MAPPING THE INTRINSIC PHOTOCHEMISTRY OF PhotoCORMS VIA GAS-PHASE LASER SPECTROSCOPY

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We perform, for the first time, gas-phase laser photodissociation spectroscopy on a series of metal carbonyls that can lose CO upon irradiation. These molecules (PhotoCORMs) can be used for delivering and releasing CO molecules for medicinal purposes, such as in cancer therapy and as antimicrobials. Photodepletion (PD) and photofragmentation (PF) spectra of $[CpRu(Ph_3)_2CO]^+$ and $[CpRu(dppe)CO]^+$ were acquired between 230 and 400 nm, and the range 230-500 nm was explored for $[Mn(CO)_4Br_2]^-$. All the PhotoCORMs lose CO after irradiation, accessing different fragmentation channels when different excited states are populated. Indeed, while scanning the wavelength range in our laser-interfaced electrospray mass spectrometer, we observe the production spectra of the photofragments and can track the variation in the intensity of their production. $[Mn(CO)_4Br_2]^-$ loses 3 CO molecules in the key visible region and 4 COs in the UV. $[CpRu(Ph_3)_2CO]^+$ fragments into $[CpRuPh_3]^+$ via the loss of CO and Ph_3. This observation can be used to improve the design of new CO-releasing molecules, as we demonstrate in the $[CpRu(dppe)CO]^+$ system where we successfully observe only the CO loss across the whole explored wavelength range. Finally, solution-phase irradiation results are presented for 365 nm photoexcitation, showing comparable photofragmentation results to the ones obtained in the gas-phase.