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Molecular understanding of adsorption mechanisms of fatty acids on fluorite

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Although fatty acids have been used for decades in many interfacial applications, their adsorption mechanisms on mineral surfaces are at the center of many largely-debated assumptions [1]. Here, we shed light on this problem by combining diffuse reflectance infrared (IR) Fourier transform spectroscopy with *Ab Initio* Molecular Dynamics (AIMD) simulations at 300 K and IR spectra calculations [2]. Using fluorite (CaF_2) and sodium octanoate – or longer-chain fatty acids - as prototypical materials, we observe that, at low fatty acids concentration, the asymmetric stretching vibration of COO^- peaks at 1560 cm^{-1} while, when the concentration increases, this IR band converts into a doublet peaking at 1535 and 1575 cm^{-1}. Using simulations, we assign the band at 1560 cm^{-1} to the adsorption of a carboxylate molecule bridged on a sodium counter-cation and the doublet at 1535 cm^{-1} and 1575 cm^{-1} to the adsorption of the sole carboxylate anion under a monodentate or a bidentate binuclear configuration, respectively. At 300 K, the bridged and monodentate configurations are stable in water conditions while the bidentate binuclear is stable either in vacuo conditions or when the surface coverage is increased. These findings unravel the mechanism of formation of an adsorbed layer on the mineral surface, which is likely to be initiated by the adsorption of a sodium carboxylate and followed by the adsorption of mixed sole anionic forms (monodentate and bidentate binuclear). This investigation also highlights the role of the carboxylate counter-cation, which was totally ignored in the literature beforehand [2]. This particularly opens the path to the development of innovative strategies to enhance the separation contrast between minerals, which is of uttermost importance for the recovery of critical raw materials [3].

[1] Foucaud, Lebègue, Filippov, Filippova & Badawi (2018), *Journal of Physical Chemistry B* 122, 12403-12410.

[2] Foucaud, Lainé, Filippov, Barrès, Kim, Filippova, Pastore, Lebègue & Badawi (2021), *Journal of Colloid and Interface Science* 583, 692–703.

[3] Foucaud, Filippov, Filippova & Badawi (2020), *Frontiers in Chemistry* 8, 230.