

## Activation of CO<sub>2</sub> through dissociative adsorption on cobalt cluster anions

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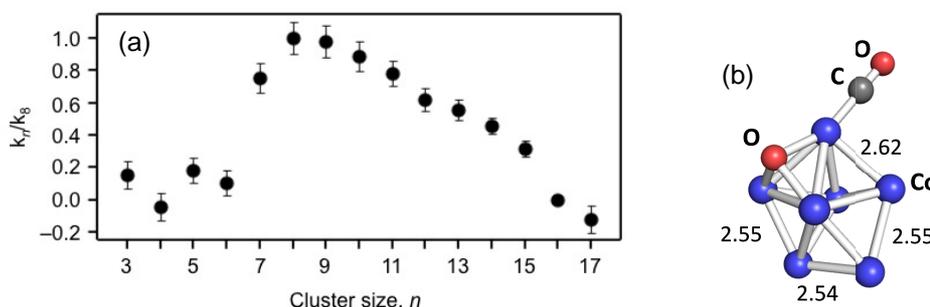
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Carbon dioxide is a primary greenhouse gas, and its emission control is a major challenge for realizing a sustainable society. A promising approach to this issue is the catalytic conversion of the chemically inert CO<sub>2</sub> molecule into useful, value-added compounds.<sup>1</sup> Here, we investigated a possibility of CO<sub>2</sub> activation by cobalt cluster anions by mass spectrometric detection and structural characterization of the reaction product using infrared multiple photon dissociation (IRMPD) spectroscopy, photoelectron spectroscopy, and DFT calculations.

The reaction of Co<sub>*n*</sub><sup>-</sup> produced by laser vaporization with CO<sub>2</sub> yielded Co<sub>*n*</sub>CO<sub>2</sub><sup>-</sup> clusters as major products. The rate constant *k<sub>n</sub>* normalized by that of the most reactive cluster *k<sub>8</sub>* was estimated by assuming a pseudo first order reaction kinetics and plotted in Fig. (a) as a function of *n*. The rate constant increases abruptly at *n* = 7, peaks around *n* = 8–10, and then decreases monotonically with increasing *n*.

The structure of the smallest product Co<sub>7</sub>CO<sub>2</sub><sup>-</sup> was characterized. The IRMPD spectrum of Co<sub>7</sub>CO<sub>2</sub><sup>-</sup> exhibited a single absorption band at 1860 cm<sup>-1</sup>. The peak position is similar to that of Co<sub>7</sub>CO<sup>-</sup>,<sup>2</sup> suggesting dissociative adsorption of CO<sub>2</sub> on Co<sub>7</sub><sup>-</sup> to form Co<sub>7</sub>(CO)O<sup>-</sup>. DFT calculation showed that structural isomers of Co<sub>7</sub>(CO)O<sup>-</sup> in which CO<sub>2</sub> is dissociatively adsorbed, see Fig. (b), are more stable than those of Co<sub>7</sub>CO<sub>2</sub><sup>-</sup> in which CO<sub>2</sub> is adsorbed non-dissociatively. Calculated vibrational spectra for the isomers of Co<sub>7</sub>(CO)O<sup>-</sup> exhibited a single IR band in the range of 1900–1930 cm<sup>-1</sup>, supporting dissociative adsorption of CO<sub>2</sub> on Co<sub>7</sub><sup>-</sup>. In addition, IRMPD spectra of larger Co<sub>*n*</sub>CO<sub>2</sub><sup>-</sup> (*n* = 8–13) have also shown single absorption bands at around 1900 cm<sup>-1</sup>, suggesting dissociative adsorption of CO<sub>2</sub> onto the larger Co<sub>*n*</sub><sup>-</sup>. This size-specific mode of CO<sub>2</sub> activation by Co<sub>*n*</sub><sup>-</sup> (*n* ≥ 7) is in sharp contrast to the non-dissociative adsorption onto the Co monomer anion to form [CO<sub>2</sub>CoCO<sub>2</sub>]<sup>-</sup>.<sup>3</sup>



Figures (a) Plot of the relative rate constants. (b) An optimized structure of Co<sub>7</sub>CO<sub>2</sub><sup>-</sup>. Bond lengths are shown in Å.

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