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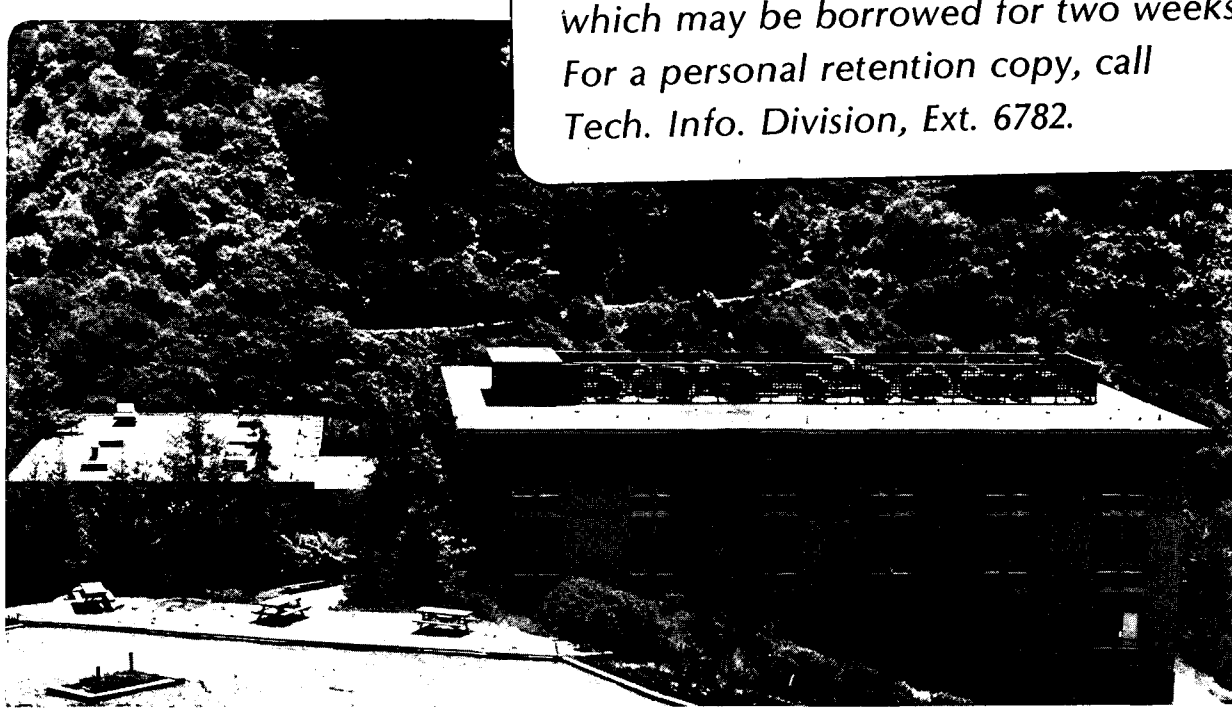

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THE ADSORPTION AND CATALYZED REACTIONS OF CO AND CO_2 ON GRAPHITE SURFACES

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1. Introduction

The use of ultra-high vacuum (10^{-10} - 10^{-11} torr) in conjunction with various electron spectroscopies has, over the past twenty years, provided considerable insight into adsorption on well-characterized transition metal surfaces. The incorporation of a high-pressure cell into the vacuum chamber has allowed surface species to be related to the mechanism of catalytic reactions.[1]

A similar approach is adopted in this work in the study of catalytic reactions of graphite with CO and CO_2. Prior to studying catalytic reactions, results are presented in this paper on the interaction of these molecules with a clean graphite surface.

The experimental probes that are brought to bear on this problem are Auger electron spectroscopy (AES) for elemental analysis of the surface, temperature programmed desorption (TPD) to examine thermal decomposition of adsorbate species and, finally, x-ray photoelectron spectroscopy (XPS) in order to identify surface entities.

2. Experimental

The experimental apparatus is shown in Figure 1, and has been described in detail elsewhere.[2] Briefly, it consists of a UHV chamber which contains a high-pressure cell, a double-pass cylindrical mirror analyzer with co-axial electron gun for Auger spectroscopy, and an X-ray source with a magnesium anode for XPS. The chamber is also equipped

with a quadrupole mass spectrometer for residual gas analysis and TPD experiments. Two types of carbon were used in these experiments: a polycrystalline carbon for high pressure reactions and TPD, and a piece of oriented graphite from the Carbon Products Division of Union Carbide for XPS.

3. Results

Oxygen was the major contaminant of both graphite samples as revealed by AES. This could be effectively removed by extensive outgassing at 1500K in UHV. Hydrogen, another possible contaminant is not detectable by AES, but since C-O bond strengths are likely to be greater than for C-H, thermal removal of oxygen implies that all hydrogen has also been removed.

3.1 CO and CO_2 Adsorption and Reaction

Shown in Figure 2 are 28 amu (CO) and 44 amu (CO_2) desorption spectra after high exposures ($>10^8$L) of CO and CO_2 onto clean polycrystalline graphite at room temperature. No other desorption species were detected. The large exposures required to saturate the surface imply very low sticking probabilities.

Surprisingly, both CO and CO_2 give rise to identical 28 and 44amu spectra above 600K, exhibiting a CO_2 peak at 740K and a CO peak at 1230K. Features below 600K may originate from "physisorbed" molecules [3] or from desorption from supports. (Platinum, the support material, has a CO desorption peak at ~500K).

The number of adsorption sites on the polycrystalline sample may be estimated at ~5×10^{14} cm^{-2} from a comparison of these data with a desorption

spectrum from a CO saturated Pt foil. The reaction between CO or CO_2 and polycrystalline graphite was investigated as a function of sample temperature in the high pressure reactor. The results for the reaction $CO_2 + C \rightarrow 2CO$, using a gas pressure of 230 torr, are shown in Figure 3. These results were obtained by measuring the gas production rate, and the turnover frequencies calculated assuming the active site concentration obtained from TPD experiments ($\sim 5 \times 10^{14}$ cm^{-2}). Measurement of the slope of this curve yields an activation energy for CO production of 67 ± 3 kcal/mole. This is in good agreement with values of 59 kcal/mole obtained in a flow reactor.[4].

Figure 4 shows a similar plot for the reverse reaction ($2CO \rightarrow CO_2 + C$). An activation energy may be extracted from the linear region and yields a value of 24 ± 2 kcal/mole. The difference between these activation energies, i.e. the enthalpy for reaction is -43 ± 5 kcal/mole, which is in good agreement with the literature value (-41.2 kcal/mole).[5]

Oriented graphite was used for X-ray photoelectron experiments since polycrystalline samples exhibited a broad feature on the high binding energy side of the C1s peak due to exitation of a plasmon.[6] This peak is sufficiently intense to effectively obscure any adsorbate induced features. However, the plasmon satellite is strongly attenuated when the X-ray beam impinges at grazing incidence onto an edge plane which allows chemically shifted species to be observed. This sample orientation is also likely to lead

to an increase in number of adsorbate sites.

Figure 5a shows a MgKα Cls x-ray photoelectron spectrum from the edge plane of an oriented graphite sample after exposure to ~ 10^8L CO_2 and flashing to 450K to remove "physisorbed" species. The solid line depicts the spectrum of clean graphite taken under identical conditions. The graphite Cls peak has a binding energy of 285.0 eV, and the adsorbate induced peaks occur at 281.7 eV and 280.6 eV constituting chemical shifts of 3.3 ± 0.2 and 4.4 ± 0.2 respectively. On heating to 850K (above the CO_2 desorption temperature) the spectrum changes to that shown in Figure 5b, the shakeup satellite disappears and only a peak at 282 eV (a chemical shift of 3.0 ± 0.1 eV) remains. This peak may be removed by heating to ~ 1400K corresponding to the desorption of CO.

4. Discussion

The use of single crystal graphite aligned so that the x-ray source impinges onto the edge plane atoms allows adsorbate induced Cls features to be observed. It is well established [7] that these shifts may be due to carbon species that can be categorized as follows: ether and hydroxyl groups ~1.6 eV, carbonyl groups ~3 eV and carboxyl groups, ~4.2 eV. The trend in Ols binding energies is less clear cut. On this basis, the peaks that arise after CO_2 exposure may be identified as being due to carboxyl (280.6 eV) and carbonyl (281.7 eV) species. The XPS data indicates that the carboxyl species disappears on heating to above 850K. CO_2 is desorbed at this temperature in TPD so that carboxyl species thermally decomposes to yield CO_2. The $\pi \rightarrow \pi^*$ shake-up satellite also disappears. Such behavior

has been observed by Schlogel after similar treatments of graphite samples.[6] Further heating to 1400K evolves CO in TPD and the remaining adsorbate induced peak due to a carbonyl species disappears. High pressure reactions on a polycrystalline graphite sample result in the formation of CO_2 from CO in the temperature range 800-900K and CO from CO_2 in the range 1000-1100K. These temperatures correspond to those at which CO_2(740K) and CO(1230K) are evolved, so that the rate limiting step for CO_2 formation may be the decomposition of carboxyl species. Similarly, the reaction to form CO may take place via carbonyl decomposition.

Further work is required to identify the exact nature of the surface carbonyl and carboxyl species so that their inconversion mechanism may be elucidated in greater detail.

5. Conclusion

The interaction of clean graphite surfaces with CO and CO_2 is amenable to investigation using conventional surface science techniques such as AES, TPD and XPS. Preliminary studies indicate that carboxyl and carbonyl species may be identified and appear to arise from exposure to either CO or CO_2. CO_2 production at similar temperatures in both high pressure reactions and in TPD suggests that carboxyl decomposition may be the rate limiting step to CO_2 formation. Analogously, carbonyl decomposition appears to be rate limiting for the formation of CO.

6. Acknowledgements

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Contract Number DE-AC03-76SF00098, through the Pittsburgh Energy Technology Center, Pittsburgh, Pa.

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8. Figures

Fig. 1 (a) Schematic diagram of apparatus with high pressure cell closed,

(b) detail with high pressure cell open.

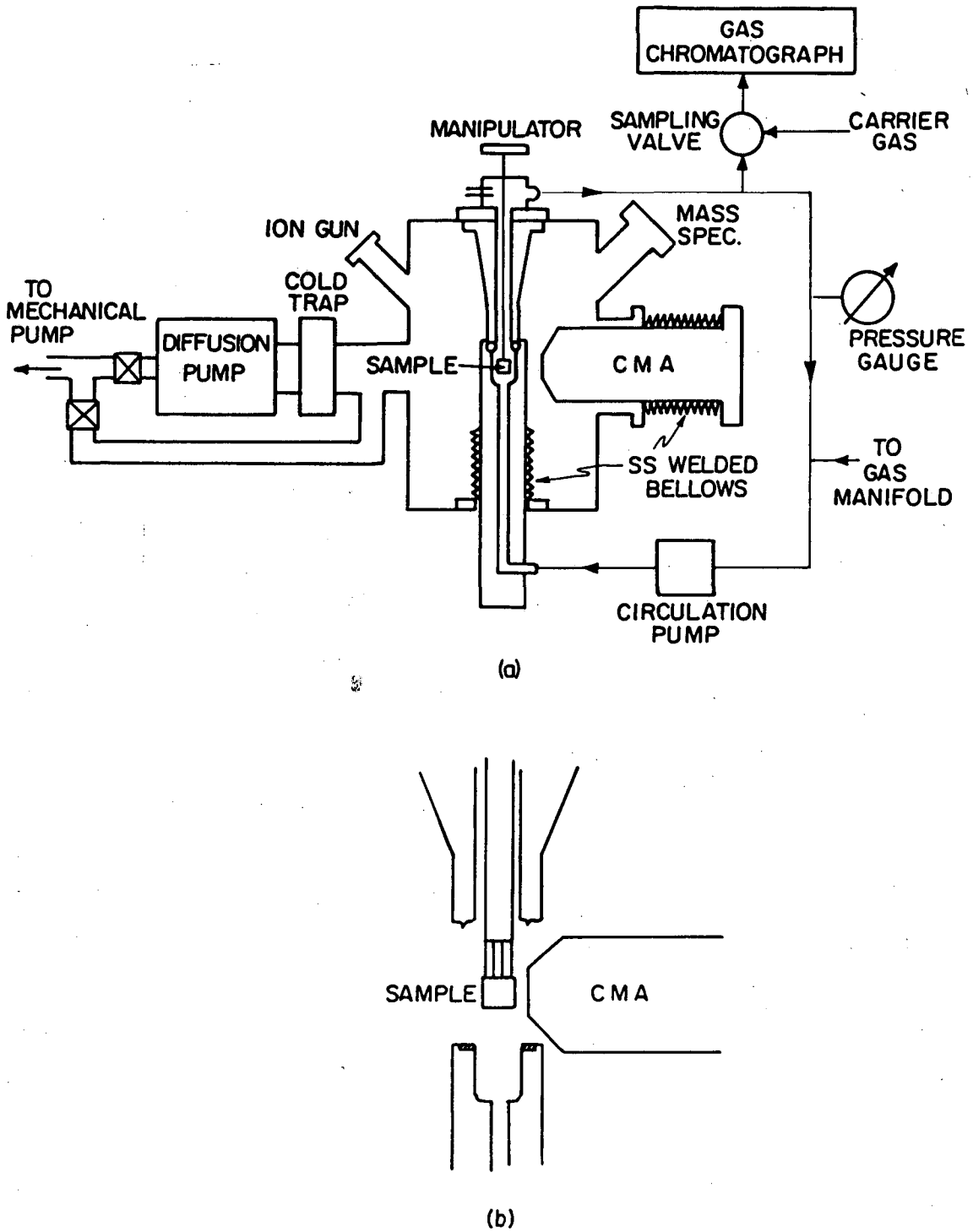
Fig. 2 28 and 44 amu desorption spectra obtained after (a) $5x10^8$L exposure of CO and (b) $5x10^8$L exposure of CO_2 onto polycrystalline graphite.

Fig. 3 Arrhenius plot for the reaction, $CO_2 + C \rightarrow 2CO$.

Fig. 4 Arrhenius plot for the reaction $2CO \rightarrow CO_2 + C$.

Fig. 5 (a) A spectrum of a graphite edge plane exposed to 10^9L CO_2 at room temperature. The spectrum of a clean surface is shown as a line.

(b) Spectrum after flashing to ~850K.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MANIPULATOR
SAMPLING VALVE
CARRIER GAS
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COLD TRAP
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SAMPLE
CMA
PRESSURE GAUGE
SS WELDED BELLOWS
TO GAS MANIFOLD
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(a)
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Fig. 1

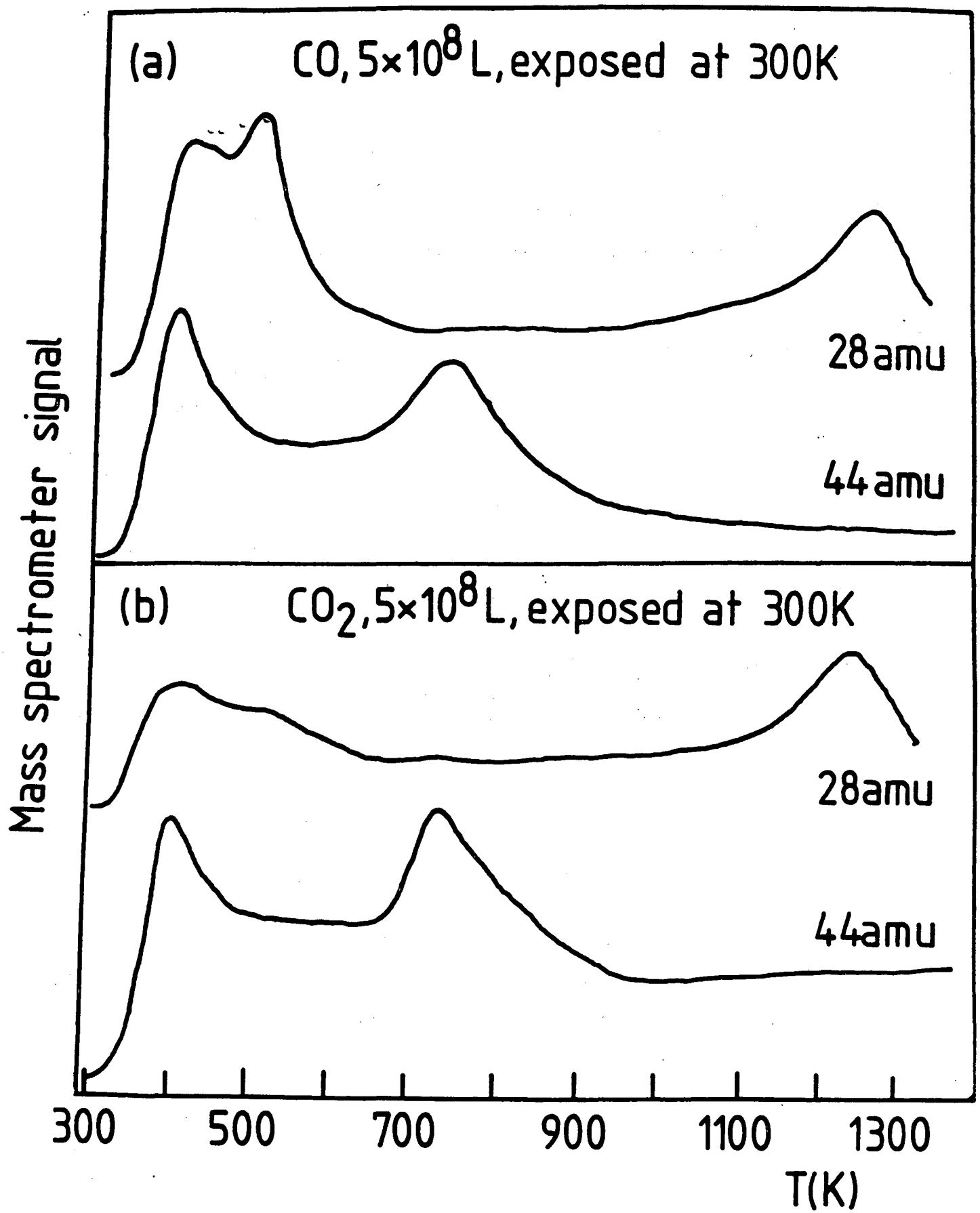

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Fig. 2

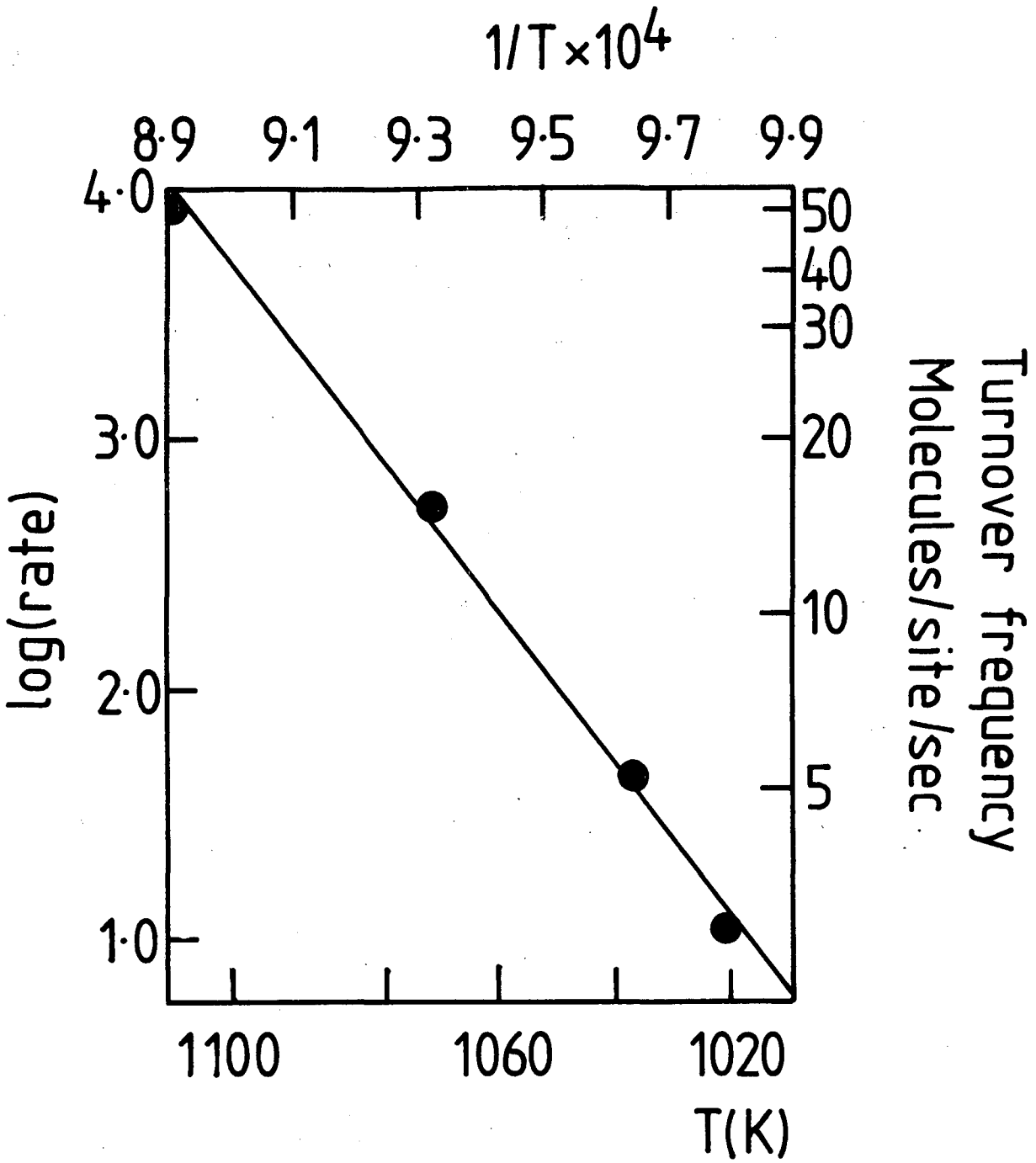

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Fig. 3

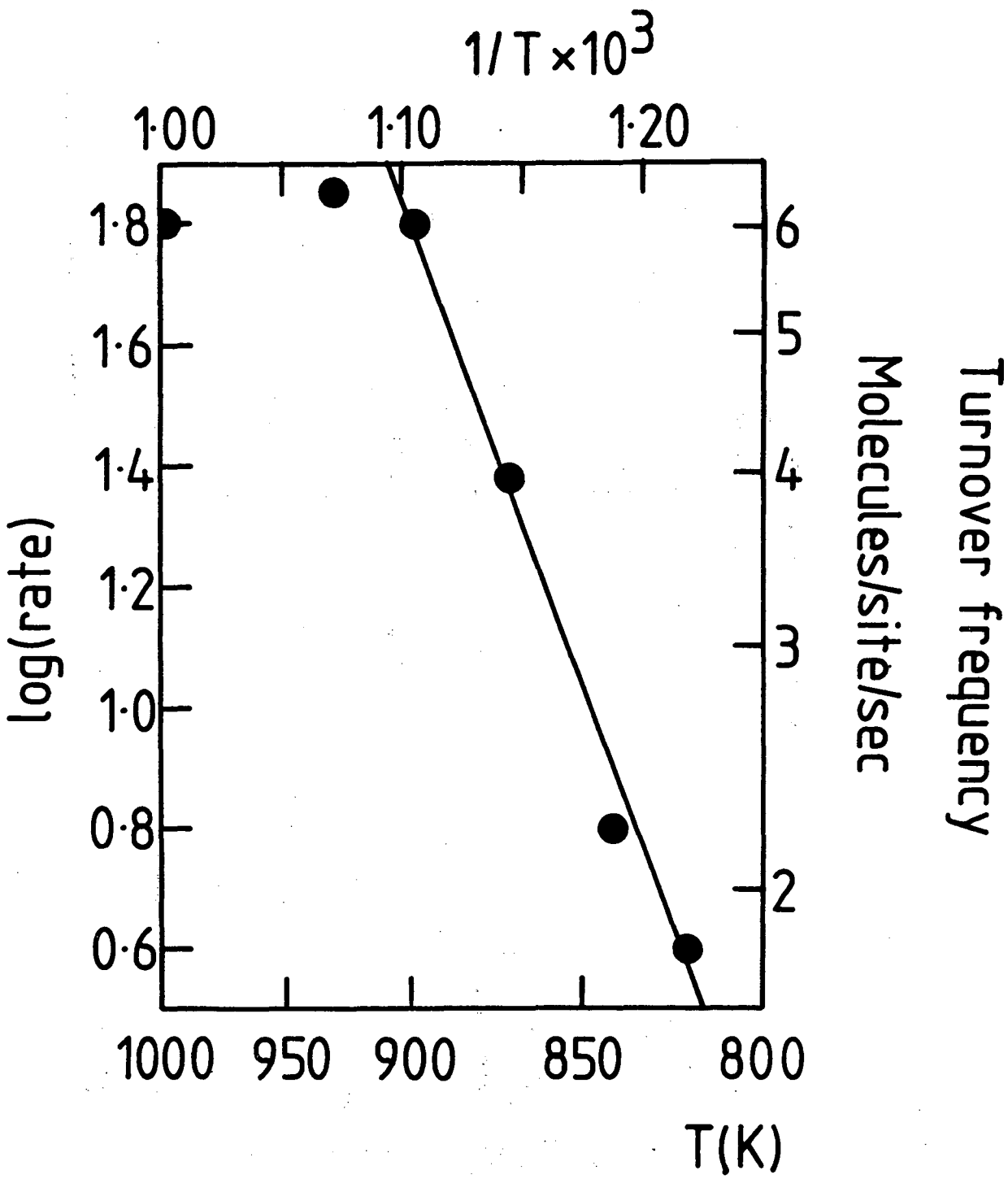

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Fig. 4

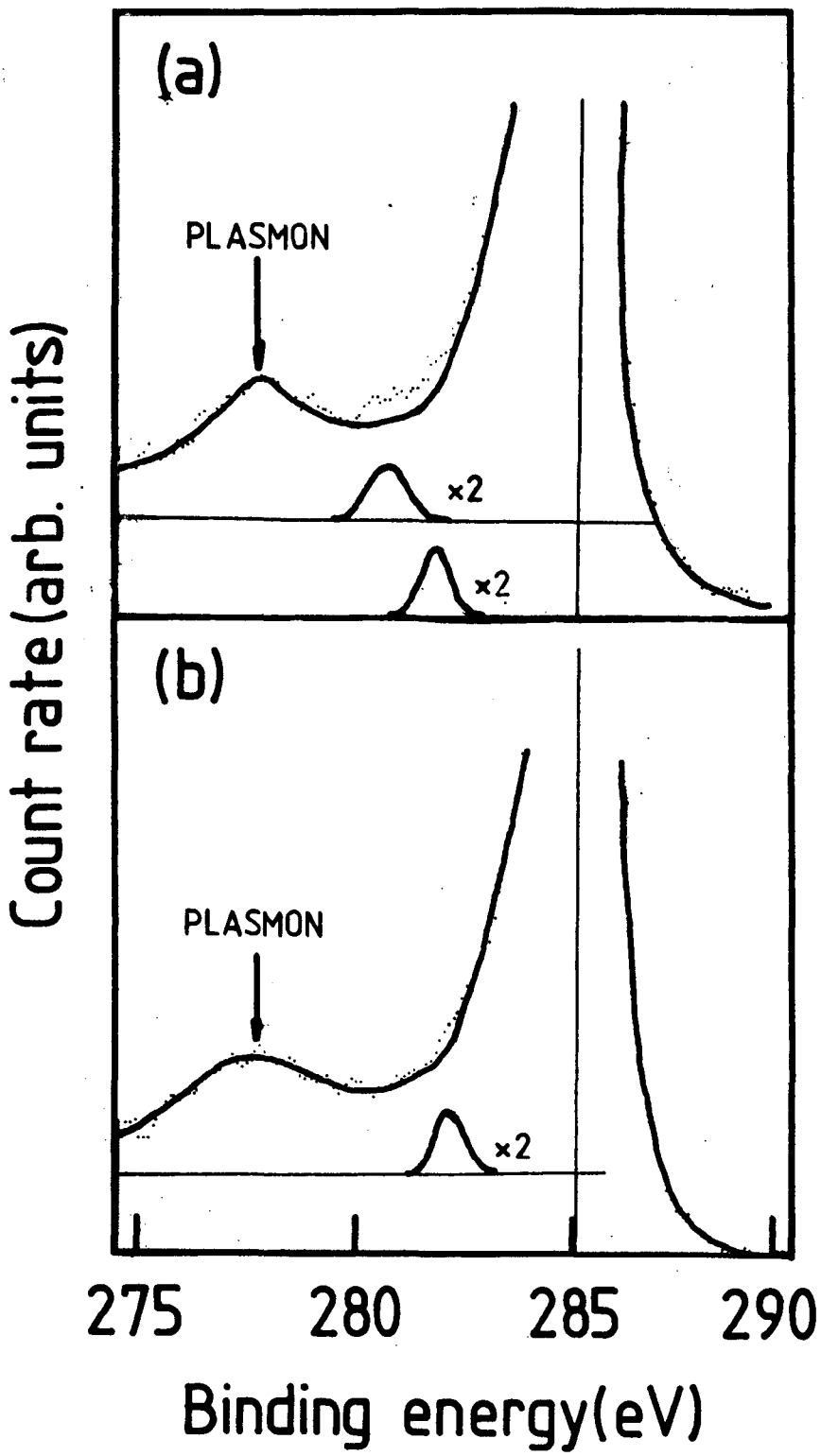

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Fig. 5

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