PHOTODISSOCIATION SPECTROSCOPY AND DISSOCIATION DYNAMICS OF $TiO^+(CO_2)$

MANORI PERERA[a], RICARDO B. METZ[b], *Department of Chemistry, University of Massachusetts Amherst[b], Amherst, MA.*

$TiO^+(CO_2)$ is produced by reaction of laser-ablated titianium atoms with CO_2 and subsequent clustering, supersonically cooled and its electronic spectroscopy characterized by photofragment spectroscopy, monitoring loss of CO_2. The photodissociation spectrum consists of a vibrationally-resolved band in the visible, with extensive progressions in the covalent Ti-O stretch (952 cm^{-1} vibrational frequency and 5 cm^{-1} anharmonicity), and in the TiO^+-(CO_2) stretch (186 cm^{-1}) and rock (45 cm^{-1}). The band origin is at 13918 cm^{-1}, assigned using titanium isotope shifts, and the spectrum extends to 17350 cm^{-1}. The excited state lifetime decreases dramatically with increasing internal energy, from 1100 ns for the lowest energy band (v_{TiO}=0), to <50 ns for v_{TiO}=3. The long photodissociation lifetime substantially reduces the photodissociation quantum yield at low energy, likely due to competition with fluorescence. Electronic structure calculations help to assign the spectrum of $TiO^+(CO_2)$ and predict allowed electronic transitions of TiO^+ in the visible, which have not been previously measured. Time-dependent density functional calculations predict that the observed transition is due to B, $^2\Pi \leftarrow$ X, $^2\Delta$ in the TiO^+ chromophore, and that binding to CO_2 red shifts the TiO^+ transition by 1508 cm^{-1}, and lowers the Ti-O stretch frequency by 16 cm^{-1}. Combining the computational and experimental results, the $^2\Pi$ state of TiO^+ is predicted to lie at $T_0 = 15426$ cm^{-1}, with frequency ωe = 968 cm^{-1} and anharmonicity ωexe = 5 cm^{-1}. The calculations also predict that there is only one low-lying $^2\Sigma$ state of TiO^+, contrary to conclusions derived from photoelectron spectroscopy of TiO. Prospects for astronomical observation of TiO^+ via the $^2\Pi$-$^2\Delta$ transition are also discussed.
[a]

[a]Department of Chemistry, University of Illinois at Urbana-Champaign