

Infrared Studies of the Influence of Alkali Metals on the C-O Bond in Chemisorbed Carbon Monoxide

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Research Scope and Objectives

This research is focussed on understanding the details of the interaction between adsorbed CO and alkali metals present together on a transition metal surface. We desire to employ the vibrational spectrum of the adsorbed CO as an indicator of the nature of the interaction. The following questions about this interaction are addressed:

- (1) Is the interaction between CO and adsorbed alkalis a long range or a short range one?
- (2) At what temperature does the interaction lead to dissociation of CO on the surface?
- (3) How much does the alkali-CO interaction shift the CO stretching frequency, and what is the meaning of this frequency shift?
- (4) How does the interaction depend upon alkali ionization potential and alkali coverage?
- (5) What is the influence of adsorbed oxygen on the alkali-CO interaction?

Description of Research Effort

An ultra high vacuum apparatus to study all of the above questions has been constructed and is working in all respects. It employs reflection IR spectroscopy as the main tool sensitive to molecular details in the surface layer. In addition, LEED, XPS, AES and temperature programmed desorption are auxiliary tools available for the investigations. A Ni(111) single crystal has been prepared and installed in the optical cell. The crystal is cleaned by Ar⁺ bombardment followed by annealing at 900K. Its temperature may be varied from 77K upwards. The reflection IR spectrometer is computer controlled, permitting spectral data to be integrated over time to enhance the signal-to-noise ratio. Using ratio recording double beam methods, we have observed the adsorbed CO-IR spectrum at 77K and at 300K, at an angle of incidence of 86°. At 77K, three infrared features are observed at

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1920 $\text{cm}^{-1}(\text{s})$, 2056 $\text{cm}^{-1}(\text{m})$ and 2112 $\text{cm}^{-1}(\text{m})$. Two of these vibrations agree with earlier EELS studies [1]. The 2112 cm^{-1} feature is a new vibrational frequency. The maximum intensity above background is 0.3%, and one can observe these bands optically with a signal-to-noise ratio of about 30:1 at a resolution of 5 cm^{-1} . [EELS resolution \sim 60 cm^{-1}].

Two sources of K are installed in the system. One is a K^+ exchanged zeolite source, mounted in an ion gun configuration. With this source, we intend to accurately measure K coverages on Ni(111) by measuring the total charge collected by the Ni(111) crystal upon bombardment by K^+ . A second source will yield mainly metallic K(g) and it will be used to check on our ability to deliver a clean deposit of K, free of oxygen contamination. These two deposition techniques, coupled with LEED and XPS/AES measurements will serve to insure that we can control our K coverage and purity. The same techniques are to be used for the other alkali metals.

Using this facility, we are planning to accurately study the coverage effect of the alkalis on the infrared line shape and frequency for the CO stretch mode. Alkali depositions will be carried out prior to CO adsorption and on top of CO layers. Based on recent measurements of the Penning spectrum of CO influenced by $\text{K}^{\delta+}$ on Ni(111) we know that increased filling of the $2\pi^*$ orbital occurs[2]. This should lead to a decrease in ν_{CO} which can be observed as the ratio of alkali-to-CO is varied.

Future Research

Our reflection IR apparatus containing an isolatable optical cell, is unique in that it permits high sensitivity studies of adsorbed layers under high gas pressures. This will permit several new experiments to be done.

- (1) Detection of weakly-bound, high coverage adsorbate states which are populated only at high pressure and low temperature.
- (2) Detection of the dynamic interactions of $\text{H}_2(\text{g})$ with CO adsorbed species at high H_2 pressures.

These new directions will be pursued simultaneously with the alkali-CO interaction studies.

References

- [1] W. E. Erley, H. Wagner, and H. Ibach. Surf. Sci. 80, 612-619 (1979).
- [2] H. Metiu, R. Martin, C. Hanrahan, and J. Arias. (private communication, August 1983).