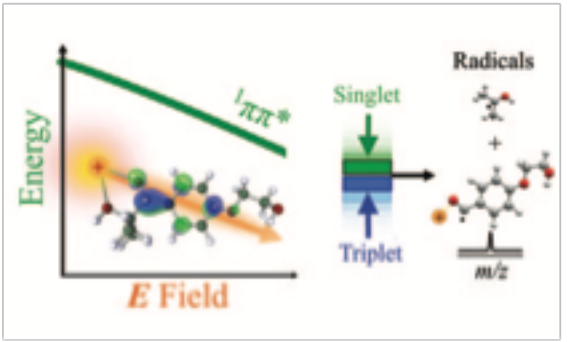
Charge up your photoinitiators

Oriented electric fields can influence chemical reactivity and recent research is applying this idea to enhance the performance of photoinitiators. Importantly for photoinitiators, shifts in the absorption transition must be considered along with shifts of other excited states that mediate activation (e.g. α-cleavage bond homolysis). Researchers at the University of Wollongong and Australian National University have shown how oriented electric fields, arising from single monatomic cations, can be used to tune the photodissociation of a common photoinitiator, Irgacure 2959 (Marlton S.J.P., McKinnon B.I., Hill N.S., Coote M.L., Trevitt A.J. *J. Am. Chem. Soc.* 2021, **143**, 2331–9). Mass-selected cation–Irgacure complexes were selectively confined within an ion trap and irradiated with tuneable laser photons. Photodissociation events were then detected by mass spectrometry. Analysis of shifts in the photodissociation action spectra with quantum-chemical calculations showed that the electric field arising from the cation perturbs the key electronic states. In some cases, the



cation caused a >1 eV red shift in the action spectra along with variations in the α-cleavage yield of up to four orders of magnitude. The study shows how oriented electric fields can shift electronic quantum states to tune photoinitiators by affecting both absorption profiles and photodissociation pathways.