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NATIONAL BUREAU OF STANDARDS WASHINGTON DC SURFACE S--ETC F/6 7/4
INFRARED SPECTROSCOPIC STUDY OF ACTIVATED SURFACE PROCESSES: CO--ETC(U)
APR 79 J T YATES, T M DUNCAN, R W VAUGHAN N00014-79-F-0014

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Technical Report #12

Infrared Spectroscopic Study of Activated Surface Processes:
CO Chemisorption on Supported Rh

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April 1979

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To be published in the Journal of Chemical Physics

AD A 069734

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
Technical Report No. 12		(14) TR-12
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED
Infrared Spectroscopic Study of Activated Surface Processes: CO Chemisorption on Supported Rh		
7. AUTHOR(s)	6. PERFORMING ORG. REPORT NUMBER	8. CONTRACT OR GRANT NUMBER(s)
10 John T. Yates, Jr., T. Michael Duncan, and R. W. Vaughan		N00014-79-E-0014 N00014-75-C-0960 CIT
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Surface Science Division National Bureau of Standards Washington, DC 20234		
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
Office of Naval Research Physical Program Office Arlington, VA 22217		Apr 1979
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES
		(12) 27 p.
		15. SECURITY CLASS. (of this report)
		Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
Approved for Public Release; Distribution Unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
Preprint; to be published in the Journal of Chemical Physics.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Carbon monoxide; chemisorption; infrared spectroscopy; isotopic exchange; rhodium.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
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Submitted to: Journal of Chemical Physics
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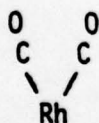
Abstract

The infrared spectrum of CO chemisorbed on alumina-supported Rh surfaces has been studied following chemisorption at cryogenic temperatures. Major differences are observed in the distribution and spectroscopic character of chemisorbed CO species produced at low temperatures (110-170K) compared to chemisorbed CO species produced on Rh at 295 K. It has been found that the species $\text{Rh}(\text{CO})_2$, formed on isolated Rh sites, is produced rapidly via an activated chemisorption process above ~ 200 K. On more "crystalline" Rh_x sites, containing chemisorbed CO, an activated CO adsorbate-conversion process has been detected in which $\tilde{\nu}_{\text{CO}}$ decreases by $\sim 50 \text{ cm}^{-1}$ on warming the adsorbed layer above ~ 265 K. Isotopic exchange between $^{13}\text{CO}(\text{g})$ and $^{12}\text{CO}(\text{ads})$ has been shown to occur rapidly at low temperature ($\sim 200\text{K}$) for $\text{Rh}(\text{CO})_2$ species, whereas $\text{Rh}_x(\text{CO})$ species exchange rapidly only at higher temperatures ($\gtrsim 250$ K). These results, taken together, serve to confirm a model in which isolated Rh sites coexist on the alumina support with crystalline Rh_x sites; the two kinds of sites are separable on the basis of the spectroscopic character of the chemisorbed CO species they adsorb as well as by means of their chemical properties.

I. Introduction

The method of transmission infrared spectroscopy for the study of adsorbed molecules on high-area surfaces has been shown to be useful in a wide variety of studies related to adsorption and heterogeneous catalysis (1,2). Through the observation of characteristic stretching frequencies, it is often possible to assign the structure of chemisorbed species. This is usually done by employing analogies between the observed vibrational frequencies and the frequencies observed in molecules of known structure. At the present time, optical spectroscopy techniques offer the highest resolution of any of the vibrational spectroscopy methods employed for surface studies. Infrared spectroscopy is therefore most suitable for the study of isotopic effects and other effects where small vibrational spectral shifts may be involved.

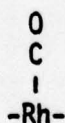
The chemisorption of CO by supported Rh has been extensively studied in the past by a number of workers, and infrared results for this system are briefly reviewed in a previous paper (3). It is believed that three generalized types of chemisorbed CO are produced on dispersed Rh surfaces at ~300 K. They are:



I

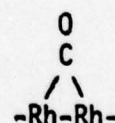
$$\tilde{\nu}_{\text{CO}} = 2104 \text{ cm}^{-1}(\text{sym})$$

$$\tilde{\nu}_{\text{CO}} = 2034 \text{ cm}^{-1}(\text{asym})$$



II

$$\tilde{\nu}_{\text{CO}} = 2070 \text{ cm}^{-1}$$



III

$$\tilde{\nu}_{\text{CO}} = 1870 \text{ cm}^{-1}$$

There is some controversy (3) regarding the degree of Rh dispersion required to allow the formation of species I. The question of the oxidation

state of the Rh in species I has also been raised (4). D. J. C. Yates (5) suggests that species I may form on the edge atoms of supported Rh "rafts" containing ~7 Rh atoms as seen in electron microscope photographs. The observed invariance of the wavenumber of the symmetric and antisymmetric stretching motion as CO coverage increases (3,6,7,8) indicates, however, that appreciable intermolecular interactions through space and through the metal do not occur for species I. This suggests that species I is formed at isolated sites (3,6,8). CO-CO interactions on bulk metal surfaces are known to produce increases of as much as 100 cm^{-1} in $\tilde{\nu}_{\text{CO}}$ as coverage increases (9). With regard to the question of the oxidation state of Rh, Primet (4) has recently suggested that CO dissociation at 200 K on Rh, producing chemisorbed oxygen, leads to the formation of Rh^+ which then adsorbs 2 CO molecules, giving the infrared doublet. The basis for this suggestion is founded on the observation of a slight intensification of the doublet when the Rh surface is treated prior to CO chemisorption with oxygen (4), as well as the need for thermal activation to produce the doublet feature during pure CO adsorption.

In contrast to species I, species II and III are thought to be associated with CO adsorption on more "crystalline" Rh sites. The observed shift of the CO stretching vibrational frequency to higher wavenumber as CO coverage is increased as interactions between neighboring CO species occur is consistent with this assignment. The chemical reactivity of sites responsible for species II and III has been shown to differ from the behavior of sites responsible for species I (3,4,7).

In this paper we employ an infrared cell which can be operated at cryogenic temperatures. It has been possible to observe new adsorption states of CO on Rh at low temperatures and to investigate activated adsorption and activated

isotopic exchange processes for CO in the various states described above. In addition, small reversible thermal effects on infrared lineshapes have been detected.

II. Experimental

The low temperature infrared cell used in this work is shown in Figure 1. It contains a recessed Cu ring in which a 2.5 cm diameter CaF_2 single crystal disk holding the Al_2O_3 -supported Rh adsorbent is snugly mounted. The Cu ring may be cooled in vacuo to ~ 100 K by conduction to a $\ell\text{-N}_2$ reservoir which is attached to the ring in the center of the cell. The infrared transmitting windows are 3.3 cm-diameter CaF_2 single crystals mounted in stainless steel "conflat" flanges (3), and sealed to the body of the cell (a double-sided stainless steel flange) using Cu gaskets. The temperature of the Cu sample holder ring may be monitored by means of a 0.025 cm diameter Fe-constantan thermocouple. It is likely that the temperature of the Rh surface may be slightly higher than the indicated thermocouple temperature during spectral measurements due to heating of the sample by the infrared beam, as discussed by Little (1). In addition, when the cell is filled above a few microns pressure with CO(g) , thermal conduction to the cooled sample causes some increase in measured temperature.

The vacuum system used in this work is a small, bakeable, all-metal, grease-free system described previously (3) capable of being pumped below 10^{-8} torr with a 20 l sec^{-1} ion pump. Provisions within the vacuum system are available for accurate volumetric measurement of the adsorption of CO by the sample.

The supported Rh samples (2.2% Rh by weight) are prepared by RhCl_3 dispersion on Alon-C alumina (3). Reduction to Rh^0 is achieved in high-purity hydrogen gas at 150°C , followed by outgassing at 175°C . The Perkin-Elmer

Model 180 infrared spectrometer was used in the double beam mode at 2.6 cm^{-1} resolution (at 2000 cm^{-1}). The absorbance scale was calibrated using standard density grids. The wavenumber scale was calibrated using the P and R branches for CO(g) when present above the sample in the IR cell. In certain cases, subtraction of related infrared spectra has been carried out, yielding difference spectra which illustrate various effects. Other experimental details are described elsewhere (3).

III. Results

A. Temperature Effects in CO Adsorption

Figure 2 shows a comparison of the spectral development for CO adsorption at low temperatures ($T \leq 173\text{ K}$) and at room temperature ($T = 295\text{ K}$). It can be seen in the carbonyl stretching region that the infrared spectra differ significantly at these two adsorption temperatures for similar exposures to CO. Three differences are noted:

- (a) The doublet at 2104 cm^{-1} and 2034 cm^{-1} is less developed at the low adsorption temperature.
- (b) The spectral feature observed between the components of the doublet is seen to shift upward in a higher wavenumber range (2065 cm^{-1} - 2082 cm^{-1}) as CO coverage increases at 173 K compared to the spectral range observed for this feature for CO adsorption at 295 K (2056 cm^{-1} - 2066 cm^{-1}) (3).
- (c) For low temperature CO adsorption the broad "bridging-CO" band occurs at slightly higher wavenumber ($\sim 1900\text{ cm}^{-1}$) than the comparable band produced at 295 K ($\sim 1870\text{ cm}^{-1}$).

Similar spectral differences are present in the spectra reported at 103 K by Primet (4) compared to his spectra obtained at 300 K for CO/Rh/ Al_2O_3 .

In order to investigate the possibility that the chemisorption of CO on Rh is an activated process, the following experiment was performed, the results

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of which are shown in Figure 3. A clean Rh surface was exposed to CO (7.1 torr) at temperatures below 178 K. The spectrum shown in Figure 3A (a;b) was obtained, and the adsorbed species were shown to be stable by repeating the spectral scan at this temperature. The spectrum 3A (a;b) agrees well with spectrum 2A (d) and demonstrates again that the carbonyl-doublet is retarded in its development during CO chemisorption at low temperature.

The Rh surface was then slowly warmed in the presence of CO(g) and the infrared spectrum was continuously rescanned as shown for spectra 3A (c,d, and e). Three effects are prominent:

- (a) The doublet at 2104 cm^{-1} and 2034 cm^{-1} develops extensively above 178 K.
- (b) The single band at 2082 cm^{-1} shifts to lower wavenumber as temperature and coverage increase. This wavenumber shift is opposite to the behavior seen for increasing coverage at $T \leq 173\text{ K}$ (Figure 2A) or at $T = 295\text{ K}$ (3).
- (c) Enhanced infrared absorption below 2000 cm^{-1} is observed.

All of these features are best visualized in the difference spectrum in Figure 3B. The slight negative feature near 2022 cm^{-1} is due to a small reversible temperature-dependent lineshape effect to be discussed later.

B. Temperature Effects Causing CO Adsorbate State Conversion at Constant Coverage

In order to investigate the possibility that activated processes may occur at constant coverage in the chemisorbed CO layer upon heating, the following experiment, yielding the infrared spectra shown in Figure 4, was carried out. A partial coverage of CO was produced by means of exposure of CO to a Rh surface at 200 K. The cell was evacuated to prevent further CO adsorption, and the surface cooled to 110 K where spectrum 4A (a) was recorded. The Rh surface

was then allowed to warm in vacuo and spectral changes were observed as shown in spectra 4A (b,c, and d). The processes which occur upon the warming of a CO layer in the absence of further CO adsorption are well illustrated in the difference spectrum, Figure 4B. Here it can be seen that an activated state conversion process takes place in which the 2082 cm^{-1} infrared feature converts into an asymmetric feature with peak maximum near 2030 cm^{-1} . In addition, some evidence for the production of a broad "bridged-CO" feature centered near 1828 cm^{-1} is seen. Little or no change occurs in the intensity of the high wavenumber component of the doublet at 2104 cm^{-1} , suggesting that the $\text{Rh}(\text{CO})_2$ species is stable in vacuum on warming from 100-314 K. Finally, a reversible temperature effect is seen for the 2104 cm^{-1} component of the doublet and possibly also for the 2034 cm^{-1} component of the doublet. This reversible phenomenon will be discussed later.

C. Kinetic Studies of Isotopic CO Exchange between Adsorbate States and the Gas Phase

We have carried out systematic spectroscopic studies of the exchange between adsorbed $^{12}\text{C}^{16}\text{O}$ species and $^{13}\text{C}^{16}\text{O}(\text{g})$ as a function of sample temperature to determine whether differences exist in the degree of lability for the different adsorbate states detected by infrared spectroscopy.

The infrared spectrum (a) shown in Figure 5A is the result of $^{12}\text{C}^{16}\text{O}$ saturation of the Rh surface at 295 K. Following spectrum 5A(a), the surface was cooled to ~200 K and $^{13}\text{C}^{16}\text{O}(\text{g})$ was admitted at ~50 torr pressure. From earlier experiments (3) at 295 K, this procedure was shown to result in extensive isotopic exchange within minutes (3). However, as seen from spectrum 5A(b), and as more clearly demonstrated from the difference spectrum 5B, only two CO species, I and III, appear to exchange readily below ~220 K. We see

that above $\sim 1960\text{ cm}^{-1}$ loss of the $\text{Rh}(^{12}\text{CO})_2$ doublet feature occurs with the production of doublet intensity for $\text{Rh}(^{13}\text{CO})_2$. The wavenumber of the two interconverting doublets agrees well with that measured for pure isotopic CO species (3). There is also a fairly featureless loss of intensity below $\sim 1960\text{ cm}^{-1}$ (species III). We cannot determine whether this is due to a shift in background intensity or whether the effect is partially real. As the Rh surface is warmed above $\sim 220\text{ K}$, further isotopic exchange occurs as shown in Figure 6. Here from the difference spectrum 6B, it can be seen that a small amount of exchange in the doublet region (species I) continues, but the dominant process is exchange of CO species II in the 2070 cm^{-1} region, with production of an exchanged broad asymmetric feature maximized near 2008 cm^{-1} . Thus, as shown by comparison of Figure 5B and 6B, this method has discriminated between the various types of chemisorbed CO species on the basis of the temperature required for rapid isotopic exchange between the gas phase and the adsorbate species.

D. Reversible Temperature Effects on Infrared Frequencies

A Rh surface fully covered with $^{12}\text{C}^{16}\text{O}$ at 295 K was cooled slowly to various temperatures, and the infrared spectrum was carefully measured as shown in Figure 7. The peak maxima for the two sharp components of the doublet (originating from species I) are both seen to shift slightly to higher wavenumber in a monotonic fashion as the surface cools. The shift is $\sim 3\text{ cm}^{-1}/200\text{ K}$. The reversible temperature effect clearly seen in Figure 4B is therefore a consequence of temperature-dependent frequency changes.

At the present time we believe that reversible temperature-dependent frequency changes observed in Figure 7 (and Figure 4) are related to coupling of the C-O oscillators in $\text{Rh}(\text{CO})_2$ to phonon modes in the Al_2O_3 support. Our data

at present do not permit a quantitative analysis of this effect.

IV. Discussion

A. Activated Adsorption of CO by Rh

Let us consider for simplicity that two general kinds of adsorption sites exist for CO chemisorption on Al_2O_3 -supported Rh. These are isolated Rh sites, designated Rh, and more compact arrangements of Rh atoms designated Rh_x (3). The Rh sites form $\text{Rh}(\text{CO})_2$ (species I) upon chemisorption while the Rh_x sites yield linear and bridge-bonded CO (species II and III).

The retardation of filling of the Rh sites to yield $\text{Rh}(\text{CO})_2$ at low temperatures ($T \leq 173$ K), as shown in Figures 2 and 3, strongly suggests that an activated process is involved for chemisorption on these sites. This activation energy could be related to the need for rehybridization of the supported Rh atoms to accommodate two CO ligands. The activated process leading to $\text{Rh}(\text{CO})_2$ was previously attributed by Primet (4) to CO decomposition, leading to the production of Rh^+ sites which were postulated to then adsorb two CO molecules. The low temperature associated with this activated process seems to argue against a model involving CO dissociation on Rh sites. In addition, Ozin, et al. (13) has reported at 15 K that $\text{Rh} + \text{CO}$ produces $\text{Rh}(\text{CO})_4$ species in CO matrices; this observation strongly suggests that activated CO dissociation is not the cause of multiple CO bonding to Rh. Furthermore, recent studies of CO interaction with Rh(111) crystals have shown that isotopic mixing does not occur between $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ in the temperature range 300 K to 800 K (14). This observation further excludes CO dissociation on Rh as being operative for the

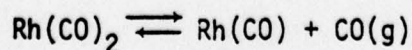
production of an adsorption site yielding $\text{Rh}(\text{CO})_2$.

The thermal ($T \geq 265$ K) conversion of the 2082 cm^{-1} - CO state to a state exhibiting $\tilde{\nu}_{\text{CO}} \approx 2030 \text{ cm}^{-1}$, (Figure 4), suggests that an activated CO state-conversion process is involved on the Rh_x sites, and that the 2082 cm^{-1} CO species produced at low temperature is metastable with respect to the final CO bonding state. The downward shift of $\sim 50 \text{ cm}^{-1}$ in $\tilde{\nu}_{\text{CO}}$ during this conversion is consistent with stronger Rh_x -CO bonding for the lower wavenumber CO state(s) produced above ~ 265 K. Similar state conversion processes, induced by heating, have been observed for CO chemisorbed on tungsten. Here the "virgin-CO" state, stable at low temperatures, converts into α -CO and β -CO upon heating (10,11). β -CO is thought to be dissociated on tungsten.

The presence of independent activated processes involving $\text{Rh}(\text{CO})_2$ formation and $\text{Rh}_x(\text{CO})$ conversion processes is consistent with the contention that Rh sites are isolated from Rh_x sites. This view was previously suggested (3) on the basis of the invariance of $\tilde{\nu}_{\text{CO}}$ (sym) and $\tilde{\nu}_{\text{CO}}$ (asym) for species I as CO coverage is increased. In addition, specific effects for H_2CO decomposition on Rh sites support this conclusion (3).

B. Activated Exchange Processes between CO(ads) and CO(g)

We have previously demonstrated that exchange between CO(g) and CO(ads) is very rapid at 295 K compared to desorption at this temperature (3). It was proposed that the rapid exchange occurred via the formation of transient adsorbed species containing extra CO moieties. Thus, a process such as $\text{Rh}(\text{CO})_2 + {}^{13}\text{CO}(\text{g}) \rightleftharpoons \text{Rh}(\text{CO})_3^* \rightleftharpoons \text{Rh}({}^{13}\text{CO})({}^{12}\text{CO}) + {}^{12}\text{CO}(\text{g})$ appears to be occurring at a rapid rate compared to isotopic exchange at a rate controlled by the desorption-limited process:



If this general mechanism, involving transient species such as $\text{Rh}(\text{CO})_3^*$ is operative, one might expect to be able to selectively exchange species I, II, and III by operation at different temperatures assuming the processes for the different species and adsorption sites are associated with different activation energies. As seen by comparison of Figure 5 and Figure 6, it has in fact been found that $\text{CO}(\text{g})$ exchanges with $\text{Rh}(\text{CO})_2$ at a lower temperature than with $\text{Rh}_x(\text{CO})$. Slow warming of the surface in $\text{CO}(\text{g})$ results in sequential isotopic exchange of species I and II. It is not clear whether bridging-CO (species III) exchange appreciably at 190-220 K (Figure 5) or whether this rather uniform decrease in intensity at this temperature is due to a shift in background during the exchange and the warming of the surface. An effect more closely resembling an exchange-induced loss of intensity in the bridged-CO region is seen in Figure 6 above ~265 K.

C. Qualitative Thermodynamic Model

Although it has not been possible to measure activation energies directly for any of the processes studied in this work, it is possible to suggest general features about the energetics of various surface processes as shown in Figure 8. Here it is postulated that the energetic features differ significantly for Rh and Rh_x sites. In particular, the activation energy E_a (or possibly E_b) for CO adsorption on Rh to yield $\text{Rh}(\text{CO})_2$ is higher than E_c for adsorption on Rh_x . There is an activation energy, E_d , for conversion from the metastable $\text{Rh}_x(\text{CO})^*$ to $\text{Rh}_x(\text{CO})$, whereas no metastable $\text{Rh}(\text{CO})_2$ was detected. There also seem to be small differences in the activation energy for CO exchange with the exchange process on isolated Rh sites occurring more readily. The activation energy for CO desorption from Rh_x sites may be estimated from the measured activation energy for CO desorption from $\text{Rh}(111)$:

in the limit of zero coverage, $32 \text{ kcal/mole}^{-1}$ (12). This value is probably greater than $(E_2 + E_a)$ since species I, $\text{Rh}(\text{CO})_2$, desorbs more rapidly than species II (7,8,3) near 300 K.

The origin of several irreversible activated processes involving CO adsorption and CO adsorbate state conversion is not understood at present. One possible view is that the final structural state achieved for CO chemisorbed at elevated temperature is the result of passage through higher energy intermediate states of chemisorbed CO. In this view, rehybridization of the Rh atoms in both isolated and "crystalline" sites may be responsible for the observed activated processes as seen by means of the infrared spectrum of the bound CO. A second model would involve activated structural rearrangements within the Rh substrate itself, caused by chemisorptive interaction with CO. In this view, one could speculate that CO chemisorption on Rh_x sites could lead to disruption of the Rh_x site, giving some isolated Rh sites which are then able to chemisorb 2 CO molecules. Similar reconstruction processes on Rh_x sites could lead to the conversion of $\text{Rh}_x(\text{CO})^*$ (2082 cm^{-1}) to a more strongly bound $\text{Rh}_x(\text{CO})$ (2030 cm^{-1}).

Structural rearrangements of single crystal surfaces due to chemisorption are now being recognized from LEED studies (15). In addition, alloy surface segregation processes induced by adsorption on the alloy surface have been observed in which the driving force is related to the formation of the chemisorption bond with one component of the alloy (16). By analogy, it is possible that the activated processes observed here may be due at least in part to structural rearrangements of the Rh substrate caused by CO chemisorption.

V. Summary

The following features related to the chemisorption of CO on Al_2O_3 -supported Rh have been observed:

1. The adsorption of CO on isolated Rh sites to form $\text{Rh}(\text{CO})_2$ species is an activated process which occurs rapidly above ~ 170 K. No evidence for oxidation of Rh via CO dissociation has been found, contrary to the conclusions of Primet (4).
2. For CO adsorption on Rh_x sites as linear species, an activated state-conversion process is observed above 265 K, causing a shift in $\tilde{\nu}_{\text{CO}}$ from $\sim 2082 \text{ cm}^{-1}$ to $\sim 2030 \text{ cm}^{-1}$. This presence of the feature at $\sim 2030 \text{ cm}^{-1}$ overlaps directly with the low frequency component of the $\text{Rh}(\text{CO})_2$ doublet, a fact which was not recognized in earlier work done at 295 K (3, 4, 6, 7, 8). This large irreversible shift implies that a major strengthening of the Rh-CO bond occurs as some type of structural rearrangement takes place on these sites.
3. Selective isotopic exchange of $^{13}\text{CO}(\text{g})$ with $\text{Rh}(\text{CO})_2$ species may be achieved at 200 K while higher temperatures are required for rapid exchange of linear CO species on Rh_x sites.
4. These results, when considered along with previous information regarding the Rh- Al_2O_3 system (3), suggest that the Rh sites responsible for $\text{Rh}(\text{CO})_2$ species are single atom sites distinct from the Rh_x sites associated with linear and bridged-CO bonding.

VI. Acknowledgment

The authors gratefully acknowledge support from ONR under contracts N00014-79-F-0014 and N00014-75-C-0960. We thank Professor George F. Rossman for his kindness in allowing us to use the infrared spectrometer. We thank Dr. Richard Cavanagh and Dr. James Hall for helpful comments.

1. L. H. Little, Infrared Spectra of Adsorbed Species (Academic Press, London, 1966).
2. M. L. Hair, Infrared Spectroscopy in Surface Chemistry (Marcel Dekker, New York, 1967).
3. J. T. Yates, Jr., T. M. Duncan, S. D. Worley, and R. W. Vaughan. J. Chem. Phys., 70, 1219 (1979); see also, J. T. Yates, Jr., S. D. Worley, T. M. Duncan, and R. W. Vaughan, J. Chem. Phys., 70, 1225 (1979).
4. M. Primet, J. Chem. Soc. Far. Trans. I, 74, 2570 (1978).
5. D. J. C. Yates, private communication.
6. A. C. Yang and C. N. Garland, J. Phys. Chem., 61, 1504 (1957).
7. H. Arai and H. Tominaga, J. Catalysis, 43, 131 (1976).
8. H. C. Yao and W. G. Rothschild, J. Chem. Phys., 68, 4774 (1978).
9. G. E. Thomas and W. H. Weinberg, J. Chem. Phys., 70, 954 (1979). See also A. M. Bradshaw and F. M. Hoffman, Sur. Sci., 72, 513 (1978).
10. R. Gomer, Proc. 2nd Internl. Conf. on Solid Surfaces, 1974, Japan J. Appl. Phys., Suppl. 2, Pt. 2, p. 213 (1974).
11. J. T. Yates, Jr., T. E. Madey, and N. E. Erickson, Surface Sci., 43, 257 (1974); J. T. Yates, Jr., N. E. Erickson, S. D. Worley, and T. E. Madey, "The Physical Basis of Heterogeneous Catalysis," ed. E. Drauglis and R. I. Jaffee, Plenum Press, p. 75 (1975).
12. P. A. Thiel, E. D. Williams, J. T. Yates, Jr., and W. H. Weinberg, Surface Science, 84, 000 (1979).
13. L. A. Hanlan and G. Ozin, J. Amer. Chem. Soc., 96, 6324 (1974).
14. J. T. Yates, Jr., E. D. Williams, and W. H. Weinberg, Surface Science, submitted.
15. R. A. Barker and P. J. Estrup, Phys. Rev. Lett., 41 (1978) 1307.
16. R. Bouwman and W.M.H. Sachtler, J. Catal., 19, 127 (1970).

Figure Captions

- Figure 1. Infrared cell for low temperature adsorption studies.
- Figure 2. Comparison of $^{12}\text{C}^{16}\text{O}$ adsorption on Rh at low temperature and high temperature. The infrared spectra correspond to approximately equivalent amounts of CO admitted to the IR cell.
- Figure 3. Activated $^{12}\text{C}^{16}\text{O}$ adsorption on Rh for increasing Rh temperature.
- Figure 4. Activated adsorbate conversion processes - $^{12}\text{C}^{16}\text{O}$ on Rh.
Spectrum (a) was measured at 110 K after CO adsorption at ~200 K.
All changes occur upon heating CO on Rh surface in vacuum.
- Figure 5. Low temperature isotopic exchange of chemisorbed CO on Rh.
- Figure 6. High temperature isotopic exchange of chemisorbed CO on Rh.
- Figure 7. Reversible temperature effects on infrared spectrum - $^{12}\text{C}^{16}\text{O}$ + Rh.
The adsorbed layer produced at 314 K was cooled to various temperatures and the infrared spectrum was measured.
- Figure 8. Qualitative free energy diagram for the adsorption of CO on Rh sites.
For the isolated Rh sites, the most stable species, $\text{Rh}(\text{CO})_2$, is inhibited from forming at low temperatures because E_a (or E_b) is larger than kT at $T \lesssim 200^\circ \text{K}$. For the crystalline Rh sites, adsorption of CO at low temperatures results in the formation of a metastable species $\text{Rh}_x(\text{CO})^*$, since $E_c < kT < E_d$ for $T \lesssim 200^\circ \text{K}$. At higher

temperatures, the reaction proceeds over the activation barrier E_d to the more stable $Rh_x(CO)$. At both sites, exchange proceeds via the proposed activated complexes $Rh(CO)_3^*$ and $Rh_x(CO)_2^*$, rather than by desorption, then re-adsorption.

INFRARED CELL FOR LOW TEMPERATURE ADSORPTION STUDIES

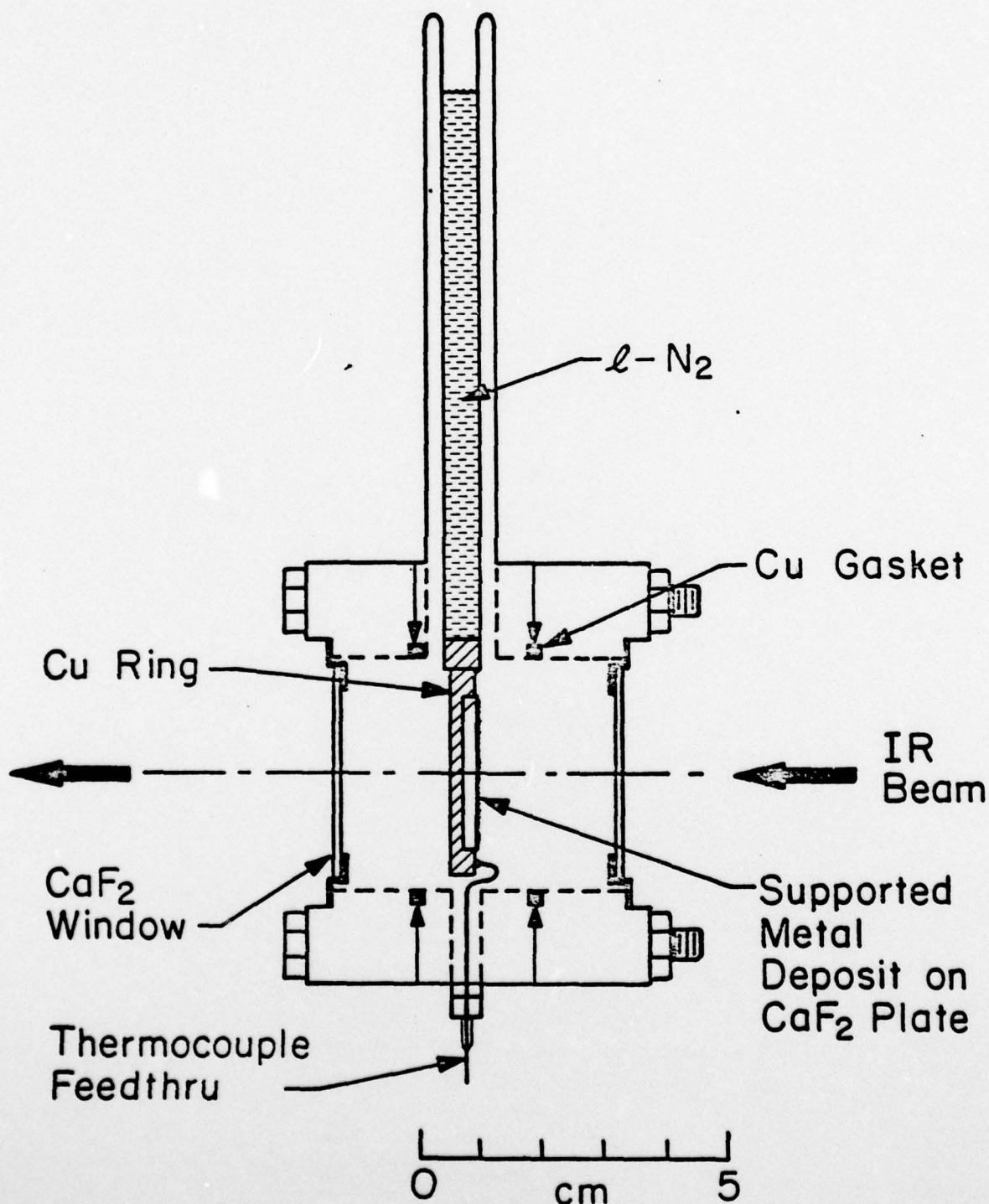


Figure 1

$^{12}\text{C}^{16}\text{O}$ SPECTRAL CHANGES DURING ADSORPTION ON Rh

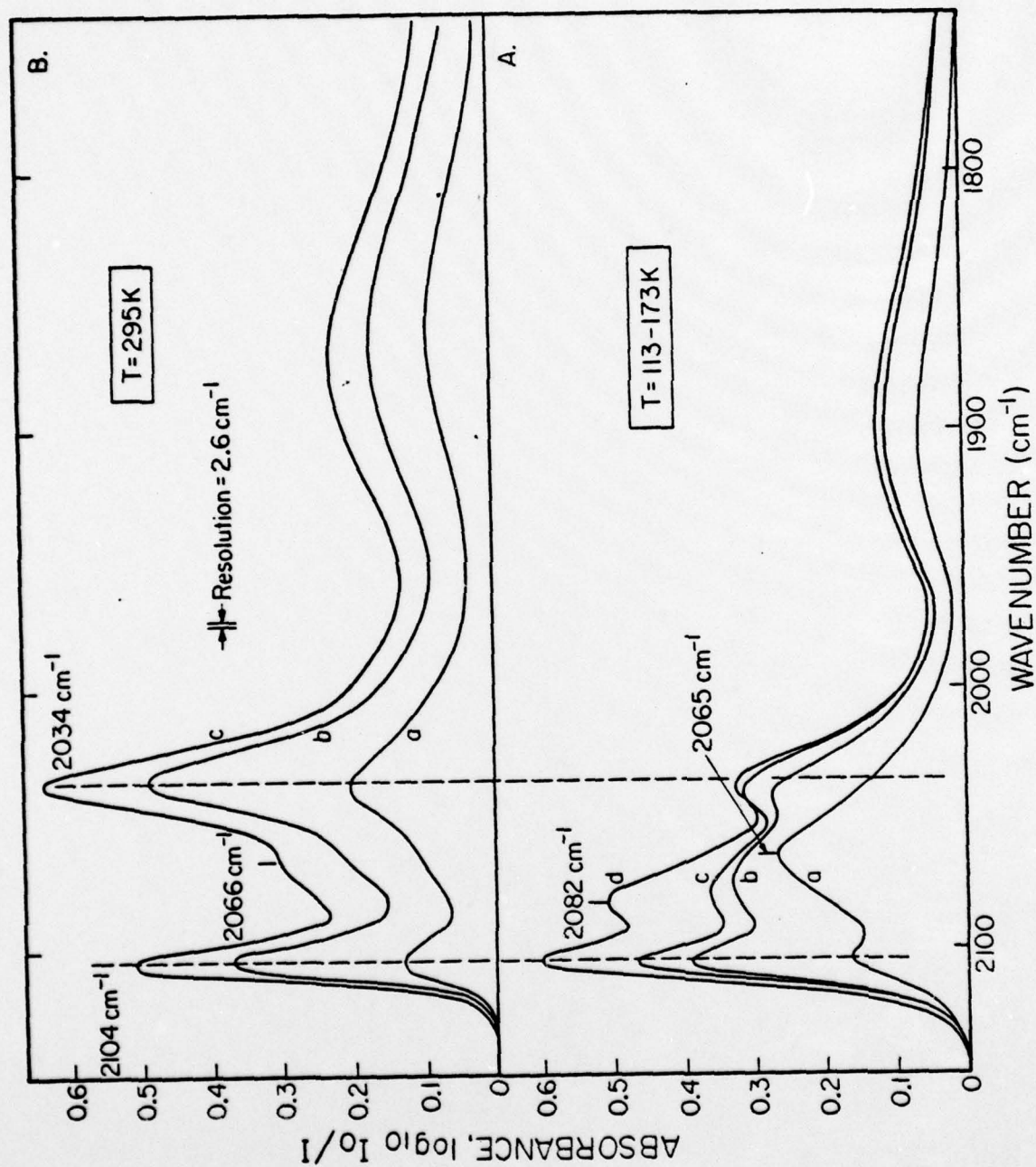


Figure 2

ACTIVATED CO ADSORPTION ON Rh

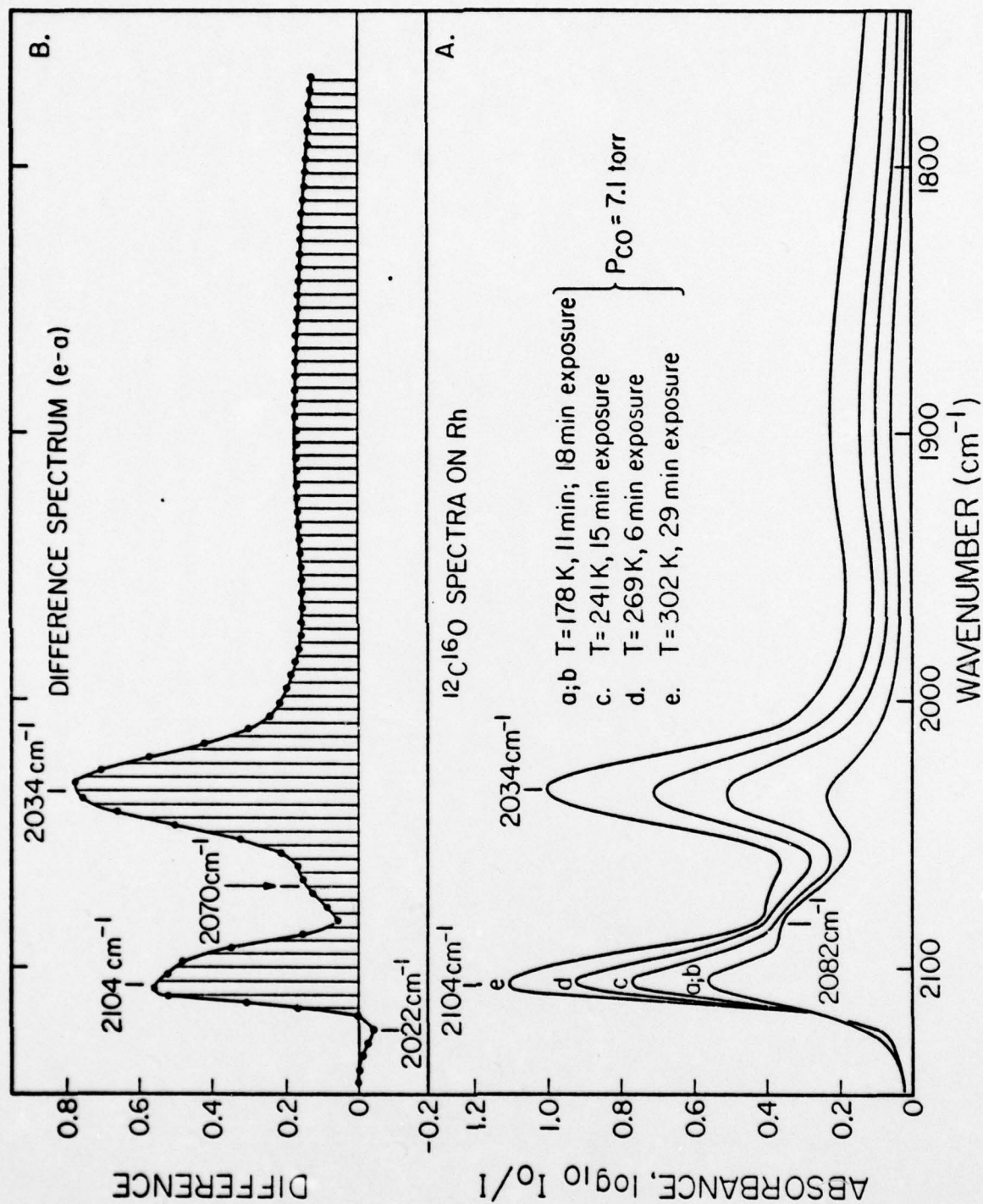


Figure 3

ACTIVATED ADSORBATE CONVERSION PROCESSES - $^{12}\text{C}^{16}\text{O}$ ON Rh

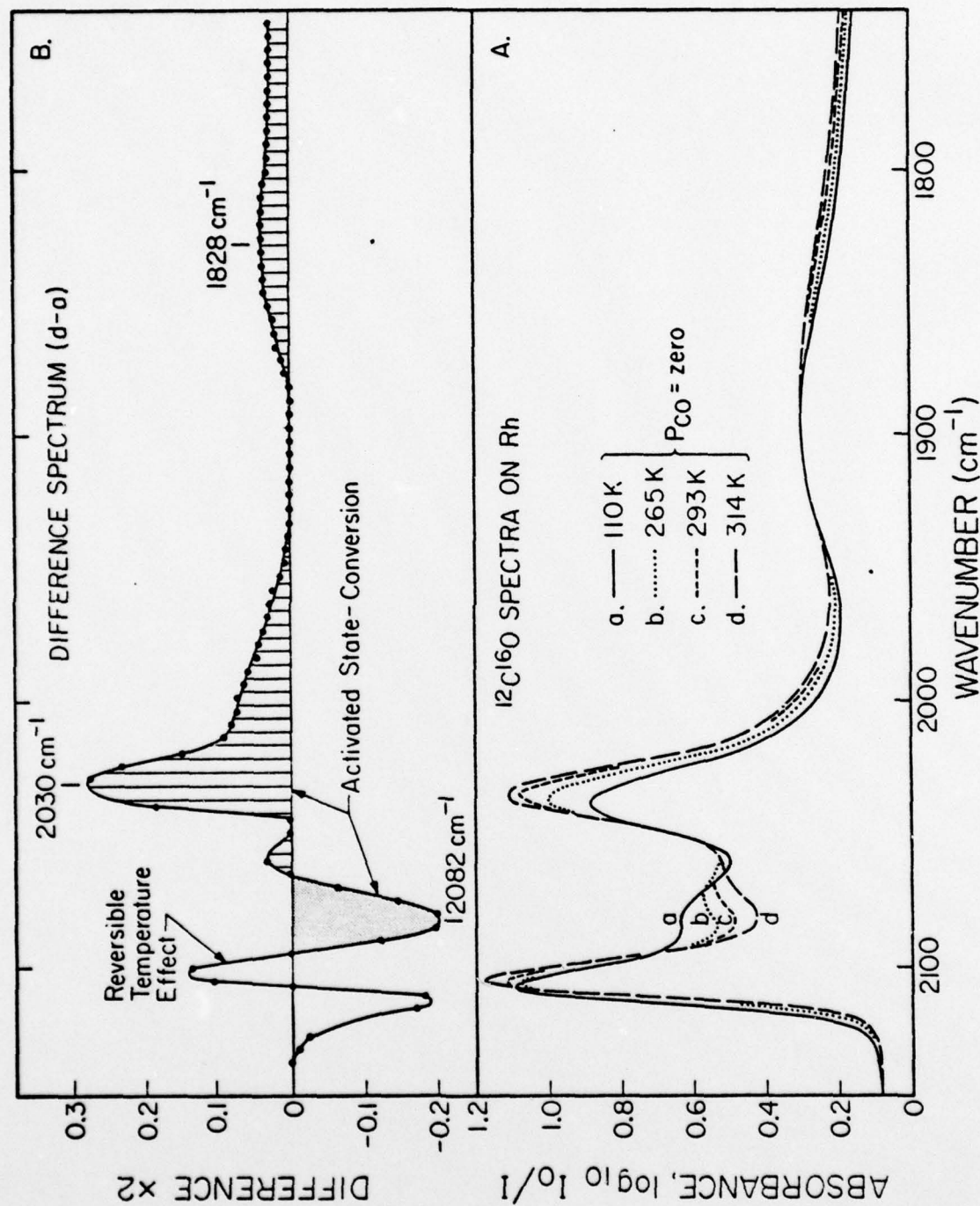


Figure 4

LOW TEMPERATURE ISOTOPIC EXCHANGE
OF CHEMISORBED CO ON Rh

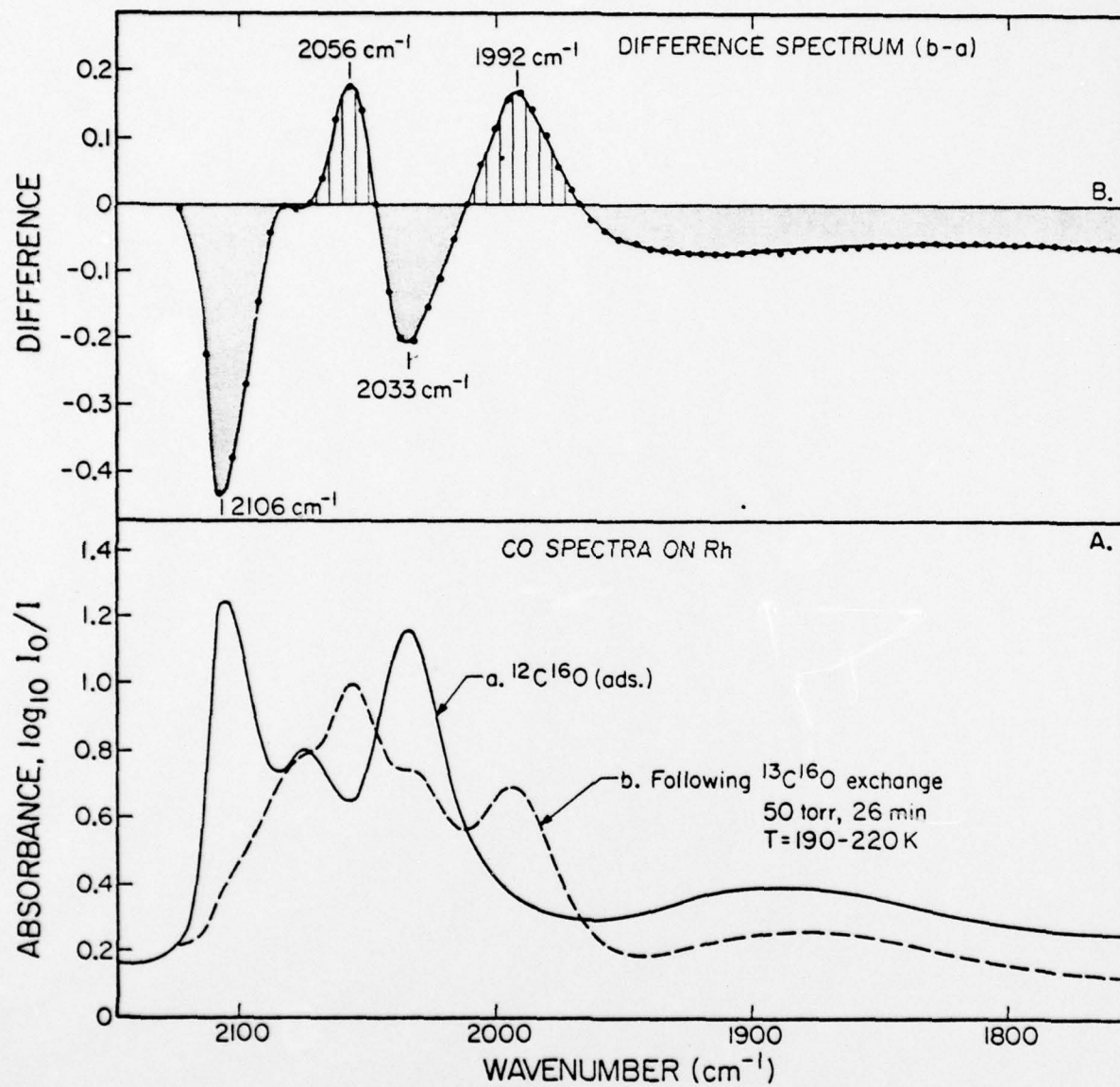


Figure 5

HIGH TEMPERATURE ISOTOPIC EXCHANGE OF CHEMISORBED CO ON Rh

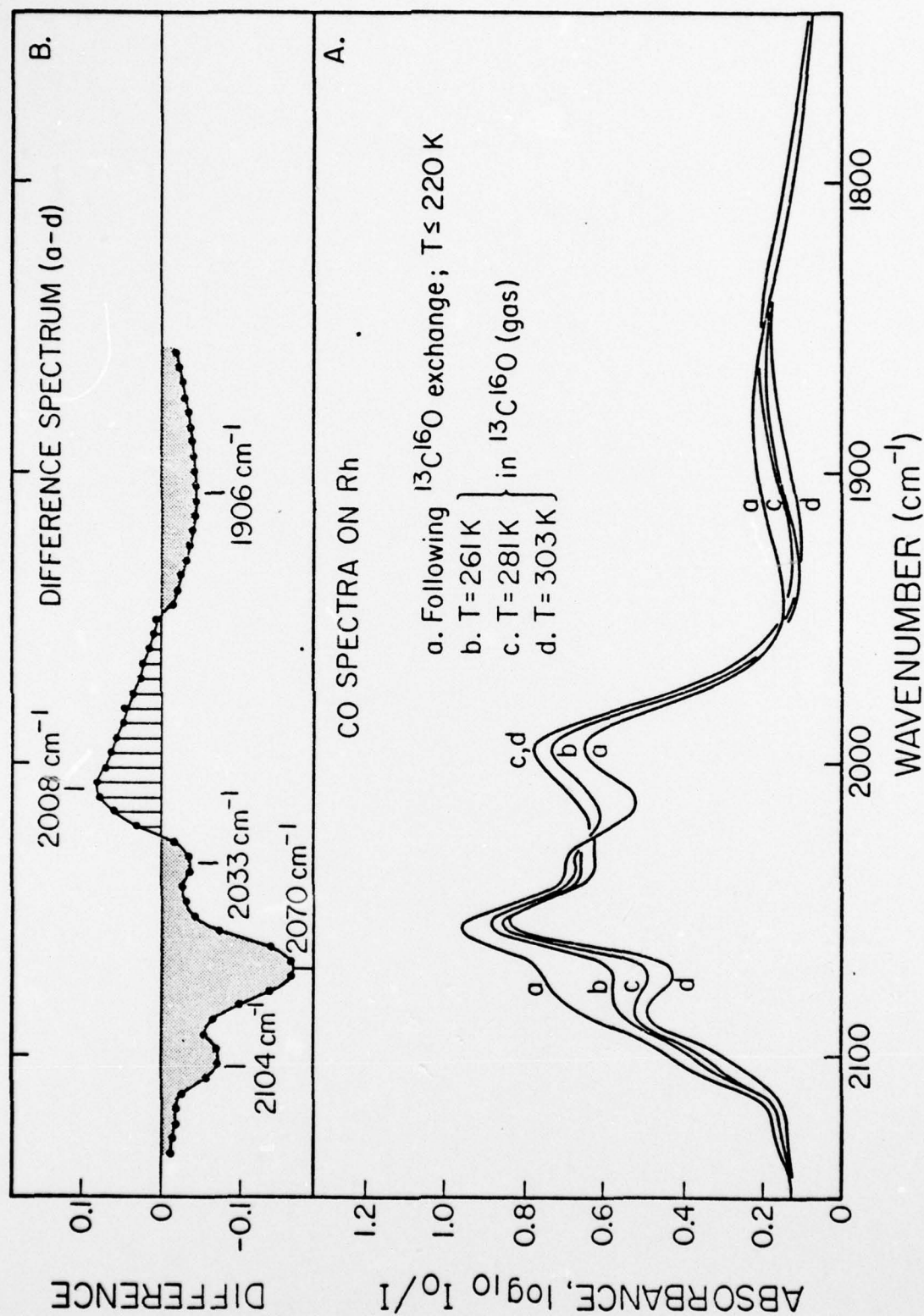


Figure 6

REVERSIBLE TEMPERATURE EFFECTS ON INFRARED SPECTRUM - $^{12}\text{C}^{16}\text{O} + \text{Rh}$

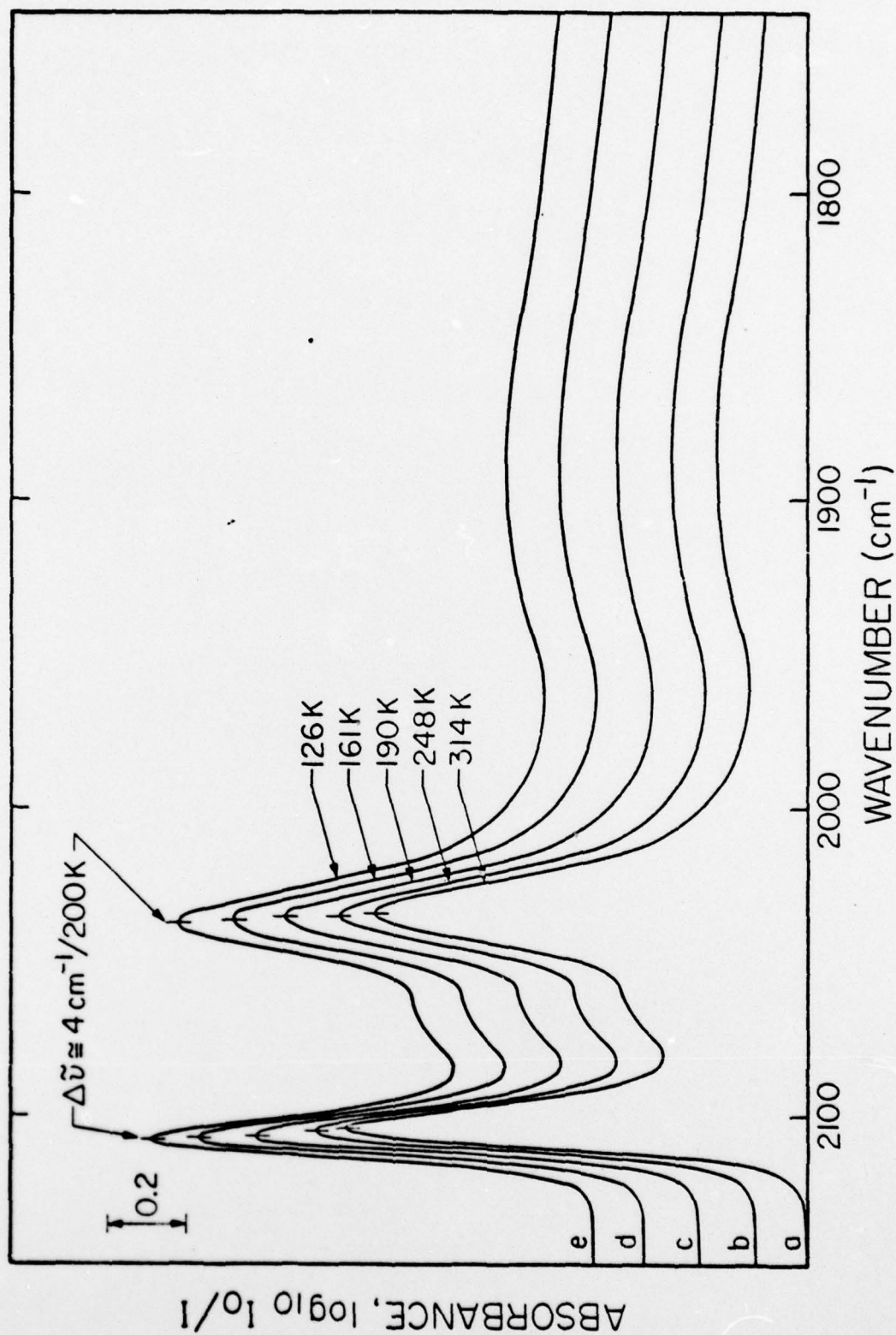


Figure 7

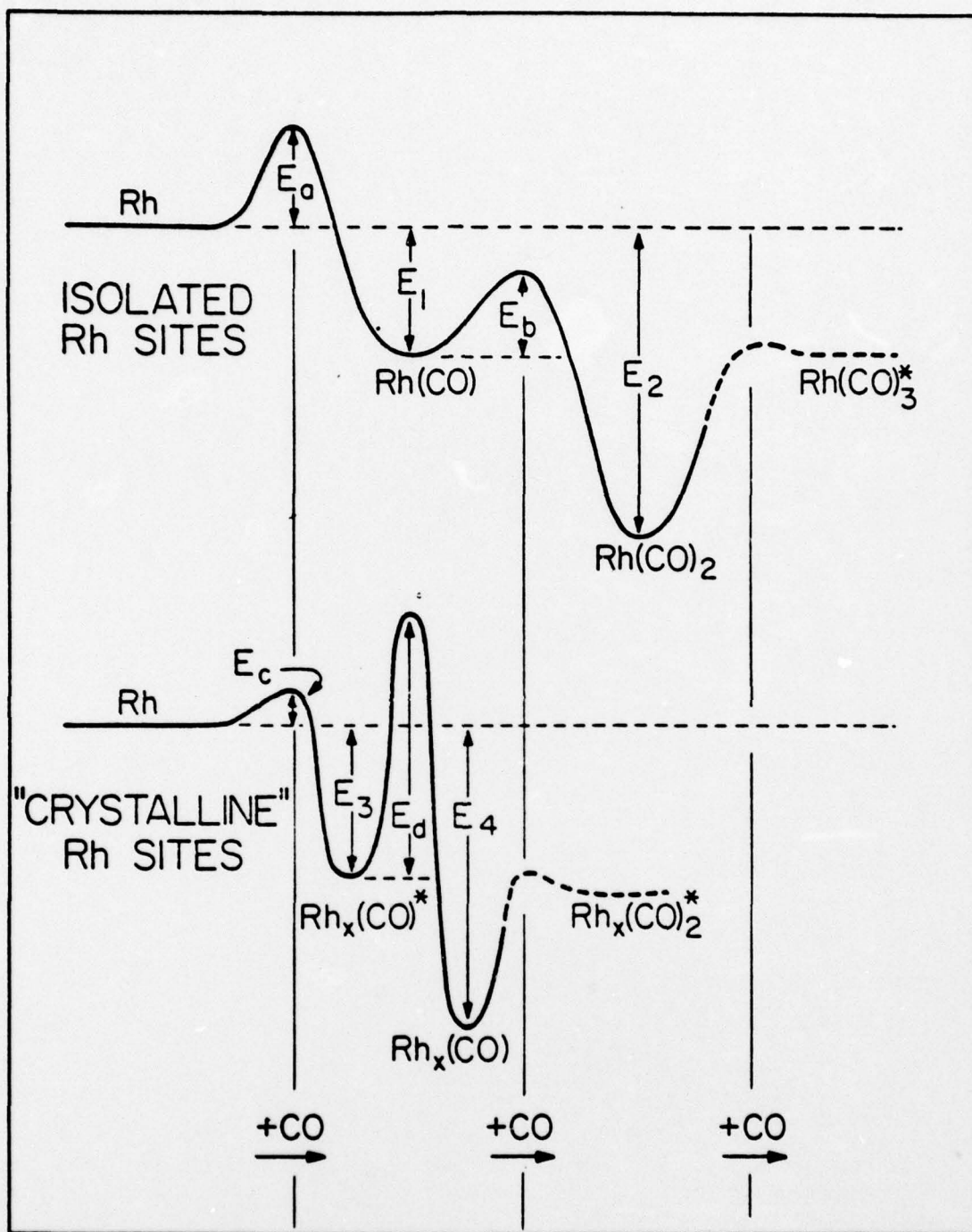


Figure 8