

1B3b Photochemistry of Transition-Metal Carbonyls in the Gas Phase

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Photochemistry of transition-metal carbonyls (TMCs) is an important research field in organometallic chemistry. Iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, is the most typical TMCs, for which many researches have been conducted to unravel the photoreaction mechanism in both gas and condensed phases.^[1-4] However, the details of the photochemical reaction is still unclear. The photoreaction mechanism dependence on metal species, configurations and ligands is also vague. We have investigated many TMCs with different metals, coordination numbers and structures by using an ion-imaging technique. In this presentation, we will treat three TMCs which are $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$ and $\text{CpCo}(\text{CO})_2$.

One-color (220 ~ 230 nm) experiments, where a single laser pulse serves as both photolysis and probe irradiation, were performed under a supersonic molecular beam condition. The internal state distributions of the CO ($X^1\Sigma^+$) fragments were measured by REMPI spectroscopy. The state-resolved scattering distributions were obtained by ion-imaging.

The observed REMPI spectra of the CO photofragments generated from $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$ and $\text{CpCo}(\text{CO})_2$ are shown in Fig. 1. The relative population in the rotational states of CO in $v = 0$ shows thermal rotational distribution for these TMCs. The rotational temperature indicate at least two components. We found that only $\text{Fe}(\text{CO})_5$ eliminates highly vibrationally excited CO products ($v = 12, 13$) with non-statistical rotational distribution. The scattering distributions of this CO products are slightly anisotropic. The energy conservation law conflicts with the generation of the CO in $v = 12$ and 13 states from one-photon absorbing $\text{Fe}(\text{CO})_5$. These results of scattering distribution and energy consideration suggest that the coordinatively unsaturated $\text{Fe}(\text{CO})_n$ ($n < 5$) produces the highly vibrated CO by further photoexcitation.

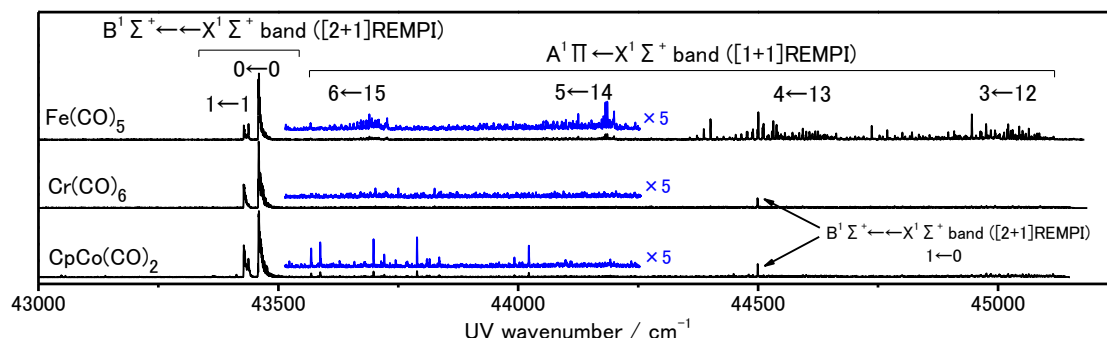


Fig. 1 REMPI spectra of CO generated by photodissociations of $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$ and $\text{CpCo}(\text{CO})_2$.

References

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