Vibrational spectroscopy of CO in gas-phase rhodium cluster-CO complexes.
André Fielicke, Gert von Helden, Gerard Meijer, Benoit Simard, Stéphane Dénommée, David M. Rayner

Supporting Information

Experimental Methods: The Rh_nCO experiments are carried out in a cluster beam apparatus that has largely been described before[1,2]. Rhodium clusters are entrained in a flow of He in a pulsed laser ablation cluster source. They pick up CO delivered through a second pulse valve in a small reactor channel before expanding to produce a beam of $Rh_n(CO)_m$ species. The extent of CO-complex formation is controlled by adjusting the CO flow through the second valve.

Neutral species in the cluster beam are probed using a time-of-flight mass spectrometer (TOFMS). Ionization is induced by an ArF excimer laser (6.42 eV/photon). The UV intensity is attenuated to minimize fragmentation induced by multiphoton absorption. The IR beam counter propagates the cluster beam and is loosely focused onto an aperture through which the cluster beam enters the detection region. This ensures that the full cross-section of the cluster beam entering the TOFMS is exposed to the IR laser beam.

IR light is generated by the "Free Electron Laser for Infrared eXperiments" (FELIX). This FEL delivers continuously tunable macropulses of infrared radiation, with 20 to 30 mJ in energy and ~6 μs in duration at a repetition rate of 5 Hz. Each macropulse consists of a train of micropulses of typically ~2 ps duration and ~4 μJ in energy separated by 1 ns. FELIX frequencies are calibrated by recording the infrared absorption spectrum of ethylene in a photoacoustic cell. The bandwidth of the IR laser radiation is measured on the Q-branch of the $\nu_7+\nu_8$ combination band of ethylene to be 10-20 cm^{-1} at 1890 cm^{-1}, which is in agreement with a Lorentz-transform limited bandwidth of the pulsed laser radiation.

The UV probe laser is timed to ionize the portion of the beam exposed to FELIX when this reaches the TOFMS. Infrared spectra are measured by recording mass spectra at fixed wavelength intervals as FELIX is scanned. The IR depletion spectra are subsequently constructed by integrating the signal intensity corresponding to a certain complex for each wavelength. The IR depletion bands are found to be up to a factor of ~2 broader than the laser bandwidth. Since the bands are caused by the absorption of multiple photons, (cross-) anharmonicities can affect the width and positions of the bands. In any case, such effects are expected not to be larger than the bandwidth of the laser.[3] Another possibility would be inhomogeneous broadening due to the presence of different isomeric cluster complexes that each could have slightly shifted line positions.

(1) Simard, B.; Dénommée, S.; Rayner, D. M.; van Heijnsbergen, D.; Meijer, G.; von Helden, G. *Chem. Phys. Lett.* **2002**, *375*, 195.
(2) von Helden, G.; Kirilyuk, A.; van Heijnsbergen, D.; Sartakov, B.; Duncan, M.A.; Meijer, G. *Chem. Phys.* **2000**, *262*, 31.
(3) von Helden, G.; van Heijnsbergen, D.; Meijer, G. *J. Phys. Chem. A* **2003**, *107*, 1671

CO stretching frequencies, ν(CO), of Rh_nCO complexes (cm^{-1})

n	ν(CO)
6	1950 ± 2
7	1961 ± 2
8	1960 ± 2
9	1962 ± 2
10	1964 ± 2
11	1964 ± 2
12	?
13	1962 ± 2
14	1962 ± 3
15	1960 ± 4
16	1960 ± 5

17	1964 ± 5
18	1964 ± 5
19	1961 ± 5
20	1965 ± 5