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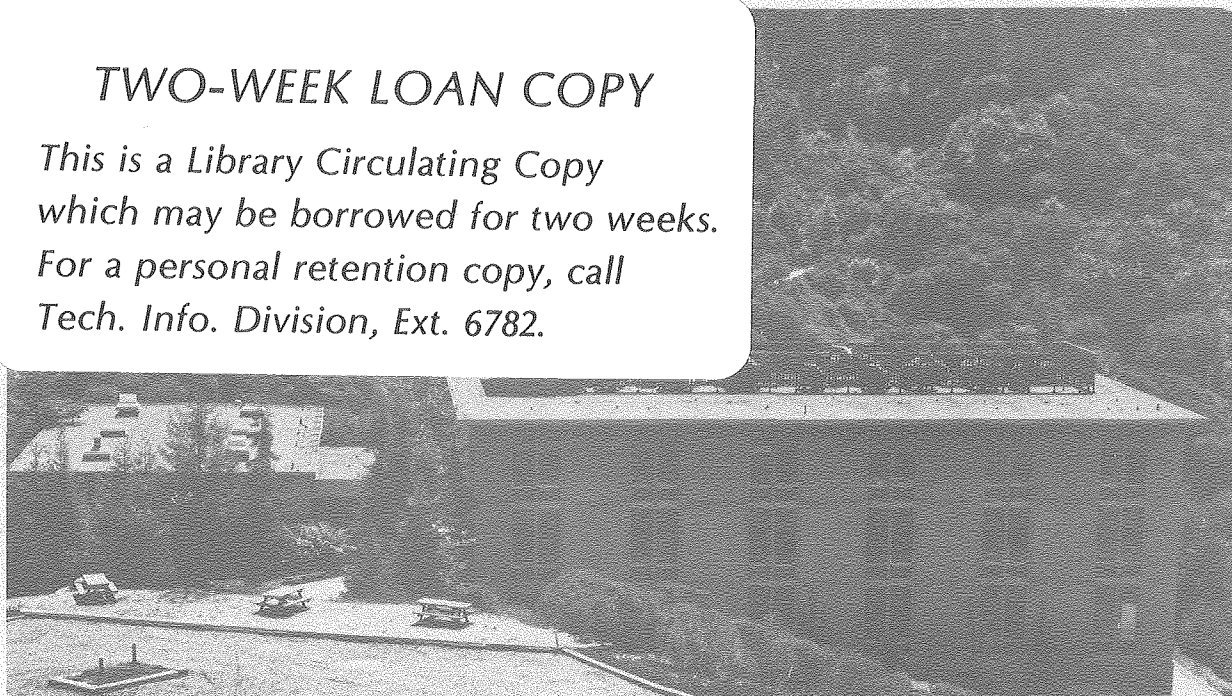
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EVIDENCE FOR AN OXYGEN INTERMEDIATE IN THE CATALYTIC
REDUCTION OF NO BY CO ON RHODIUM SURFACES

by

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Abstract

Evidence for an oxygen intermediate in the reaction of NO and CO to form N₂ and CO₂ over rhodium surfaces is presented. High resolution electron energy loss spectroscopy (ELS) measurements indicate that both NO and CO molecules associatively adsorb on the Rh(331) single crystal surface at 300 K. Chemisorbed NO readily dissociates on this surface upon heating to 450 K. At 700 K high resolution ELS and Auger electron spectroscopy (AES) both indicate that only oxygen is present on the catalyst surface. N₂ desorption below this temperature is easily detected by mass spectroscopy. The addition of CO to this surface oxygen at 700 K results in the formation of gaseous CO₂ and the removal of the surface oxygen species. Similar results were obtained when O₂ was substituted for NO as a control indicating that oxygen is indeed a surface intermediate under our experimental conditions. The reaction mechanism to reduce NO to N₂ by CO over rhodium surfaces may then be expressed as $2\text{NO}_{(g)} \longrightarrow \text{N}_{2(g)} + 2\text{O}_{(ads)}$ and $2\text{O}_{(ads)} + 2\text{CO} \longrightarrow 2\text{CO}_{2(g)}$.

Introduction

The desire for clean air has stimulated both legislation and research on the reduction of nitrogen oxides (NO_x) in fossil fuel combustion exhaust. Recent interest has focused on the catalytic reduction of NO to N_2 by carbon monoxide in automobile exhaust. A promising catalyst for this reaction is rhodium.^{1, 2} The mechanism of nitric oxide reduction over Rh has been illuminated in several recent publications. Campbell and White used thermal desorption mass spectrometry (TDS), surface titration and steady state reaction kinetics to study the chemisorption and reactivity of nitric oxide on a polycrystalline rhodium wire at temperatures between 330 and 950 K and at pressures below 2×10^{-8} torr.³ They concluded that the mechanism must involve NO dissociation and a subsequent reaction of CO with the atomic oxygen intermediates remaining on the surface. No direct evidence for this surface oxygen species was presented, however.

Unland,⁴ Arai and Tominaga⁵ and more recently Solymosi and Sárkány⁶ applied infrared (IR) spectroscopy to a study of NO and CO chemisorption on alumina supported rhodium particles. In addition to observing stretching vibrations for numerous molecular NO and CO species between 300 and 670 K and at pressures up to 150 torr, they found an absorption band which they associated with a surface isocyanate (NCO) complex. There now is evidence for a migration of this isocyanate species from the rhodium particles to the support.^{6, 7} Finally, Iizuka and Lunsford studied the reduction of nitric oxide by carbon monoxide to form N_2O and CO_2 over rhodium-Y zeolites.⁸ They proposed a $[\text{Rh}^{\text{I}}(\text{CO})_2\text{NO}]^+$ complex as a reaction intermediate based on infrared spectroscopic evidence. The spectral range of all of these studies did not extend to the region below 1000 cm^{-1} where vibrations from surface N and O atoms from dissociated nitric oxide would be expected. Thus these studies neither supported nor contradicted the previous evidence for the presence of a surface oxygen intermediate.

An adsorbed oxygen species from NO dissociation has been observed on the surface of other transition metals. Thomas and Weinberg reported such a species on the Ru(001) single crystal surface using high resolution electron energy loss spectroscopy (ELS).⁹ Zhdan et al. observed a similar species on the Ir(111) surface with X-ray and ultraviolet photoelectron spectroscopy.^{10, 11} These authors argue convincingly for a surface oxygen intermediate in the reduction of NO by CO over iridium catalysts.

In this paper we report on studies of the molecular chemisorption and subsequent dissociation of nitric oxide on a Rh(331) single crystal surface. Here we combine high resolution ELS and Auger electron spectroscopy(AES) to determine the structure and chemical composition of the adsorbed species with TDS and kinetic studies to monitor the reaction products after desorption into the gas phase. These new high resolution ELS and AES measurements on a single crystal rhodium surface complement the previous studies^{1-6, 8} to present a complete picture of a reaction mechanism involving a surface oxygen intermediate.

Experimental

Experiments were carried out in an ion pumped stainless steel ultrahigh vacuum chamber built in two levels. The upper portion contained the standard single crystal surface analysis equipment (four grid LEED/Auger optics, glancing incidence electron gun and quadrupole mass spectrometer). After dosing, the sample was lowered into the high resolution electron energy loss spectrometer by an extended travel precision manipulator. The spectrometer has been described in more detail elsewhere.¹² In the present series of experiments the angle of incidence was fixed at 65° to the surface normal and electrons were collected in the specular direction. The elastic scattering peak had a full width at half

maximum between 60 and 100 cm^{-1} and a maximum intensity of 1×10^5 counts per second.

The procedures for sample preparation, mounting and cleaning have been described previously.¹³ Briefly, the Rh(331) crystal, oriented to $\pm 1/2^\circ$, was cleaned by a combination of argon ion bombardment (1000-2000 eV.) followed by annealing in vacuum and O_2 (800-1000 K) to remove carbon, sulfur and boron.

NO , CO and O_2 adsorption were studied at pressures between 1×10^{-8} and 1×10^{-7} torr and at temperatures between 300 and 900 K. Neither gas exposures nor background pressures were corrected for ion gauge sensitivity.

TDS spectra were recorded at an initial heating rate of 40 K/sec. Kinetic studies were performed by predosing the Rh(331) surface with either O_2 or NO at 700 K and turning on the CO flow at $t = 0$. The CO_2 partial pressure ($m/e = 44$) was monitored with a mass spectrometer located approximately 15 cm. from the crystal.

Results and Discussion

A. The molecular chemisorption and subsequent dissociation of NO on rhodium

The lowest trace of fig. 1 shows the high resolution ELS spectrum from the adsorption of 1 L (1L = 1 Langmuir = 10^{-6} torr·sec. = 1.33×10^{-4} Pascal·sec.) of NO on the Rh(331) single crystal surface at 300 K. The strong band above 1700 cm^{-1} is typical of a N-O stretching vibration for molecularly adsorbed nitric oxide.¹⁴ The weak band at 403 cm^{-1} is characteristic of the metal-nitrogen stretch for an associatively adsorbed species.^{9, 15, 16} Both the relative intensities and the positions of the energy loss peaks were found to be essentially independent of gas exposure (from 0.1 to 10 L). As the rhodium substrate is heated to 450 K these bands disappear and a single peak near 520 cm^{-1} appears (middle trace).

The disappearance of the high frequency mode and the simultaneous appearance of the 520 cm^{-1} band clearly indicates the dissociation of nitric oxide. Furthermore, at least one of the dissociation products must remain on the surface. The upper trace in fig. 1 shows the vibrational spectrum from the adsorption of 1L of O_2 on the Rh(331) surface at room temperature. A single band at 520 cm^{-1} due to dissociatively chemisorbed oxygen is visible. This suggests that the 520 cm^{-1} band produced from NO dissociation is due to surface oxygen. The absence of a second peak is not necessarily evidence for nitrogen desorption since it is thought that the M-N stretch from dissociated NO should be weak.⁹ This peak could be hidden beneath the relatively intense rhodium-oxygen stretch. The absence of surface nitrogen, however, can be confirmed by thermal desorption mass spectrometry and Auger electron spectroscopy.

Fig. 2 displays TDS spectra for N_2 and O_2 desorption from the Rh(331) single crystal after exposing the surface to 1L of NO. Note that if NO is adsorbed at room temperature the nitrogen desorbs as N_2 ($m/e = 28$) below 500 K while the oxygen desorbs as O_2 ($m/e = 32$) only at much higher temperatures. Furthermore, fig. 2a shows that O_2 desorption is similar whether the rhodium surface is exposed to gaseous nitric oxide or to oxygen. The NO ($m/e = 30$) TDS spectrum showed only one peak near 460 K. Similar thermal desorption results have been obtained previously both by Campbell and White on polycrystalline rhodium wire³ and by Castner and Somorjai on stepped rhodium single crystal surfaces¹³ during NO chemisorption studies. Finally note that if NO is adsorbed on the rhodium surface at 700 K (a typical reaction temperature for an automobile catalytic converter) and the crystal cooled to 300 K; subsequent flashing yields negligible nitrogen desorption from the surface (fig. 2b). This is consistent with the relatively low temperature found for N_2 desorption from adsorbed NO.

The absence of surface nitrogen is also confirmed by Auger electron spectroscopy.

copy (see fig. 3). The chemisorption of 1L of NO on the Rh(331) single crystal surface at 300 K (lower trace) results in both nitrogen and oxygen present on the surface. This is consistent with the molecular chemisorption of nitric oxide indicated by the vibrational spectra in fig. 1. Chemisorption of 1L of NO at 700 K results in only oxygen present on the surface (upper trace). Both the TDS and AES results lead us to conclude that the peak at 520 cm^{-1} in the middle trace of fig. 1 is due solely to adsorbed oxygen.

Thus at a typical operating temperature for a catalytic converter (700 K), the adsorption of NO results in the liberation of N_2 gas and in the formation of a stable surface oxygen species. Vibrational spectra recorded after flashing the crystal to successively higher temperatures indicate that the metal-oxygen stretch is visible until above 850 K.

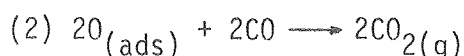
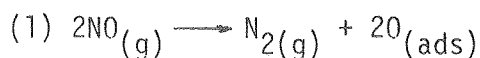
B. The reaction of CO with dissociated NO

Carbon monoxide readily reacts with the oxygen remaining on the surface after NO dissociation. Fig. 4 shows what happens to the Rh-O stretching vibration as CO is added to either dissociatively chemisorbed O_2 (a) or NO (b) at 700 K. Note that in both cases the intensity of the 520 cm^{-1} loss is measurably decreased by a 1L CO exposure and has disappeared into the noise by a 5L CO exposure. Surface oxygen produced during O_2 chemisorption is more easily removed than surface oxygen formed as a result of the dissociation of NO. This is a reproducible effect that will be discussed in more detail below.

We carried out a kinetic study to determine which gases are produced when CO reacts with surface oxygen. In fig. 5 the rhodium substrate was first heated to 700 K and then dosed with either 1 L of O_2 (lower trace) or NO (upper trace) to produce a surface oxygen species. The reaction products were monitored with a mass spectrometer as 4×10^{-8} torr of CO was admitted to the vacuum chamber at $t = 0$. As one might expect, carbon dioxide ($m/e = 44$) was the primary product.

CO₂ was produced until the CO exposure was of order 5 L (2 min. at 4 x 10⁻⁸ torr). This observation correlates with the high resolution electron energy loss results of fig. 4 which showed that the surface oxygen disappeared by a 5 L CO exposure. The dashed lines in fig. 5 represent the background reactivity of both the rhodium single crystal surface and the mass spectrometer filaments without predosing the sample with either O₂ or NO.

From the above we conclude that the reaction of NO and CO to form N₂ and CO₂ proceeds by the following two consecutive steps:



There is evidence that CO reacts with adsorbed oxygen directly from the gas phase (an Eley-Rideal mechanism) as well as after being adsorbed on the surface (a Langmuir-Hinshelwood mechanism). Campbell and White studied the reaction between adsorbed oxygen and carbon monoxide over polycrystalline rhodium wires.¹⁷ They concluded that the formation of carbon dioxide proceeded by both Langmuir-Hinshelwood and Eley-Rideal kinetics, depending on substrate temperature and gas pressure. They also found both mechanisms to be operative in their recent investigation of the catalytic reduction of NO by CO over polycrystalline rhodium wires.³

An interesting feature of the data is that surface oxygen from NO desorbs at a slightly higher temperature (fig. 2; refs. 3 and 13) and reacts somewhat less readily with CO (figs. 4 and 5) than the surface oxygen from dissociated O₂. Though we do not understand this effect, it is consistent with recent kinetic studies on supported rhodium catalysts under simulated reaction conditions. Specifically, the rate of conversion of NO to N₂ and CO₂ by the reaction with CO is less than the rate of conversion of O₂ to CO₂ by CO under identical experimental conditions.¹ In contrast, on iridium, the rate of reaction of NO with CO is higher than that of O₂.¹ Further research into the mechanism of this reaction selectivity might be

both scientifically interesting and technologically important.

Summary

The following evidence for a surface oxygen intermediate in the reaction $2\text{NO}_{(g)} + 2\text{CO}_{(g)} \longrightarrow \text{N}_{2(g)} + \text{CO}_{2(g)}$ was presented:

- a) NO dissociates on the Rh(331) single crystal surface below 450 K, well below typical catalytic converter reaction temperatures of 600-800 K (fig. 1).
- b) The nitrogen from dissociated NO desorbs as N_2 below 500 K (fig. 2).
- c) The oxygen from dissociated NO is stable on the surface at typical reaction temperatures in vacuum (figs. 2, 3 and 4).
- d) The oxygen from dissociated NO is readily removed by CO under our experimental conditions (fig. 4).
- e) The reaction of CO with the surface oxygen produces gaseous CO_2 (fig. 5).

The reaction mechanism may now be expressed as $2\text{NO}_{(g)} \longrightarrow \text{N}_{2(g)} + 2\text{O}_{(ads)}$ and $2\text{O}_{(ads)} + 2\text{CO} \longrightarrow 2\text{CO}_{2(g)}$. Key to this mechanism is the identification of the 520 cm^{-1} peak as surface oxygen in the high resolution electron energy loss spectrum resulting from the dissociation of adsorbed NO (fig. 1). This identification is supported by:

- a) The presence of a similar 520 cm^{-1} peak from the adsorption of O_2 (fig. 1);
- b) Thermal desorption traces indicating that nitrogen from dissociated NO desorbs at a temperature below temperatures at which this peak is stable (fig. 2);
- c) AES results showing only oxygen and the clean rhodium surface features when the 520 cm^{-1} peak is present (fig. 3) and
- d) Kinetic studies indicating that the 520 cm^{-1} peak from dissociated NO was removed with similar (but not identical) kinetics to that from adsorbed O_2 (figs. 4 and 5).

Although there can be little doubt that this reaction mechanism operates in high vacuum, it is not clear that it is the predominant mechanism on rhodium catalysts under automobile exhaust operating conditions. However, recent studies on Pt/SiO₂ catalysts under high pressure reducing conditions found kinetics and product selectivities in good agreement with a mechanism based upon the dissociation of NO as the rate limiting step.⁷

Acknowledgements

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14. Vibrational spectra of associatively adsorbed NO have been recorded on the Pt(111),¹⁵ Ru(001)⁹ and Rh(111)¹⁶ single crystal surfaces.
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Figure Captions

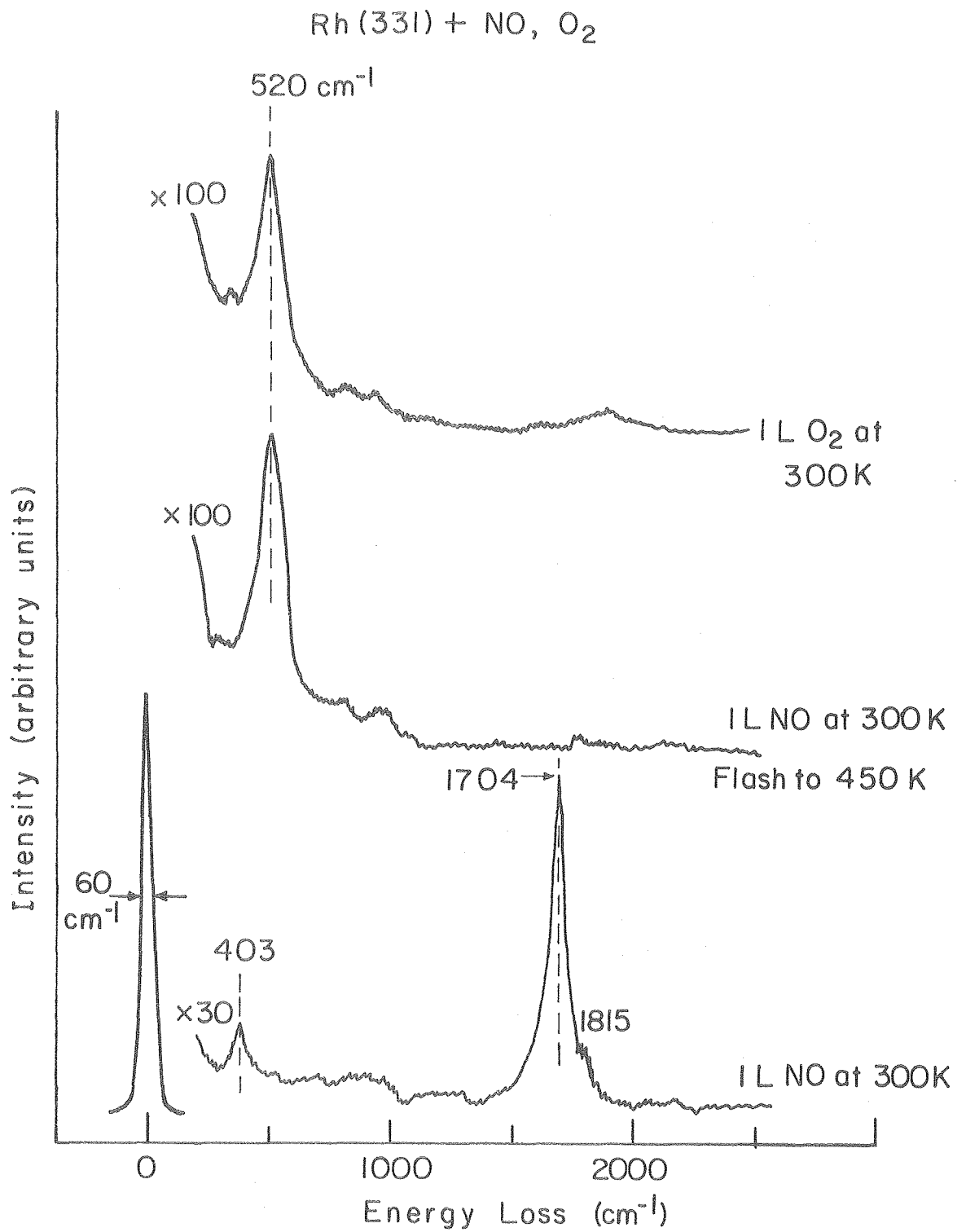
1a) Nitric oxide molecularly adsorbs on the Rh(331) single crystal surface at 300 K as shown by the presence of N-O stretching vibrations ($1704, 1815 \text{ cm}^{-1}$) in the bottom high resolution ELS spectrum. This species dissociates by 450 K as indicated by the absence of the N-O stretching vibrations in the middle spectrum. The 520 cm^{-1} peak in this spectrum is similar to that obtained from the adsorption of O_2 gas at 300 K (top spectrum).

2a) O_2 desorption ($m/e = 32$) from the adsorption of 1 L of either O_2 (lower trace) or NO (upper trace) on the Rh(331) single crystal surface at 300 K. (b) N_2 desorption ($m/e = 28$) from the adsorption of 1 L of NO at either 300 K (lower trace) or 700 K (upper trace). The small peak at 325 K is presumably due to nitrogen desorption from the crystal support rods.

3. The Auger spectrum of NO chemisorbed on the initially clean Rh(331) single crystal surface shows both nitrogen and oxygen peaks when adsorbed at 300 K, but only oxygen transitions when adsorbed at 700 K. The fine structure between the primary peaks is irreproducible and presumably due to noise.

4. The 520 cm^{-1} peak in the high resolution ELS spectra of either O_2 (a) or NO (b) adsorbed on the Rh(331) single crystal surface at 700 K decreases rapidly upon exposure to gas phase carbon monoxide.

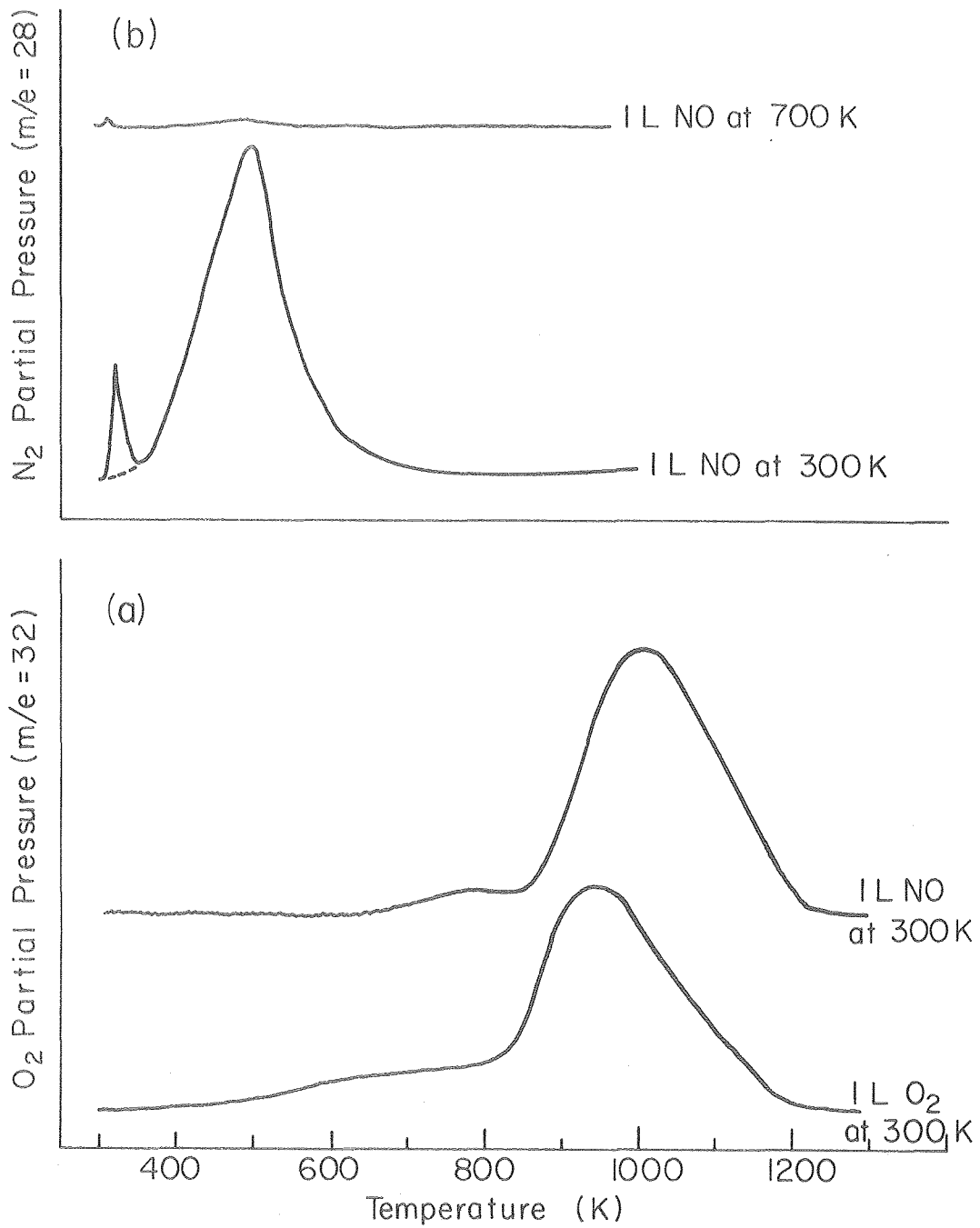
5. Gaseous CO_2 production on the Rh(331) surface at 700 K after predosing the crystal with 1 L of either O_2 (lower trace) or NO (upper trace). 4×10^{-8} torr of CO is admitted to the vacuum chamber at $t = 0$ and CO_2 production is monitored by mass spectroscopy ($m/e = 44$). The dotted curves show the background CO_2 liberation if the surface was not pre-exposed to either NO or O_2 before CO admission.



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Fig. 1

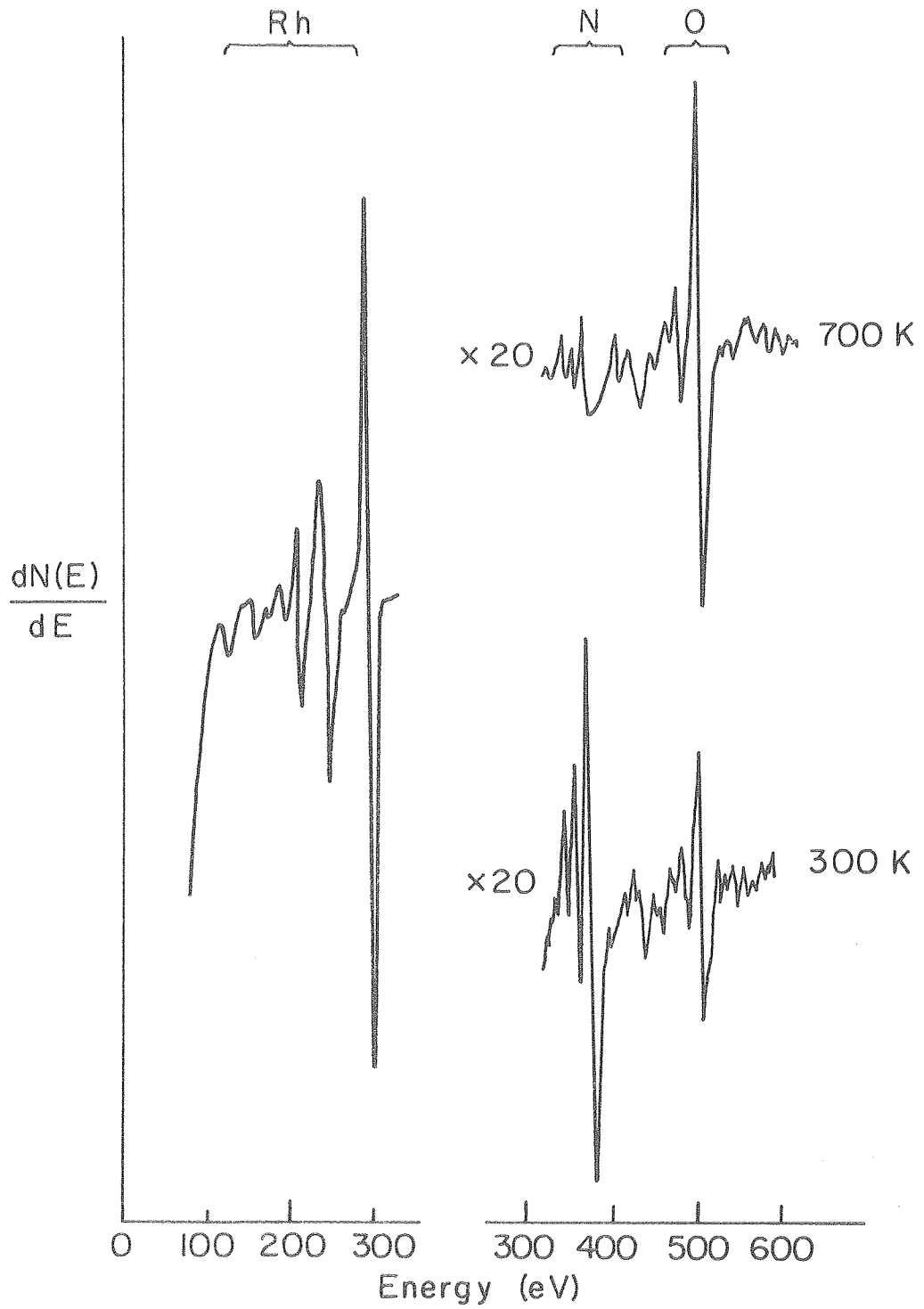
Rh (33I) + NO, O₂



XBL 7910-7252

Fig. 2

Rh (331) + 1 L NO



XBL 7910-7253

Fig. 3

Rh(331) + O_{ads} + CO at 700K

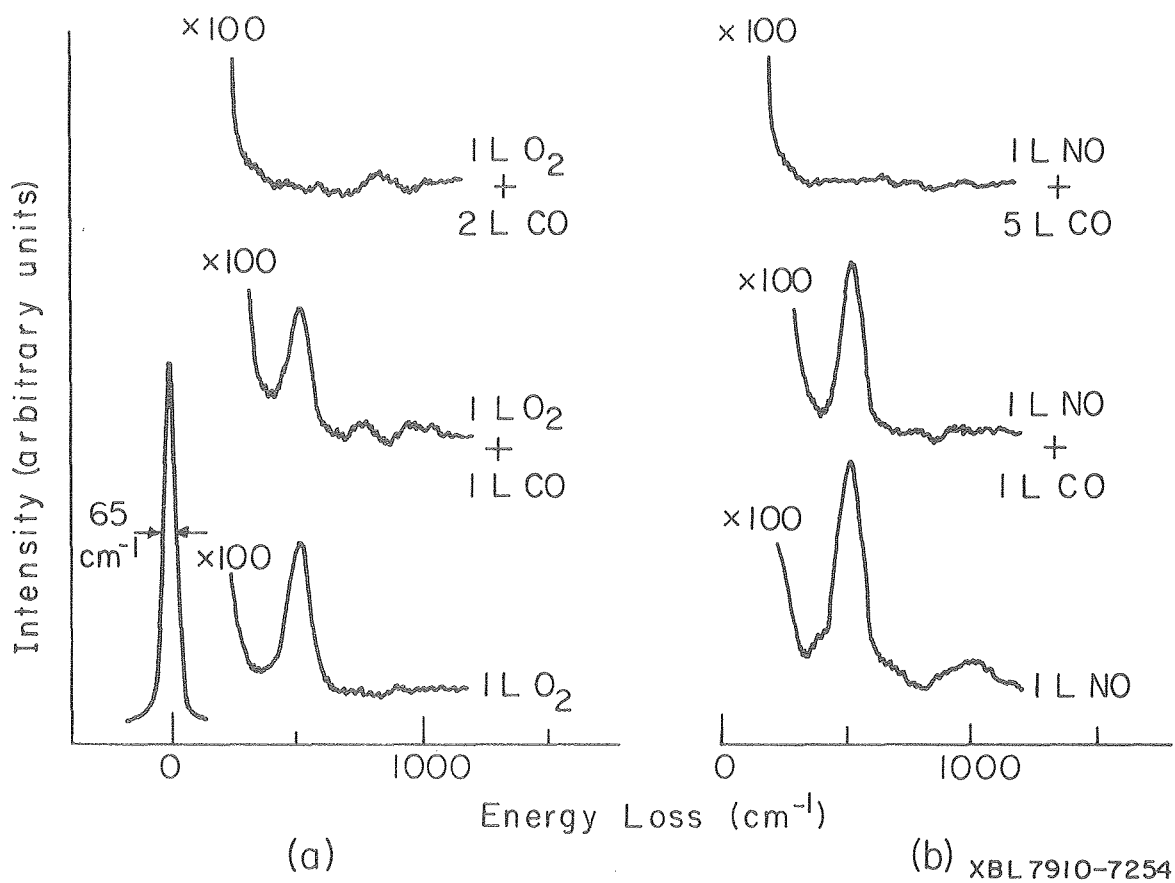
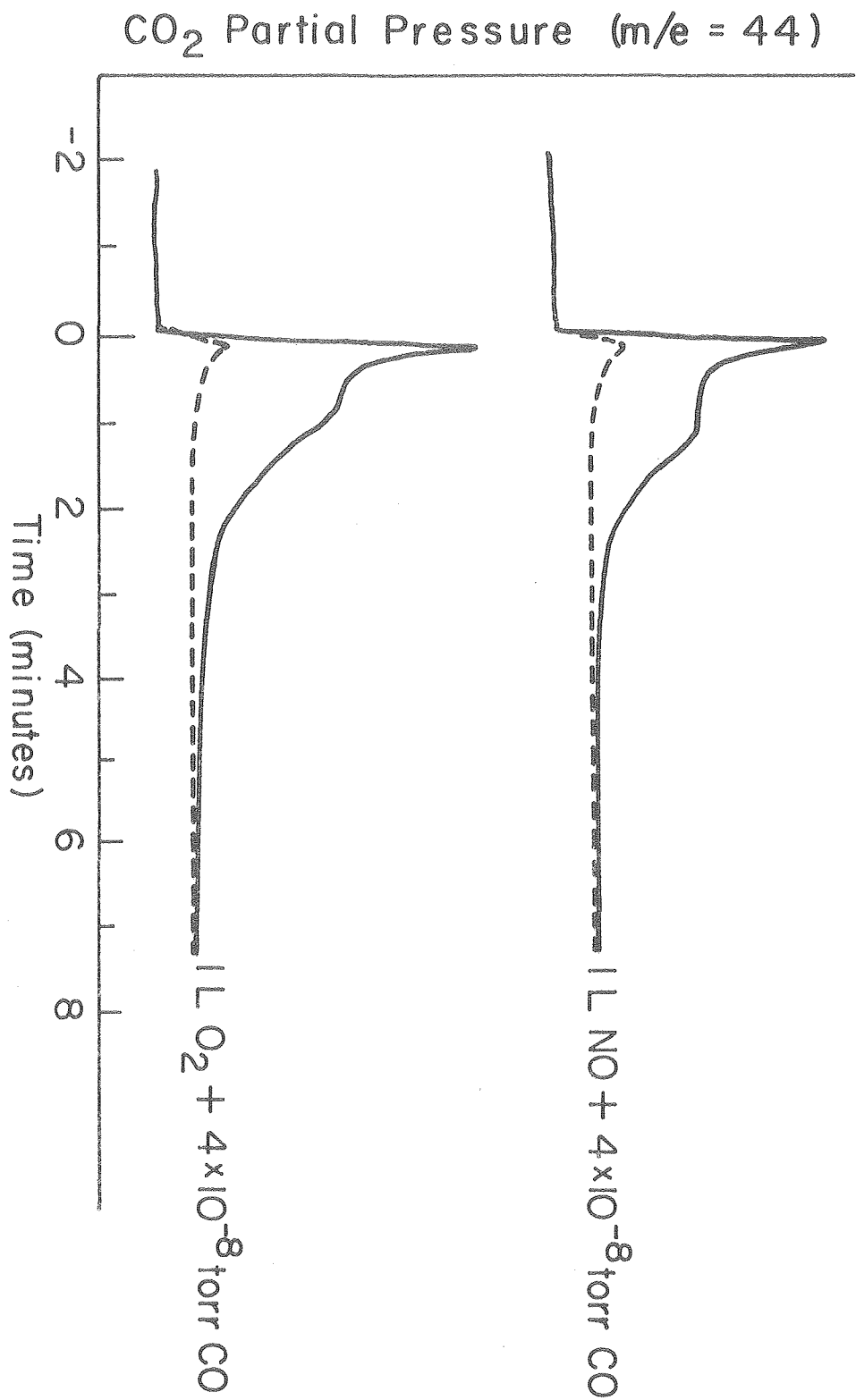


Fig. 4

CO₂ Production on Rh (331) at 700 K



XBL 7910-7255

Fig. 5

