Adsorption Feature of Hydrogen on Rhodium Cationic Clusters investigated by infrared multiple photon dissociation and gas-phase thermal desorption spectrometry

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The study of the reactions between hydrogen and transition metal clusters reveals the fundamental insight of elementary steps in the field of catalysis and hydrogen storage. Rhodium serves as an effective catalyst in many chemical reactions,[1,2] and previous study has proved the hydrogen-storage capability of Rh nanoparticles.[3] In this study, we investigated the adsorption and desorption features of D_2 on Rh_n^+ clusters using infrared multiple photon dissociation (IRMPD) and thermal desorption spectrometry (TDS).

$Rh_nAr_k^+$ clusters were prepared by laser ablation of a rhodium rod in the Ar/He carrier gas, then reacted with the D_2/He reactant gas and generated $Rh_nD_mAr_k^+$ (k = 0–2) clusters.

For the $Rh_8D_2^+$ clusters, an intense broad band at 970 cm^{-1}, two weak bands at 620 and 730 cm^{-1} and possibly very weak bands at 400 and 480 cm^{-1} were observed (Figure 1). Based on the relative intensities and the wavenumbers of the adsorption bands, the most stable isomer (b), and meta-stable isomers (d) and (f) are regarded as possible structures. The band at 970 cm^{-1} corresponds to the stretching vibration of the bridge-site D atom. Bands around 620 and 730 cm^{-1} can be assigned to the stretching vibration of the bridge-site D atom, and out-of-plane wagging vibration of the other hollow-site D atom, respectively. Weak bands at 400 and 480 cm^{-1} corresponds to the stretching vibration of hollow-site D atom.

These results show that the first D_2 molecule tends to adsorb dissociatively on the Rh_8^+ clusters on a bridge site and/or a hollow site. Hydrogen adsorption forms with more D_2 attachment and desorption process will be discussed in detail.

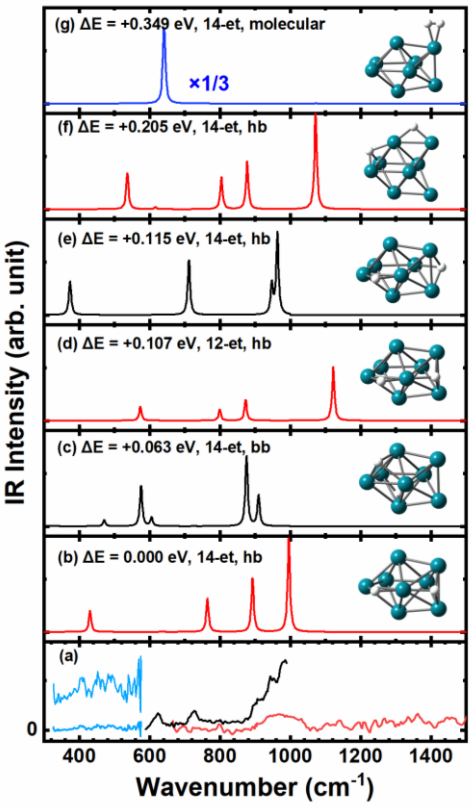

Figure 1. (a) IRMPD spectrum of $Rh_8D_2^+$ and (b–g) vibration spectra of stable isomers of $Rh_8D_2^+$ obtained by the DFT calculation. Blue, black and red curves indicate the experiments with different settings of the IR beam.

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