Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Time-Resolved Observation of Transient Precursor State of CO on Ru(0001) using Carbon K-edge spectroscopy

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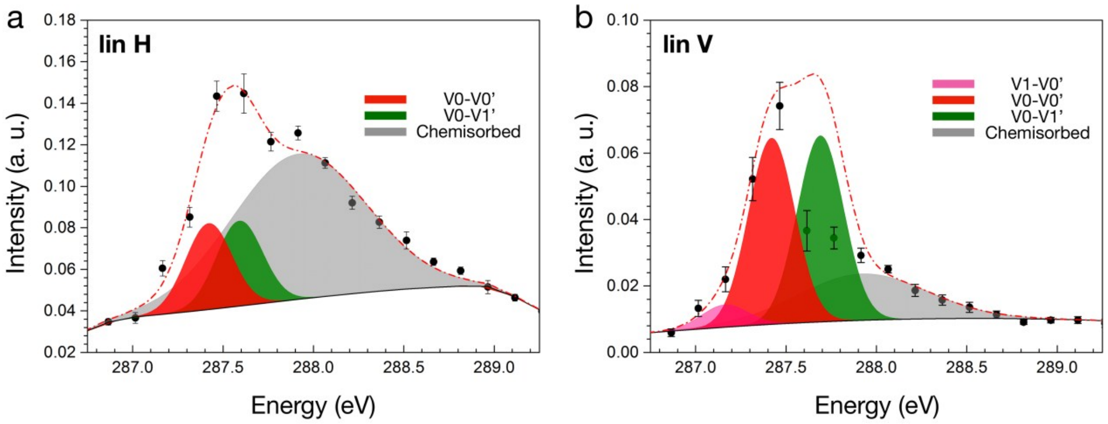

Fig. S1. Results of fits without adding the NAS state in (a) lin H and (b) lin V XA spectra at 8-10 ps pump-probe delay. The red dashed curve in (a) and (b) shows the resulting fit which is to be compared with the data points (black, with error bars).

We want to first clarify that the peak position at ~287.4 eV coinciding with the known gas-phase energy position is not just simply defined by one single data point. Each data point is an averaged result which usually contains 50 - 90 meaningful shots after data analysis. After we obtain the raw data, an obvious trend of intensity growing at 287.4 eV with time ranging from 0 ps to 10 ps can thus be clearly identified in Figure 1. Due to the fact that 0.3 eV is the resolution of the FEL, we first tried to fit a Gaussian peak centered at 284.4 eV with a linewidth of 0.3 eV, and we found this sharp peak indeed can only be ascribed to one species, which was defined as the precursor state. Again, although the linewidth for both the $v_0 - v_0$’ and $v_0 - v_1$’ resonance is usually smaller than 0.18 eV (ref. 14), the linewidth used in the fitting is restricted to 0.3 eV because of the 0.3 eV FEL resolution. Based on this premise, the linewidth of 0.3 eV for the “hot state” of the $v_1 - v_0$’ resonance as well as the NAS should also be reasonable.

After we fixed the energy position for the precursor state, owing to the fact that the CO molecule in the precursor state is free to isotropically rotate, all corresponding spectral features of the precursor state must be equally seen in the lin V and lin H spectra, which means we should always see the same ratio of the $v_0 - v_0$’ and $v_0 - v_1$’ resonance intensities of the precursor state in both spectra. If we allow the relative intensities of $v_0 - v_0$’ and $v_0 - v_1$’ resonance to relax yet still keep the same ratio value for both lin V and lin H spectra, as demonstrated in Fig. S1 where the ratio of the $v_0 - v_0$’ and $v_0 - v_1$’ resonance intensities is 1:1, we can have a good fit in the lin V spectrum but a very poor result in lin V spectrum. In other words, if we modify the ratio to have a good fit in the lin V spectra, then we must add an additional resonance intensity for the lin H spectra to satisfy the spectral profile. Therefore, it should be reasonable to adopt a known value of the $v_0 - v_0$’ and $v_0 - v_1$’ resonance peaks based on Ref. 14 as reference, and the need of NAS as well as $v_1 - v_0$’ resonance is thus necessary since the combination of $v_0 - v_0$’ and $v_0 -$

v_1’ resonance intensities is not enough to satisfy the data profile distribution.

The broad feature of the chemisorbed state can always be well-fitted by a wide Gaussian peak with a small standard error of < 0.003. Overall, the R^2 is usually > 97% for all fitting results, and there is only one exception for 4-6 ps delay in the lin V spectrum where R^2 is ~ 95%. The line through the data points is obtained by convoluting all the fitting peaks to have a cumulative spectral profile.”

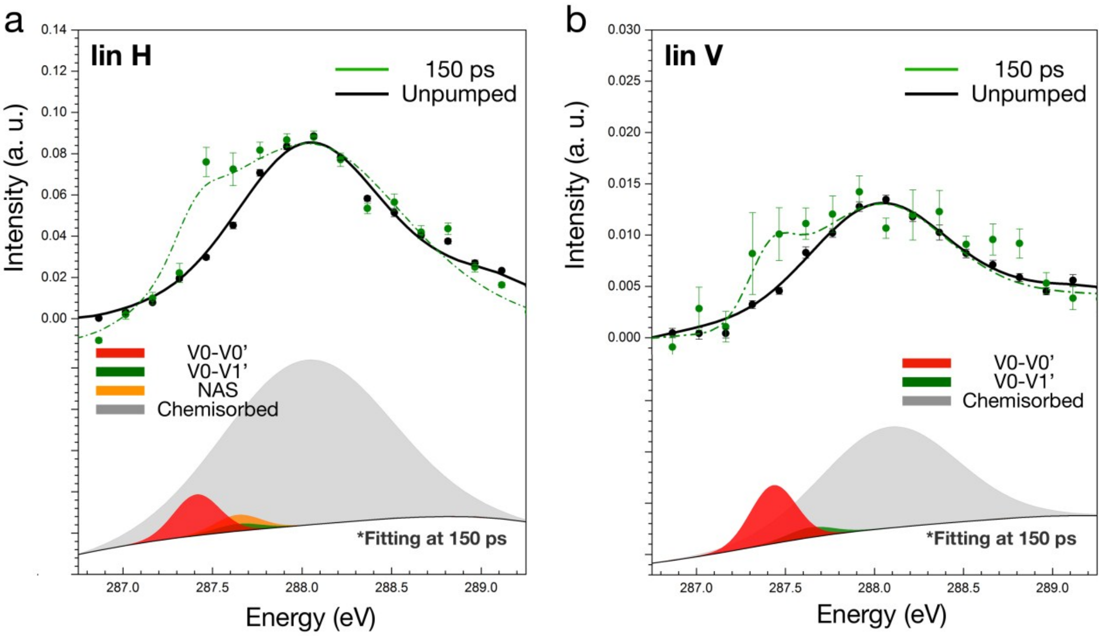

Fig. S2. Comparison between unpumped and 150 ps in (a) lin H and (b) lin V XA spectra. The corresponding fitting results in (a) and (b) show that we can still see some NAS intensity in the lin H spectra, while in the lin V spectra the NAS intensity is absent due to the upright orientation of the CO molecule as the surface temperature rapidly becomes lower. Note the different scales in the lin H and lin V spectra.

The fitting result indicates that some NAS resonance can still be seen in the lin H spectra at 150 ps delay, as seen from the shape of the overall spectral profile. In the lin V spectra, due to the relatively large error bar of the spectrum at 150 ps, it is difficult to precisely determine the real spectral profile. Besides, since the resonance intensity at 287.4 eV (ascribed as gas phase position at 150 ps delay) is still clearly visible, then the v_0 -v_1' transition could also affect the shape of the chemisorbed state intensity. The percentage of CO that desorbs from the surface is only a rough estimation. Therefore the error is still quite huge (14.5 ± 5 % means there could be a maximum of 66% error). The escaping fraction is only estimated based on the intensity changes of the peak at 287.4 eV without considering NAS and chemisorbed state since NAS and chemisorbed sate are still the bonded state on the surface, and both intensities area affected by each other due to the frustrated translation of CO on the on-top sites. On the other hand, the intensity at 287.4 eV is much clear and reliable for the estimation since there is no doubt that we have a new species there. At 8-10 ps delay, the intensity at 287.4 eV reached its maximum where it could include both precursor state and gas phase signal. However, at 150 ps delay, the surface should be cold enough that the intensity can only be ascribed to free gas molecules. Therefore, we believe that the intensity changes of the peak at 287.4 eV should be a good reference for the estimation.