Supporting Information

The analyses shown in Figures 2-5 are here repeated using methylammonium as the perturbation, as shown in Figures S1 and S3. The bond capacities for methylammonium have been assigned to reproduce the polarizability of the isolated molecule for the $J_{ii} = 0$ BC model while for fluoromethane the bond capacity parameters are taken from Table 4.

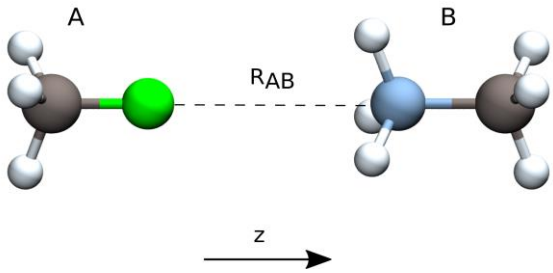

Figure S1: Fluoromethane and methylammonium used to probe intramolecular polarization

The interfragment distance is changed analogous to Figure 2, with the results shown in Figure S2.

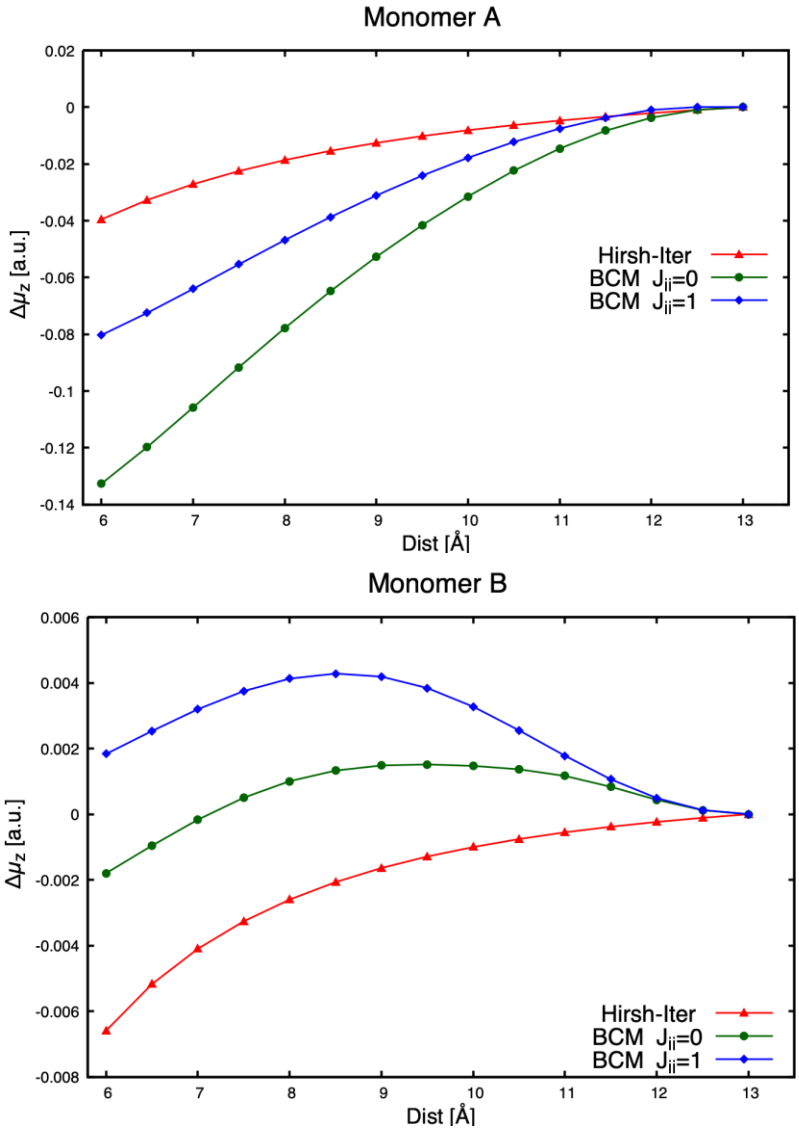

Figure S2: Change in the dipole moment component for monomer A and B with zero set at 13 Å

The charged case behaves similar to the neutral one, although the larger perturbation due to the presence of a net charge leads to an overpolarization of fluoromethane both for the $J_{ii} = 0$ and $J_{ii} = 1$ BC models.

The charged system analogues to Figure 4 and 5 are shown in Figures S3 and S4.

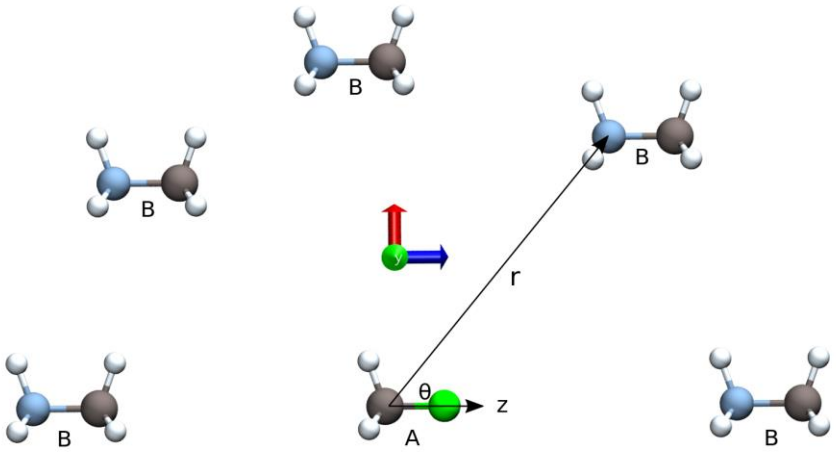

Figure S3: Five illustrative CH_3F-$NH_3CH_3^+$ geometries used to probe intermolecular polarization in the charged case.

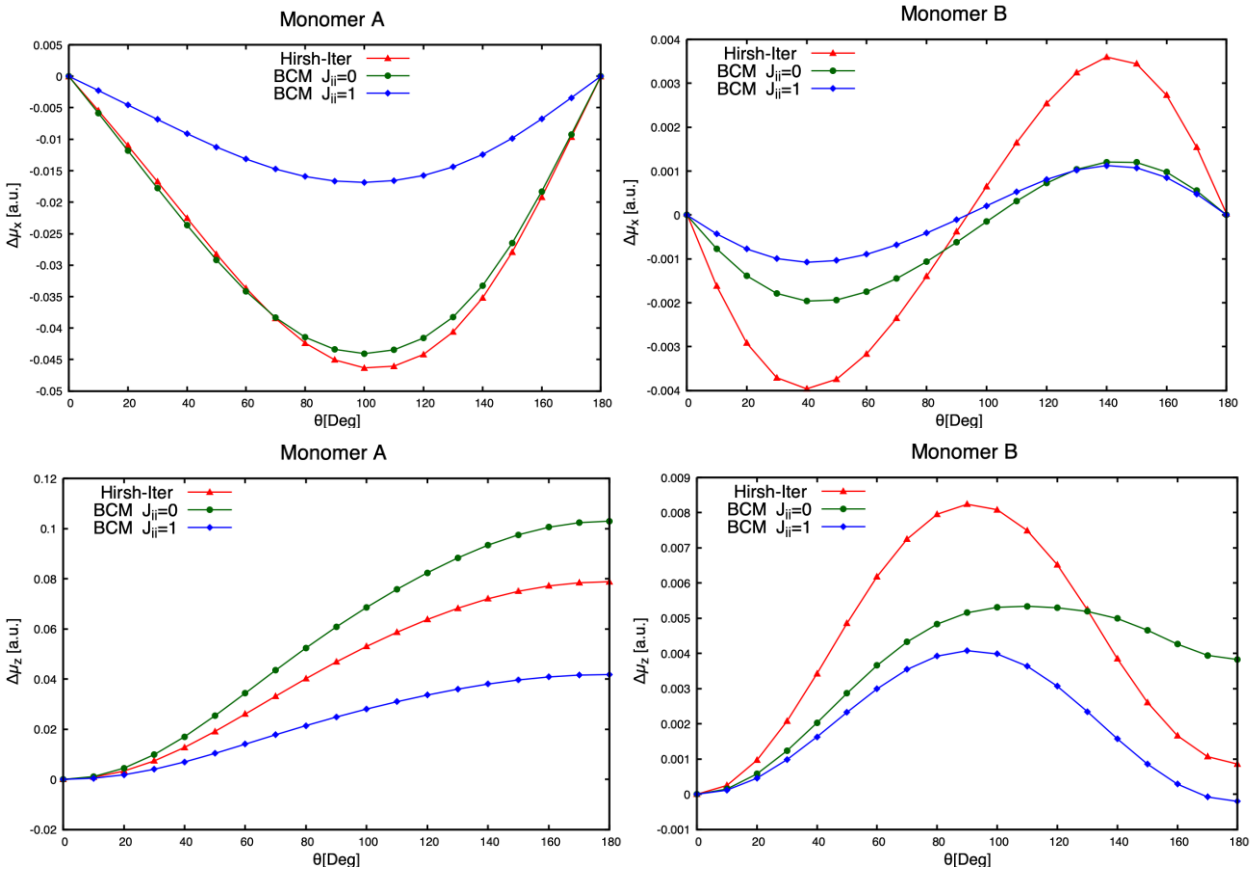

Figure S4: Change in the dipole moment components with zero taken at θ=0.

The overall geometry trends are reproduced, with the over/under-polarization modulated by the Coulomb self-interaction term.

The intramolecular equivalent of Figure 6 is shown in Figure S5, with Figure S6 providing the results corresponding to Figure 7.

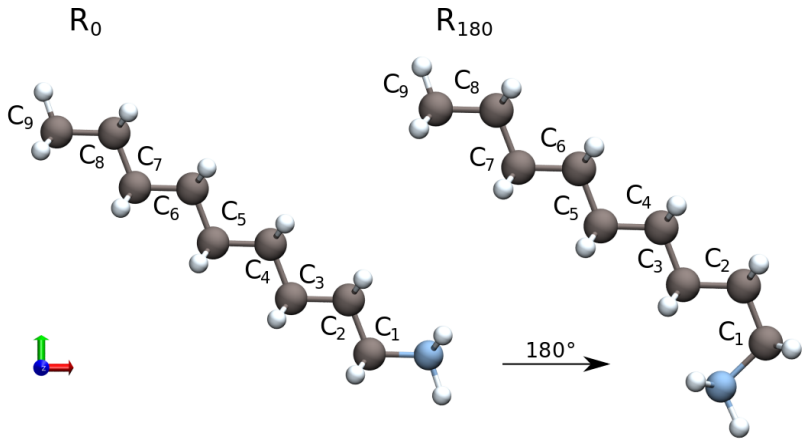

Figure S5: Alkylammonium molecule used for probing intramolecular polarization with the backbone laying on the xy plane.

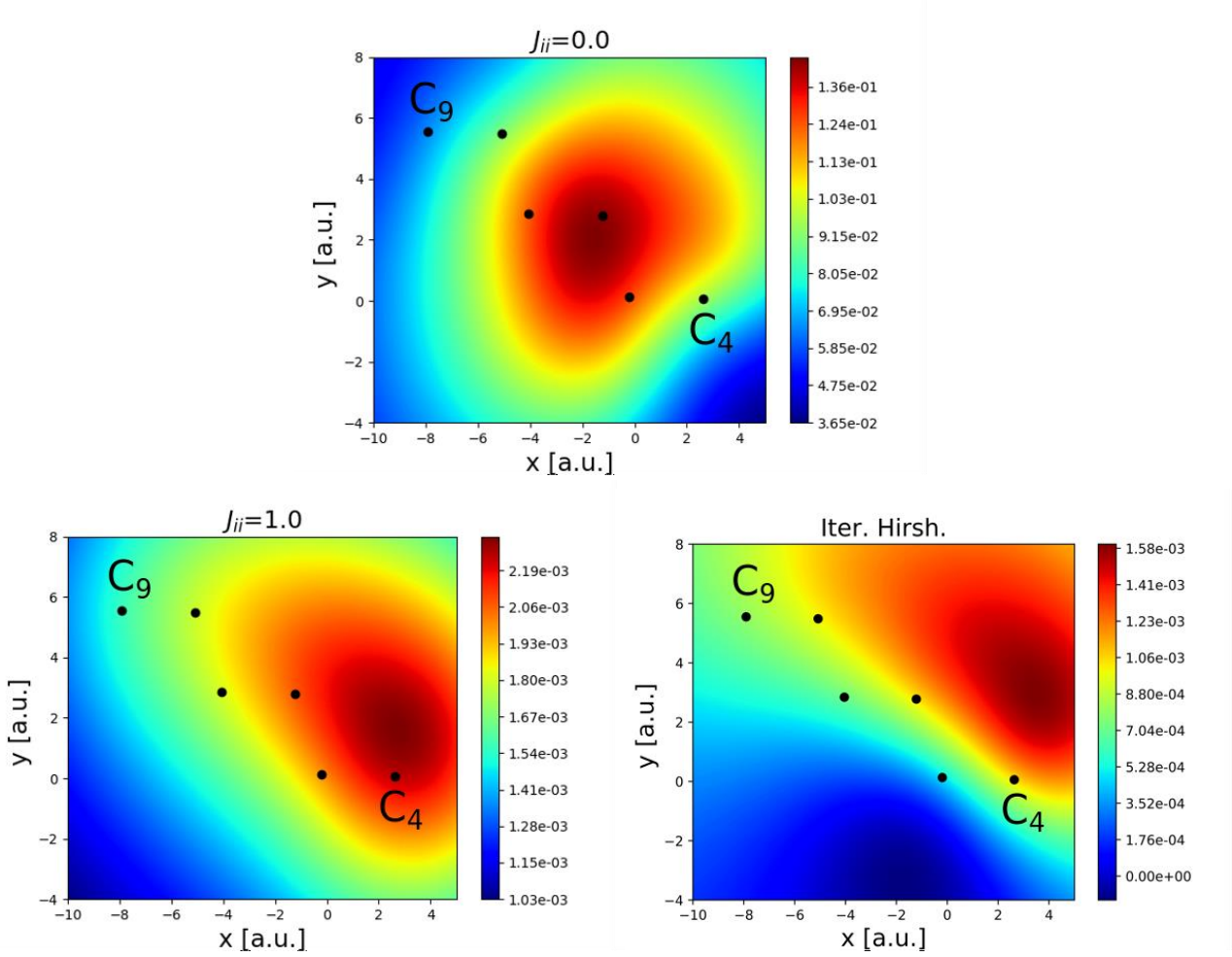

Figure S6: Electrostatic potential in atomic units on the xy plane arising from the atomic charges difference for the C_5-C_{10} atoms and their bonded hydrogens for the J_{ii}=0, J_{ii}=1 BC models and the iterative Hirshfeld.

The BC model qualitatively reproduce the geometry variation of the induced dipole moments for both the neutral and charged systems, and the magnitude of the polarization can be modulated by the Coulomb self-interaction parameter. A non-zero value of the latter is strongly suggested by the present results but the optimum value, and possibly atom specific values, will have to await testing for a larger variety of systems.