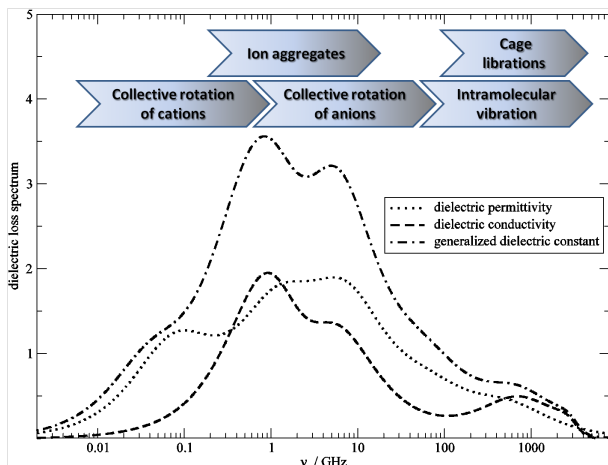


# Computational dielectric spectra of polarizable ionic liquids

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Classical molecular dynamics simulations on molecular ionic liquids are based on pairwise additive Coulomb forces with fixed partial atomic charges which cannot respond to a local environment. In order to circumvent this problem we introduce polarizable forces in our simulations by means of Drude oscillators:<sup>1</sup> In addition to the atoms virtual mobile Drude particles are added which carry a “Drude charge” and are bound by a harmonic spring to their reference atoms. This “spring” mimics an additional induced atomic dipole and its strength is correlated to the polarizability of the reference atom. These induced dipole moments are orientated by the local electric field. The complex interplay between strength and orientation of the induced and permanent dipole moments differs between imidazolium based cations and classical anions like triflate.



Polarizable forces in molecular dynamics simulation enhances the single-particle dynamics of the molecular ionic liquids, e. g. the diffusion coefficients, by a factor of two and more without changing the structure significantly. However, although polarization forces model the response to the local environment, their influence has a much longer range affecting the collective dynamics of the molecular ionic liquid which can be best seen in spectra of the generalized dielectric constant  $\Sigma^*(\nu)$ . These spectra can be measured experimentally from tens of MHz to several THz covering more or less the whole range of collective dynamics. Furthermore, they comprise information on polarity, viscosity, conductivity and the refractive index of the ionic liquids. On the one hand, these experimental spectra validate our underlying force field. On the other hand, the computational spectrum can be decomposed in various con-

tributions not directly accessible by the experiment:<sup>2</sup> The induced collective dipole moments behave like the rovibrational collective dipole moments with respect to the shape of the correlation functions and their relaxation time constants.<sup>1</sup> Consequently, the influence of both collective dipole moments are attributed to the dielectric permittivity  $\epsilon(\nu)$  in our interpretation. The inclusion of polarizability shifts  $\epsilon(\nu)$  to higher frequencies without altering the shape of the peaks. The counterpart of  $\epsilon(\nu)$  is the dielectric conductivity  $\vartheta(\nu)$  characterizing the collective translational phenomena beyond the static conductivity  $\sigma(0)$ .<sup>3,4</sup> Only its low frequency peaks in the low GHz-regime are affected by the polarizability leaving the high frequency region beyond 100 GHz almost untouched.

<sup>1</sup>C. Schröder and O. Steinhauser, *J. Chem. Phys.* **133**, 154511 (2010).

<sup>2</sup>C. Schröder, J. Hunger, A. Stoppa, R. Buchner, and O. Steinhauser, *J. Chem. Phys.* **129**, 184501 (2008).

<sup>3</sup>C. Schröder and O. Steinhauser, *J. Chem. Phys.* **131**, 114504 (2009).

<sup>4</sup>C. Schröder and O. Steinhauser, *J. Chem. Phys.* **132**, 244109 (2010).