BOND DISSOCIATION DYNAMICS AND THERMODYNAMICS OF NiO^+ AND NiS^+

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Transition metal oxide and sulfide cations activate C-H bonds in the gas phase; several oxide cations activate methane and convert it to methanol at room temperature. However, a lack of experimental data on the energetics and dynamics of these species makes it difficult to model their reactions with hydrocarbons. We perform photofragment ion imaging experiments and ab initio calculations to determine the bond strength and photodissociation dynamics of the nickel oxide (NiO^+) and nickel sulfide (NiS^+) cations.

NiO^+ photodissociates broadly from 25000 to 32000 cm^{-1}via an excited $^4\Sigma^-$ state, exclusively forming Ni^+ (^{4}F) + O (^{3}P) products at photolysis energies above 29000 cm^{-1}. Photofragment images of NiO^+ show resolved Ni^+ ($^4F_{9/2}$) + O (^{3}P) and Ni^+ ($^4F_{7/2}$) + O (^{3}P) product spin-orbit channels; the lower energy (J = 9/2) channel dominates at photolysis energies of 29000 to 32000 cm^{-1}. The photofragment spectrum of NiS^+ from 19800 to 23200 $\mathrm{cm}^{-1}$is highly structured, with 12 distinct vibronic peaks each containing underlying spin-orbit structure. Photofragment images of NiS^+ collected over this region show slight parallel anisotropy, suggesting the highly structured photodissociation spectrum of NiS^+ in this region predominantly arises from a $\Delta\Lambda$ = 0 transition. Above 21600 cm^{-1}, the Ni^+ ($^2D_{5/2}$) + S (^{3}P) and Ni^+ ($^2D_{3/2}$) + S (^{3}P) product spin-orbit channels compete, with a branching ratio of 0.5. Temperature-dependent spectra suggest peaks below 20150 cm^{-1}result from hot bands. Images taken slightly above the dissociation threshold (20600 cm^{-1}) show resolved S ($^3P_2$) and S ($^3P_1$) spin-orbit channels. Our D_0 measurements for NiO^+ (D_0 = 244.6 +/- 2.4 kJ/mol) and NiS^+ (D_0 = 240.3 +/- 1.4 kJ/mol) are more precise and closer to each other than previously reported values.