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THE DISSOCIATIVE CHEMISORPTION OF
CARBON DIOXIDE ON RHODIUM SURFACES

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There is much uncertainty in the literature concerning the nature of carbon dioxide chemisorption on rhodium surfaces. Recent results from our laboratory which show the dissociation of $\text{CO}_2(\text{g})$ to $\text{CO}_{\text{ads}}^{\dagger}$ and O_{ads} on several single crystal^{1,2,3} and polycrystalline samples⁴ do not agree with those of others indicating the absence of chemisorption for carbon dioxide.^{5,6,7,8} In order to obtain additional proof of CO_2 dissociation on rhodium surfaces we have applied high resolution electron energy loss spectroscopy (ELS) and thermal desorption spectroscopy (TDS) to a study of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ chemisorption on the Rh(111) single crystal surface. The combination of these two techniques allows one to determine the nature of the adsorbed species while on the metal surface and after desorption into the gas phase. We present convincing evidence for the dissociative chemisorption of carbon dioxide to $\text{CO}_{\text{ads}}^{\dagger}$ and O_{ads} at 300 K. The difficulty in detecting CO_2 dissociation upon adsorption is due to the low sticking probability of the molecule on rhodium¹⁻⁸ and to the rapid back reaction $\text{CO}_{\text{ads}}^{\dagger} + \text{O}_{\text{ads}} \rightarrow \text{CO}_2(\text{g})$ at elevated temperatures in the presence of excess chemisorbed oxygen.^{1,2,7,8}

Early infrared studies employing alumina supported rhodium samples

[†] ads denotes an adsorbed species

showed no evidence for CO₂ chemisorption--either molecular or dissociative.⁵ Similarly, volumetric uptake measurements on evaporated rhodium films indicate that very little CO₂ chemisorption is taking place.⁶ Simple calculations of heats of adsorption for dissociatively chemisorbed CO₂ yield values between 10 and 29 kcal/mole, implying only weak chemisorption, if any.^{6,9} Kinetic studies on polycrystalline rhodium wires by Campbell and White also show no CO₂ adsorption at 330 K.⁷ A small CO peak was observed in the thermal desorption spectrum, but it was attributed to chemisorption from the ambient. More recently, Primet found no evidence for carbon dioxide chemisorption on zeolite supported rhodium catalysts at 300 K using infrared spectroscopy.⁸ Samples on an alumina support under identical conditions, however, showed bands at 1860 and 2025 cm⁻¹. This was interpreted in terms of a very low coverage of carbon monoxide derived from dissociatively chemisorbed CO₂. Finally, he found that preadsorbed oxygen inhibited the dissociation of carbon dioxide at 300 K.

Low energy electron diffraction (LEED) studies on rhodium single crystal surfaces provided the first evidence for CO₂ chemisorption. Grant and Haas observed a "rather complex" diffraction pattern after exposing an initially clean Rh(111) surface to 60L (1L = 1 Langmuir = 10⁻⁶ Torr·sec) of CO₂.¹⁰ Castner, Sexton and Somorjai showed that CO and CO₂ gave an identical series of LEED patterns and thermal desorption spectra on both the (111) and (100) rhodium surfaces.¹ The only difference noted between the two adsorbates was that CO₂ required an approximately five-fold higher exposure to achieve the same surface structures. They interpreted these findings in terms of carbon dioxide dissociation into adsorbed CO and oxygen. Further studies on stepped rhodium surfaces are in full agreement with this interpretation.² Recent catalytic experiments on rhodium foils indicate that CO₂ does indeed dissociatively chemisorb and is extremely

reactive toward hydrogen.⁴

To clarify the nature of carbon dioxide adsorption on rhodium we have studied the chemisorption of both $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ on Rh(111) by high resolution ELS and thermal desorption spectroscopy. The lower portion of Figure 1 shows a comparison between the ELS spectra of ^{12}CO and $^{12}\text{CO}_2$ chemisorbed on a rhodium (111) single crystal surface at 5×10^{-7} torr background pressure and 300 K. It is clear that the vibrational spectra are almost identical, indicating dissociative chemisorption of carbon dioxide.

For the case of molecular CO_2 adsorption one would expect several extra peaks in the $800\text{-}1600\text{ cm}^{-1}$ region. Such stretching vibrations have been seen for two distinct types of carbon dioxide bonding in rhodium - CO_2 coordination complexes,¹¹ but are clearly not visible here, even at high scale expansions. One can now assign all of the observed losses by comparison with several rhodium carbonyls,^{12,13} with matrix isolation experiments,¹⁴ and with previous infrared studies on supported rhodium catalysts;^{5,8,15} $430\text{ cm}^{-1} : \nu_{\text{Rh-C}}$, $1870\text{ cm}^{-1} : \nu_{\text{C=O}}$ (multiply coordinated site) and $2060\text{ cm}^{-1} : \nu_{\text{C=O}}$ (atop site). A complete study of the vibrational spectra of CO and CO_2 chemisorbed on Rh(111) as a function of crystal temperature, surface pretreatment and background pressure will be published elsewhere.³

The position of the carbon-oxygen stretch at 2060 cm^{-1} is a strong function of coverage³ and is therefore not well suited for isotopic studies. The peak at 1870 cm^{-1} grows in at constant frequency, however, and is ideal for labelling experiments. Relatively high pressures of ^{12}CO , $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ were applied in order to insure adequate population of this site. It is clear from the $^{13}\text{CO}_2$ chemisorption spectrum in the top of Figure 1 that $^{13}\text{CO}_2$ dissociatively chemisorbs on Rh(111) and forms $^{13}\text{CO}_{\text{ads}}$. This result eliminates the possibility that CO_{ads}

is produced by the chemisorption of background CO in the vacuum system. Mass spectral analysis of both $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ showed no major CO impurities. The calculated shifts of the vibrational frequencies presented in Table I agree quite well with the predicted values, despite the limited resolution of ELS. They are also in excellent agreement with the recent infrared results of Yates, et al. for ^{12}CO and ^{13}CO chemisorbed on alumina supported rhodium.¹⁵ Further studies have shown that the weak Rh-O stretch from adsorbed oxygen at 520 cm^{-1} is probably hidden beneath the $\nu_{\text{Rh-C}}$ peak.³ Oxygen is soluble in bulk rhodium and therefore may be residing beneath the surface.^{1,2,16}

The TDS spectra of chemisorbed CO and CO_2 are also quite similar (see Figure 2). $^{13}\text{CO}_2$ yields only ^{13}CO , as expected. Again, an approximately five- to ten-fold higher exposure is required for the adsorption of carbon dioxide. No molecular CO_2 (either $m/e = 44$ or 45) was observed desorbing from the surface and this is consistent with the solubility of oxygen in bulk rhodium samples.^{1,2,16} These labelling studies provide clear evidence that background adsorption is not causing the observed LEED, ELS or TDS features.

The question still remains: Why was it difficult to detect the dissociative chemisorption of carbon dioxide on rhodium in other experiments? It appears that relatively high gas exposures are necessary to detect any chemisorption due to the low sticking probability of CO_2 . Also CO readily reacts with, and is easily removed by, excess chemisorbed oxygen, even at 320 K.^{1,2,7,8} Thus, if the rhodium surface is partially oxygen covered, the rate of the association reaction $\text{CO}_{\text{ads}} + \text{O}_{\text{ads}} \rightarrow \text{CO}_2(\text{g})$ will be rapid and yield the apparent result that CO_2 does not adsorb.

Acknowledgement

We would like to thank Professor C.B. Moore for lending us a sample of $^{13}\text{CO}_2$ (Merck Isotopes, 90.5% purity).

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T A B L E I

Isotopic Frequency Shifts for CO₂ Chemisorption on Rhodium ^a

Mode	Observed on Rh(111) ^b		Calculated ^c	Observed on Supported Rhodium ¹⁵	
	¹² CO ₂	¹³ CO ₂	¹³ CO	¹² CO	¹³ CO
$\nu_{\text{Rh-C}}$	430	420	423	--	--
$\nu_{\text{C=O}}$ (multiply coordinated)	1870	1820	1828	1870	1832
$\nu_{\text{C=O}}$ (atop)	2060	2010	2014	2070	2024

a. All frequencies in cm⁻¹

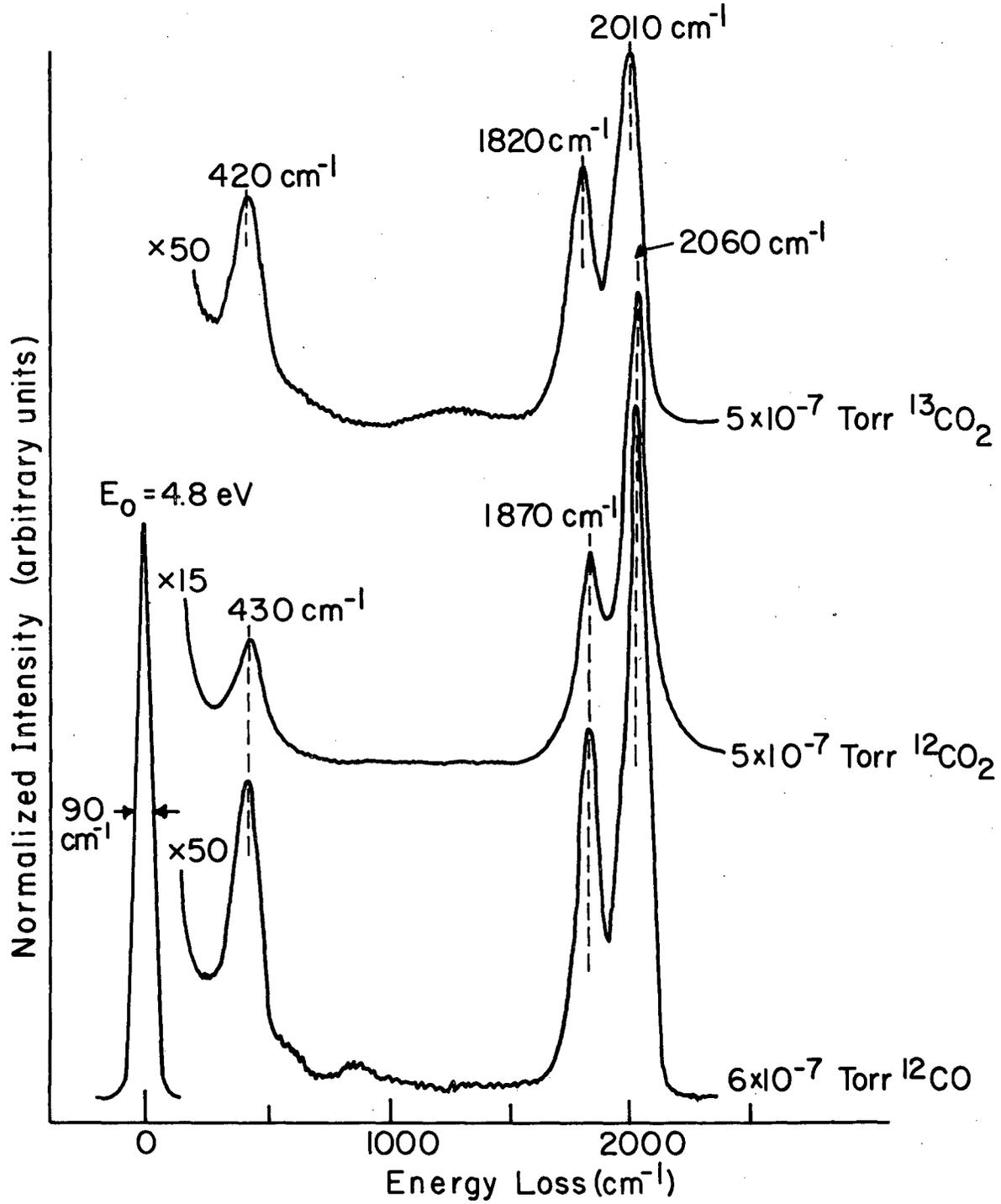
b. Observed values are reproducible to ± 7 cm⁻¹

c. $\nu^* = \left(\frac{\mu}{\mu^*} \right)^{1/2} \nu$, where μ is the reduced mass for the vibrational mode of interest and * refers to the labeled species.

Figure Captions

1. High resolution ELS spectra of chemisorbed ^{12}CO , $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ on Rh(111) at 300 K under approximately 5×10^{-7} torr background pressure. Note the absence of extra peaks for carbon dioxide chemisorption. The frequency shifts are summarized in Table I.
2. Thermal desorption spectra for ^{12}CO , $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ chemisorbed on Rh(111). The heating rate was approximately 20 K/sec. CO ($m/e = 28$ or 29) was the only species detected desorbing from the surface.

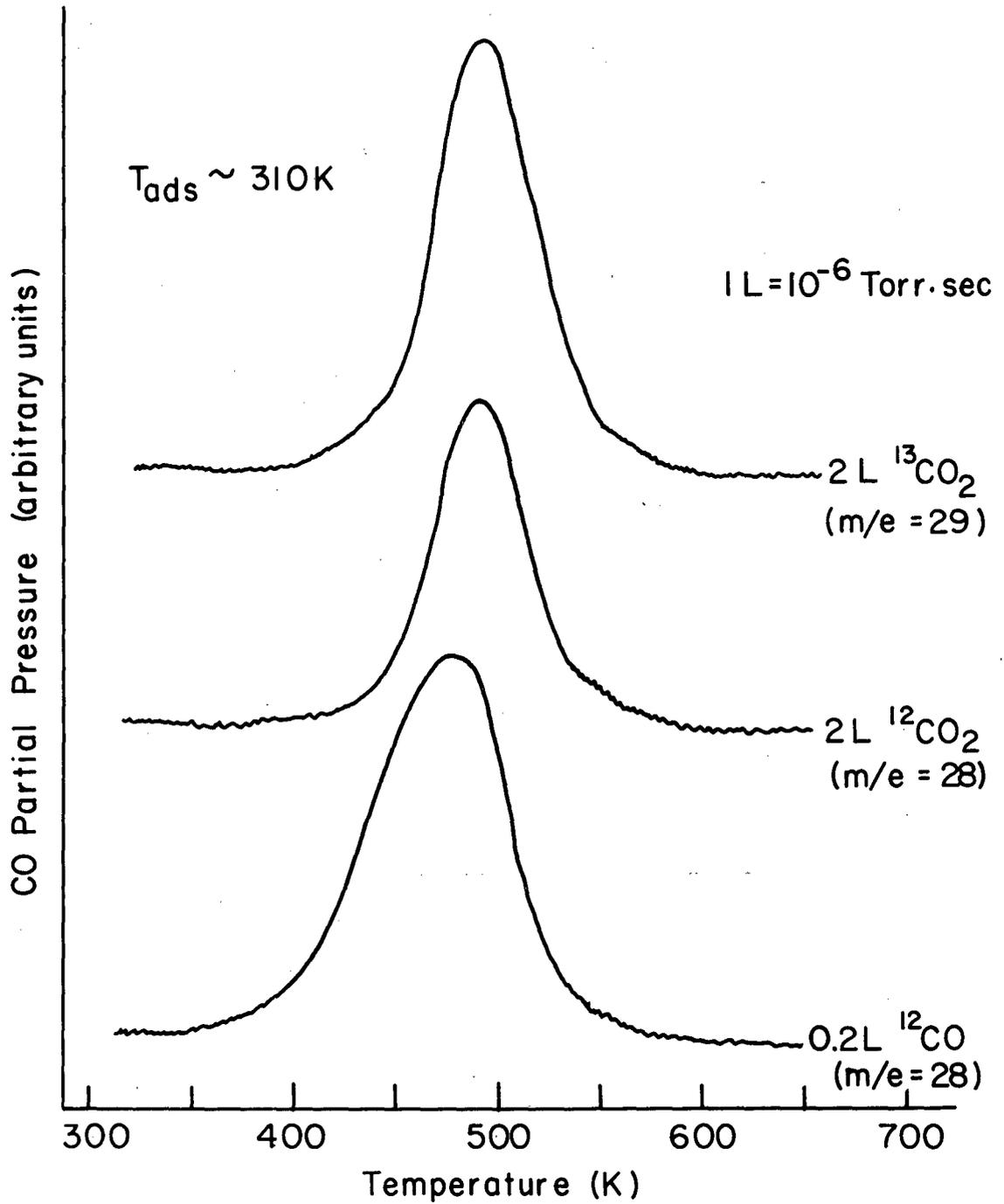
Rh (III) with ^{12}CO , $^{12}\text{CO}_2$ or $^{13}\text{CO}_2$
 $T \sim 300\text{ K}$



XBL 793-5974

Fig.1

^{12}CO , $^{12}\text{CO}_2$, $^{13}\text{CO}_2$ on Rh (III)



XBL793-5972

Fig.2

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