



First measurement of the dissociative recombination of CaO^+ with electrons brings closure to Ca ion recycling chemistry in the lower thermosphere

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Modelling the temporal and spatial extent of the metal layers in the mesosphere/lower thermosphere requires knowledge of the rate coefficients of dissociative recombination of metal oxide ions with electrons. Previously, these coefficients have been assumed to be $3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 200 K. In this study the coefficient has been measured directly for the dissociative recombination of CaO^+ .

Measurements are made in a flowing afterglow system with a Langmuir probe. Calcium oxide ions are introduced into an argon ion/electron plasma by pulsed laser ablation of a solid target. The relative concentration of CaO^+ is measured by a quadrupole mass spectrometer as a function of flow rate (3 – 5 slm), which is inversely proportional to the reaction time of the CaO^+ ions with the electrons in the plasma (2.1 to 3.5 ms).

Charge transfer reactions between argon ions and neutral molecules complicate the analysis. A kinetic model describing gas-phase chemistry and diffusion to the reactor walls was fitted to the experimental data to extract the DR rate coefficient for CaO^+ . Unlike other metals present in the atmosphere, Ca^+ ions are far more abundant than neutral Ca. The new DR rate coefficient is used to explore possible reasons for this anomaly in a model of meteor-ablated calcium in the mesosphere and lower thermosphere.