# Supplementary Materials

## Infrared Photodissociation Spectroscopic and Theoretical Study of Mass-selected Heteronuclear Iron-Rhodium and Iron-Iridium Carbonyl Cluster Cations

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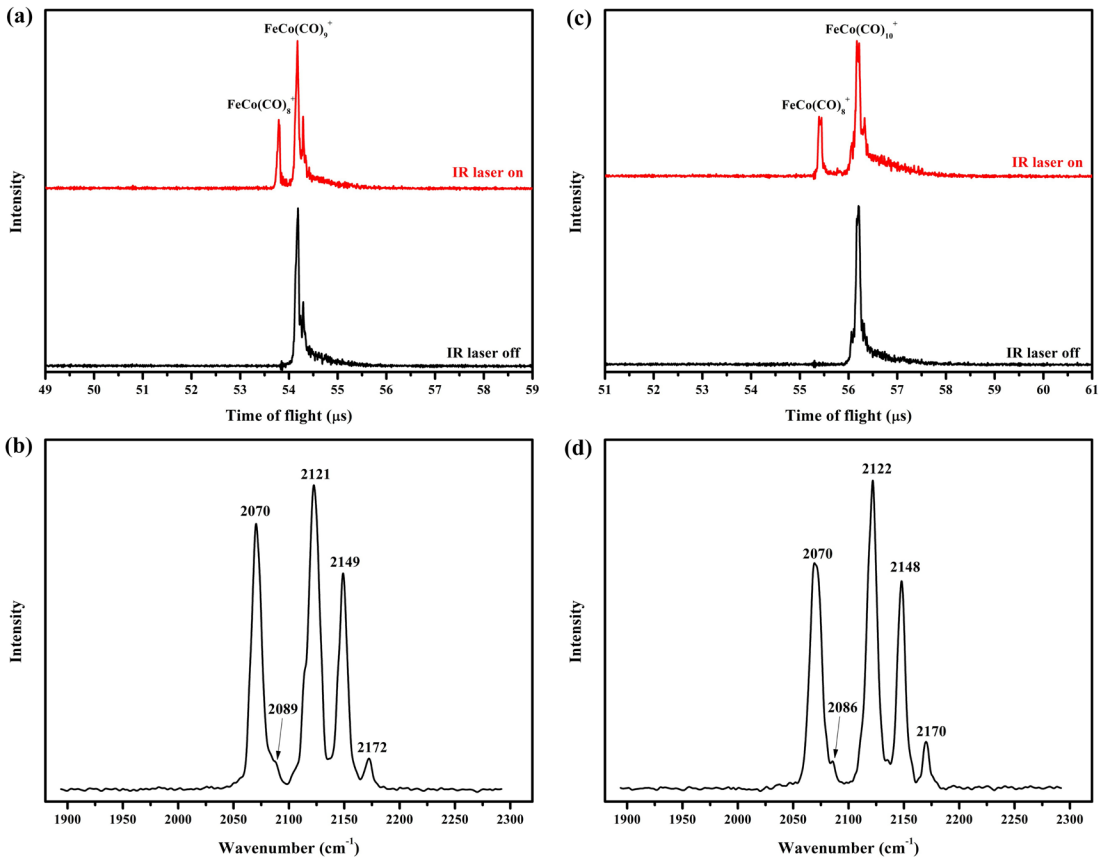



**Figure S1**. The laser-induced photofragmentation mass spectrum of mass-selected $FeCo(CO)_9^+$ (a) and the resulting infrared photodissociation spectrum (b); the laser-induced photofragmentation mass spectrum of mass-selected $FeCo(CO)_{10}^+$ (c) and the resulting infrared photodissociation spectrum (d).

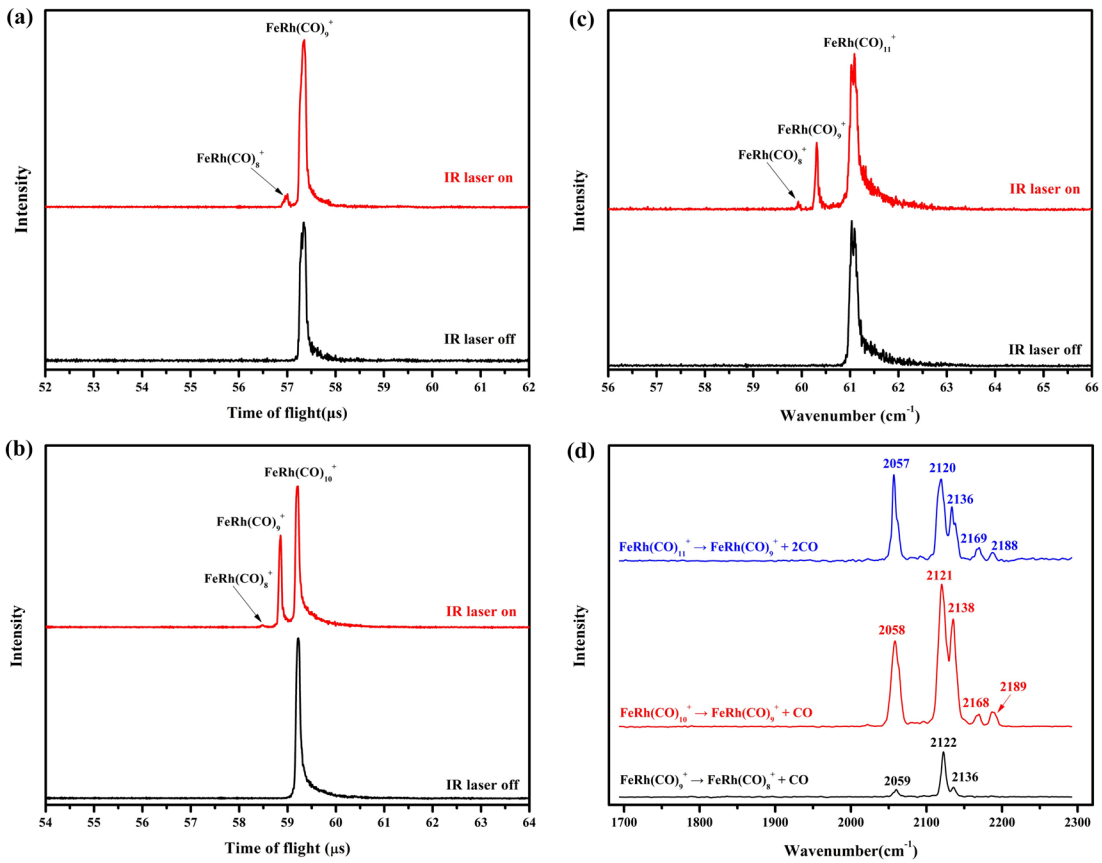



**Figure S2**. The laser-induced photofragmentation mass spectra of mass-selected $FeRh(CO)_9^+$ (a), $FeRh(CO)_{10}^+$ (b), $FeRh(CO)_{11}^+$ (c), as well as the resulting infrared photodissociation spectra (d).

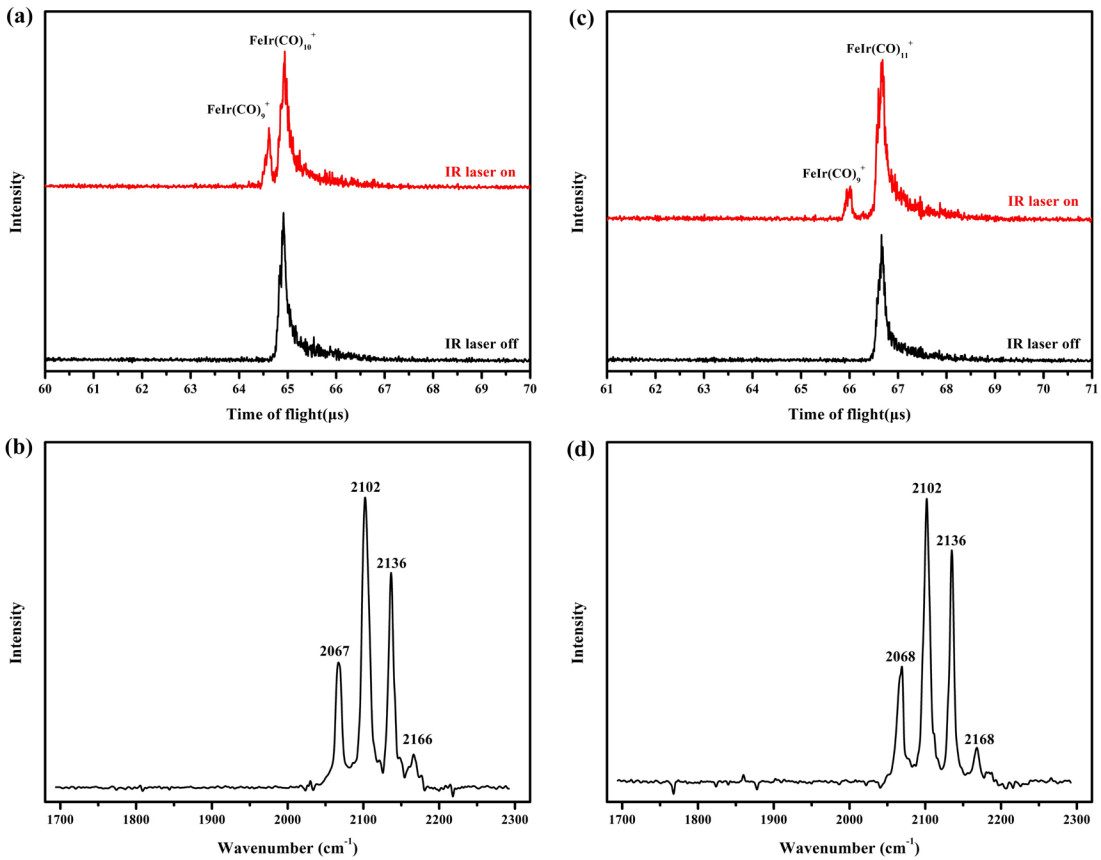



**Figure S3**. The laser-induced photofragmentation mass spectrum of mass-selected $FeIr(CO)_{10}^{+}$ (a) and the resulting infrared photodissociation spectrum (b); the laser-induced photofragmentation mass spectrum of mass-selected $FeIrCO)_{11}^{+}$ (c) and the resulting infrared photodissociation spectrum (d).

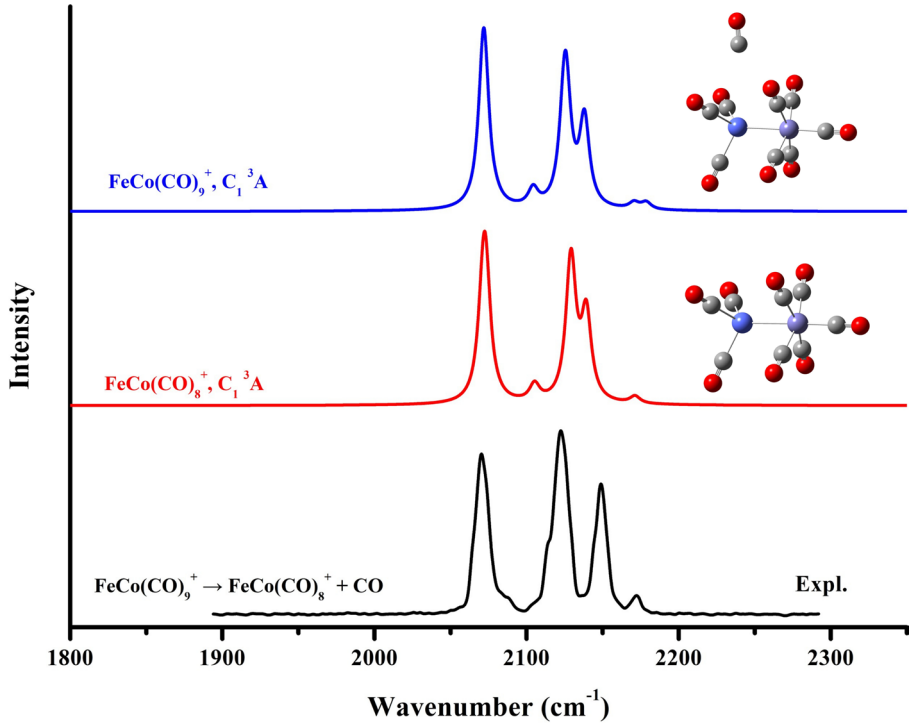



**Figure S4**. The experimental infrared photodissociation spectrum of $FeCo(CO)_9^+$ and the simulated vibrational spectra of the saturated $FeCo(CO)_8^+$ and solvated $FeCo(CO)_9^+$ cation complexes in the carbonyl stretching frequency region.

**Table S1.** The calculated charge distribution of $FeM(CO)_9^+$ based on natural population analysis.

| Complex | Site | NPA charge | Spin population |
|---|---|---|---|
| $FeRh(CO)_9^+$ | Fe1 | -2.221 | - |
| ($C_{4v}$ $^1A_1$) | Rh2 | -1.068 | - |
| | C7-O8 | 0.572 | - |
| | C9-O10 | 0.519 | - |
| | C3-O4 | 0.412 | - |
| $FeIr(CO)_9^+$ | Fe1 | -2.228 | - |
| ($C_{4v}$ $^1A_1$) | Ir2 | -0.837 | - |
| | C7-O8 | 0.581 | - |
| | C9-O10 | 0.531 | - |
| | C3-O4 | 0.340 | - |
| $FeCo(CO)_8^+$ | Fe1 | -2.341 | 0.020 |
| ($C_1$ $^3A$) | Co2 | -0.300 | 1.816 |
| | C7-O8 | 0.573 | -0.006 |
| | C9-O10 | 0.539 | 0.002 |
| | C3-O4 | 0.305 | 0.055 |

**Table S2.** Calculated thermodynamic energy (electronic energy including zero-point vibration energy correction) of free CO, triplet $FeCo(CO)_8^+$, and singlet $FeCo(CO)_9^+$, as well as the relative energy of singlet $FeCo(CO)_9^+$ to $FeCo(CO)_8^+$ plus CO at the B3LYP, TPSSh, TPSS, and PBE level with def2-TZVPP basis set, respectively.

| | $FeCo(CO)_8^+$ (a.u.) | CO (a.u.) | $FeCo(CO)_9^+$ (a.u.) | ΔE (eV) |
|---|---|---|---|---|
| B3LYP | -3553.428911 | -113.340223 | -3666.786101 | -0.462 |
| TPSSh | -3553.450647 | -113.354550 | -3666.833857 | -0.780 |
| TPSS | -3553.682697 | -113.369579 | -3667.086705 | -0.937 |
| PBE | -3552.033234 | -113.229441 | -3665.308458 | -1.246 |

**Table S3.** The cartesian coordinates (Å) of the structures of $FeM(CO)_9^+$ optimized at B3LYP/def2-TZVPP level.

| Complex | Atom | x | y | z |
|---|---|---|---|---|
| $FeRh(CO)_9^+$ | Fe | 0 | 0 | -1.64778 |
| ($C_{4v}$, $^1A_1$) | Rh | 0 | 0 | 1.519343 |
| | C | 1.372805 | 1.372805 | 1.794769 |
| | O | 2.158761 | 2.158761 | 1.978374 |
| | C | -1.37281 | -1.37281 | 1.794769 |
| | O | -2.15876 | -2.15876 | 1.978374 |
| | C | 0 | 0 | -3.49269 |
| | O | 0 | 0 | -4.62126 |
| | C | 0 | 1.827068 | -1.39055 |
| | O | 0 | 2.953495 | -1.26911 |
| | C | 1.372805 | -1.37281 | 1.794769 |
| | O | 2.158761 | -2.15876 | 1.978374 |
| | C | 1.827068 | 0 | -1.39055 |
| | O | 2.953495 | 0 | -1.26911 |
| | C | 0 | -1.82707 | -1.39055 |
| | O | 0 | -2.9535 | -1.26911 |
| | C | -1.37281 | 1.372805 | 1.794769 |
| | O | -2.15876 | 2.158761 | 1.978374 |
| | C | -1.82707 | 0 | -1.39055 |
| | O | -2.9535 | 0 | -1.26911 |
| $FeIr(CO)_9^+$ | Fe | 0 | 0 | -1.80691 |
| ($C_{4v}$, $^1A_1$) | Ir | 0 | 0 | 1.266732 |
| | C | 1.369596 | 1.369596 | 1.564447 |
| | O | 2.153904 | 2.153904 | 1.779444 |
| | C | -1.3696 | -1.3696 | 1.564447 |
| | O | -2.1539 | -2.1539 | 1.779444 |
| | C | 0 | 0 | -3.65234 |
| | O | 0 | 0 | -4.78032 |
| | C | 0 | 1.835664 | -1.57353 |
| | O | 0 | 2.962645 | -1.47269 |
| | C | 1.369596 | -1.3696 | 1.564447 |
| | O | 2.153904 | -2.1539 | 1.779444 |
| | C | 1.835664 | 0 | -1.57353 |
| | O | 2.962645 | 0 | -1.47269 |
| | C | 0 | -1.83566 | -1.57353 |
| | O | 0 | -2.96265 | -1.47269 |
| | C | -1.3696 | 1.369596 | 1.564447 |
| | O | -2.1539 | 2.153904 | 1.779444 |
| | C | -1.83566 | 0 | -1.57353 |
| | O | -2.96265 | 0 | -1.47269 |