

Photoinduced Elimination of CO and NO Ligands from the Heteroleptic Transition-Metal Complex: $\text{Co}(\text{CO})_3\text{NO}$

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Transition-metal (TM) complexes are characterized by highly symmetric structures, dense electronic structures, and low bond dissociation energies (100-200 kJ/mol) compared to organic compounds. Photoexcitation of TM complexes into the dense electronic states arising from the *d*-orbitals shows ultrafast relaxation (> 10 fs), and sequential loss of a variety of ligands, which are poorly understood. Photoinduced elimination of heteroleptic TM complexes provide understandings of the reactivity and bond-selectivity for photocatalysis. We have investigated photodissociation of $\text{Co}(\text{CO})_3\text{NO}$ from the viewpoint of nascent distributions of liberated ligands.

A supersonic jet of $\text{Co}(\text{CO})_3\text{NO}$ generated in a vacuum chamber was irradiated with ultraviolet laser to induce ligand elimination. Dissociated CO and NO fragments were state-selectively photoionized and detected as CO^+ and NO^+ with an ion-imaging apparatus. The REMPI spectra, which reflects nascent state distributions of the photofragments, were recorded by monitoring the ion yields by varying the probe laser wavelength. State-resolved scattering images were observed by fixing the ionization laser wavelength at a particular rovibrational state and recording arrival positions of the ionized fragments on a two-dimensional detector.

Translational energy distributions for CO and NO channels are shown in Fig. 1. The translationally lower components (~2 kJ/mol) were observed similarly for both NO and CO fragments, while the translationally higher component (~67 kJ/mol) was observed only for the NO fragment. Angular distributions for the translationally lower components of the CO and NO fragments were nearly isotropic, indicating that the dissociation lifetime is longer than the rotational period of $\text{Co}(\text{CO})_3\text{NO}$ (sub-nanoseconds). Several tens of nanoseconds is sufficiently long for the photoexcited $\text{Co}(\text{CO})_3\text{NO}$ to relax into the electronic ground state by internal conversion.

The translational energy distributions were well fitted by a model proposed by Klots^[1] on the basis of an orbiting transition state / phase space theory (OTS/PST). Calculations based on OTS/PST predict translational energy distributions from the height of centrifugal barrier. The angular distribution for the translationally higher component of NO were highly anisotropic expressed by zeroth, second, and fourth order of Legendre polynomials, demonstrating fast dissociation from the electronic excited states and rotational alignment of the eliminated NO. In conclusion, for ultraviolet photoelimination of $\text{Co}(\text{CO})_3\text{NO}$, fast elimination from electronic excited states is peculiar to NO, while slow eliminations from electronic ground state are common to CO and NO.

Reference

[1] C. E. Klots, *J. Phys. Chem.* **99**, 1748 (1995).

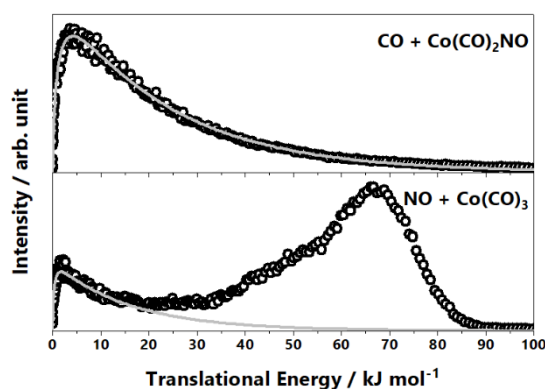


Fig. 1 Translational energy distributions for (upper) CO ($X^1\Sigma^+$, $v=0$, $J=36$) channel and (lower) NO ($X^2\Pi_{3/2}$, $v=0$, $J=35.5$) channel. Gray curves represent the Klots's model^[1].