortho*-chlorophenol (oCP). The calculations were performed with the Schwinger multichannel method with pseudopotentials, and analysis of the computed integral cross sections and virtual orbitals revealed one σ^*_{CCl}, one σ^*_{OH}, and three π^* shape resonances. We show that electron capture into the two lower lying π^* orbitals initiates dissociative processes that lead to the elimination of the chloride ion, accounting for the two overlapping peaks where this fragment was observed. Despite the relatively small differences on the energetics of the π^* resonances, a major isomeric effect was found on their corresponding autodetachment lifetimes, which accounts for the observed increasing cross sections in the progression pCP < mCP < oCP. In particular, dissociation from the π^*_1 anion of pCP is largely suppressed because of the unfavorable mixing with the σ^*_{CCl} state. We found the intramolecular hydrogen bond present in oCP to have the opposite effects of stabilizing the σ^*_{CCl} resonance and destabilizing the σ^*_{OH} resonance. We also suggest that the hydrogen abstraction observed in chlorophenols and phenol actually takes place by a mechanism in which the incoming electron is directly attached to the dissociative σ^*_{OH} orbital.

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