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Temperature effects on the infrared spectrum of chemisorbed CO

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The temperature dependence of the infrared spectrum of CO chemisorbed on Rh supported by Al_2O_3 has been measured. A shift in the CO stretching mode of $1.4 \times 10^{-2} \text{ cm}^{-1} \text{ K}^{-1}$ to higher wave number is observed on cooling. An electrodynamic model of the surface interactions is presented. The model accounts for both the magnitude and direction of the observed shift.

INTRODUCTION

The observation of normal mode frequencies of chemisorbed molecules is commonly employed to gain an understanding of the molecular structure of the chemisorbed species.^{1,2} Studies of the vibrational spectra of adsorbed species may now be carried out on highly dispersed substrates as well as on single crystals. Both optical and electron energy loss³ spectroscopies are commonly employed in these studies, the optical studies providing the higher resolution. Recently, using transmission infrared spectroscopy, a small temperature dependent line shift on the carbonyl stretching mode has been observed for CO chemisorbed on Al_2O_3 -supported Rh surfaces.⁴ In this paper we report further measurements and present an electrodynamic model of the effect. This model accounts for both the direction and the magnitude of the observed frequency shifts.

EXPERIMENTAL

Experimental details regarding sample preparation appear in an earlier paper.⁵ In brief, a dispersed sample of Rh^{3+} on Al_2O_3 is reduced in hydrogen at 420 K and cooled to room temperature while under vacuum. The supported Rh sample is subsequently exposed to 50 Torr of CO for 1 h at $\sim 300 \text{ K}$ to achieve full coverage and then evacuated to 3×10^{-3} Torr. A sequence of infrared spectra of the chemisorbed CO is recorded as the sample is first cooled to 100 K and then warmed to room temperature. Typical spectra are shown in Fig. 1 for the carbonyl stretching region. Four spectra features are observed in the range from 2300 to 1750 cm^{-1} . Coverage dependent features occur near 1870 and 2070 cm^{-1} and have been previously assigned.^{5,6} The low wave number feature is attributed to bridge bonded CO on Rh_x sites while the 2070 cm^{-1} feature is assigned to CO bound terminally to a Rh atom of a Rh_x cluster. The remaining features at 2104 and 2034 cm^{-1} do not shift in wave number with changes in CO coverage. These features have therefore been assigned as the symmetric and antisymmetric stretching modes of a pair of CO ligands bound to *isolated* noninteracting Rh sites.⁵⁻⁷ There is some controversy regarding the latter assignment.⁸

The peak position and band edge position of the high

wave number peak are given as a function of temperature in Fig. 2, where spectra recorded at higher dispersion than in Fig. 1 were used to accurately determine the wave number shift. Although both peaks were observed to shift to higher wave number as the temperature is decreased, only the 2104 cm^{-1} feature has been analyzed because of its lack of overlap with other features.

THEORY

In order to understand the observed temperature shift, we consider the electrodynamic interaction of the dynamic dipole moment of the CO with the Al_2O_3 substrate. This interaction, described below, leads to a plausible, although possibly not unique, explanation of the observed temperature shift.

The vibrating CO molecule has a dynamic dipole moment which couples to the infrared radiation. This same dynamic dipole moment, however, also couples to itself and its neighbor since the charge distribution of the CO sets up an image charge distribution in the dielectric Al_2O_3 substrate. The image field is smaller than for the case of a metal substrate by a factor of about 2 at the CO stretch frequency. This image field interacts with the CO charge distribution leading to frequency shifts in the normal modes of the system. Considerations of CO dynamic dipole interactions on metal single crystal substrates have been invoked^{9,10} to explain the wave number shifts observed as a function of CO coverage.

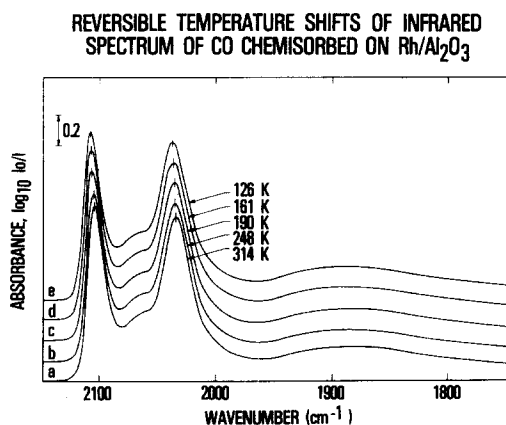


FIG. 1. Reversible temperature shifts of the infrared spectrum of CO chemisorbed on $\text{Rh}/\text{Al}_2\text{O}_3$.

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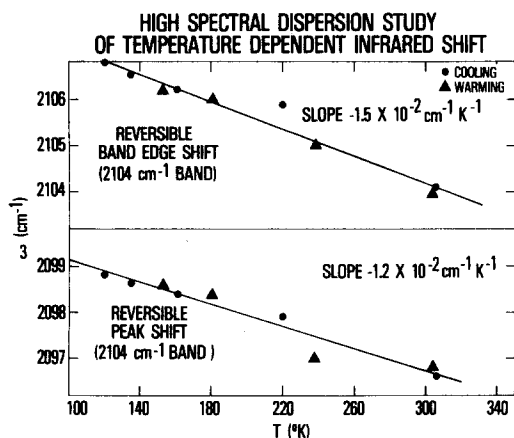


FIG. 2. High spectral dispersion study of the temperature dependent infrared frequency shift.

The model of the system which we will use is shown in Fig. 3. The dynamic dipole moments will be considered as point dipoles located halfway between the C and O atoms in the adsorbed species and oriented along the axis of the CO ligands. In the molecule $\text{Rh}_2(\text{CO})_4\text{Cl}_2$, which contains two $\text{Rh}(\text{CO})_2$ moieties, one observes a splitting of the degenerate CO stretch frequency due to CO-CO coupling, resulting in a symmetric and an anti-symmetric mode.^{5,6} The coupling may be electrodynamic in origin due to the dipole-dipole coupling, or it may be due to coupling through the rhodium atom.

For the case of adsorbed CO on dispersed Rh on an Al_2O_3 substrate similar splitting is observed, and it is believed that a $\text{Rh}(\text{CO})_2$ complex exists on the substrate as well as bridged and terminal CO species chemisorbed on Rh crystallites, Rh_x .⁴⁻⁶ The adsorbed $\text{Rh}(\text{CO})_2$ complex can librate, or tilt back and forth, about the Rh-substrate bond. There are two possible modes of oscillation: (a) the in and out rocking motion with respect to the plane of the paper [see Fig. 3(C.a)]; and (b) the left and right wagging motion in the plane of the figure [see Fig. 3(C.b)]. In each case the displacement from the equilibrium position brings at least one of the CO ligands closer to the Al_2O_3 substrate, thereby changing the coupling with the substrate. Since the amplitude of the motion is temperature dependent, one might suspect that this is the source of the observed temperature dependent shift in the CO stretching modes.

The CO molecules may also librate on the Rh atom, i.e., as if the $\text{Rh}(\text{CO})_2$ complex were waving its "arms." One mode (c) (scissor) is due to bending in the plane of Fig. 3(A) about the C-Rh-C bond [see Fig. 3(C.c)] and the other is due to motion out of the plane of the figure [see Fig. 3(C.d)]. The motion (d) is a torsion about the substrate to rhodium bond and should not show a temperature dependent shift contribution. We will therefore disregard the torsional mode 3(C.d).

The rock, wag, scissor, and CO stretch modes of the Al_2O_3 -supported $\text{Rh}(\text{CO})_2$ complex are coupled through the electrodynamic interaction with the substrate. At room temperature and below the CO stretching motion is in its vibrational ground state. This CO stretching

frequency is much higher than the other modes of the $\text{Rh}(\text{CO})_2$ complex and, consequently, we will treat the motions separately, i.e., for a given angular excursion, we solve the equation of motion for the vibrational modes of the coupled CO molecules in the $\text{Rh}(\text{CO})_2$ species and then average over the motion of the remaining modes (i.e., the rock, wag, and scissor modes).

Since we are interested only in the shift of CO vibrational frequency, we will use classical equations of motion to describe the behavior of the molecules. A similar approach, for instance, has been used to analyze Raman scattering of molecules in the vicinity of a metal surface.¹¹ The parameter of interest is the intrinsic dynamic dipole moment $\mu = xq$, where $x = |\mathbf{r} - \mathbf{r}_0|$ is the displacement with respect to equilibrium separation $|\mathbf{r}_0|$ and q is the effective dynamic charge of the oscillating dipole. The equation of motion of the intrinsic dynamic dipole moment of a gas phase CO molecule is¹¹

$$\ddot{\mu} + \omega_0^2 \mu + 2\Gamma \dot{\mu} = \frac{q^2}{m} E_e, \quad (1)$$

where ω_0 is the resonant frequency, Γ is a damping constant, m is the effective mass of the vibrational motion, and E_e is the component of the driving electric field along the dipole axis. It should be noted that the intrinsic dynamic dipole moment appears whenever the molecule is

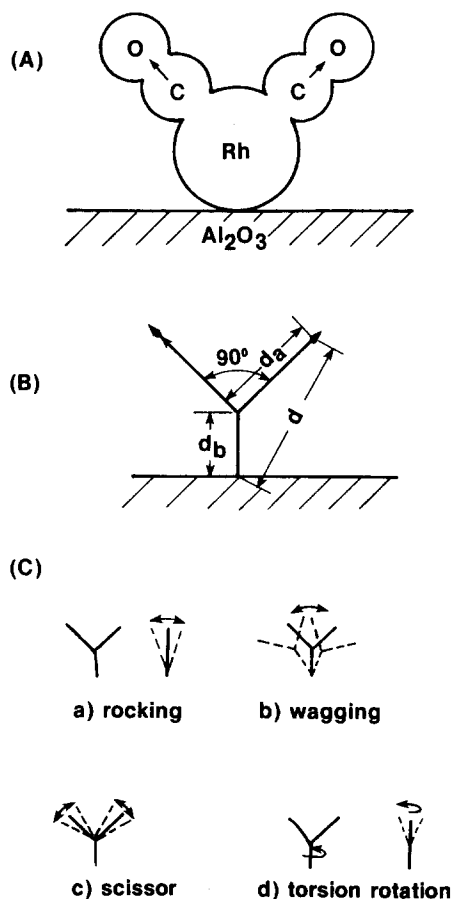


FIG. 3. Models for the calculation of infrared frequency shift: (A) $\text{Rh}(\text{CO})_2$ complex supported on Al_2O_3 ; (b) definition of coordinates; (c) description of low frequency motion of the $\text{Rh}(\text{CO})_2$ complex.

oscillating. On the other hand, in the presence of an external electric field, the electronic charge distribution is polarized irrespective of the vibrational motion of the molecule. Since we are dealing with frequencies much smaller than those necessary for electronic excitation, we consider the electronic response to be independent of frequency.

The total dynamic dipole moment of a driven molecule is

$$\mu_T = \mu + \mu_e, \quad (2)$$

where μ is the intrinsic dynamic dipole moment of Eq. (1) and μ_e is the induced electronic dipole moment

$$\mu_e = \alpha_e E_e, \quad (3)$$

where α_e is the electronic polarizability of the molecule along the long axis of the molecule. The total polarizability of the gas phase molecule along this axis is⁶

$$\alpha = \alpha_e + \frac{q^2/m}{\omega_0^2 - \omega^2 - 2i\Gamma\omega}. \quad (4)$$

The vibrational motions of the two CO molecules residing on a Rh atom, as shown in Fig. 3(C), are coupled together by several mechanisms both electronic and electrodynamic in origin. All except the interaction through the substrate would be present in a hypothetical $\text{Rh}(\text{CO})_2$ gas phase molecule. The overall coupling leads to the splitting of the two degenerate CO stretch vibrational modes into two normal modes. The two intense peaks in Fig. 1 are the symmetric (high frequency) and antisymmetric (low frequency) modes of the $\text{Rh}(\text{CO})_2$ complex.

Since the dynamic dipole moment of the normal modes produces an image in the substrate, the image field couples with the dynamic dipole moment leading to change in the normal mode frequency. The shift is dependent on the magnitude of the image field which is in turn strongly dependent on the distance to the substrate. This coupling is included in the equation of motion described next.

The equations of motion of the intrinsic dipole moment of the two coupled CO oscillators including interactions with the substrate are

$$\begin{aligned} \ddot{\mu}_1 + \omega_0^2 \mu_1 + 2\Gamma \dot{\mu}_1 &= q^2/m [E_{e1} + f \mu_2 + (g_a + g_b + g_c) \mu_1 + (h_a + h_b) \mu_2], \\ \ddot{\mu}_2 + \omega_0^2 \mu_2 + 2\Gamma \dot{\mu}_2 &= q^2/m [E_{e2} + f \mu_1 + (g_a + g_b + g_c) \mu_2 + (h_a + h_b) \mu_1], \end{aligned} \quad (5)$$

with the following parameters and limiting conditions: f is the coupling between the oscillators ignoring the electrodynamic interaction with the substrate, g is the coupling of the dynamic dipole to its own image in the substrate, and h is the coupling of its neighbor's image. The subscripts a , b , and c refer to the librational modes a , b , and c described previously. The scissor mode c has a much higher frequency than the rocking and wagging modes of the $\text{Rh}(\text{CO})_2$ complex. Consequently, the contribution of the scissor mode to the temperature dependent frequency shift of the CO stretch mode is negligible.

We keep the g_c coupling term to show this explicitly; the coupling term h_c which would give a result of the same order of magnitude is neglected.

The dipole moments in the above equation which are multiplied by g and h should be the total dipole moment μ_{T1} and μ_{T2} . We will not consider this refinement since it makes less than a 10% difference in the final result.

Using the geometry as shown in Fig. 3 and after some tedious algebra, we find the coupling parameters to order θ^2 to be

$$g_a + g_b + g_c = \frac{0.282}{d^3} (1 + 1.17\theta_a^2 - 0.557\theta_b^2 - 0.279\theta_c^2) \delta, \quad (6)$$

$$h_a + h_b = \frac{0.222}{d^3} (1 + 0.508\theta_a^2 + 0.938\theta_b^2) \delta, \quad (7)$$

where θ_a , θ_b , θ_c are the angles from equilibrium of the various modes and

$$\delta = \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1}. \quad (8)$$

$\delta = 0.453$ for sapphire (Al_2O_3)¹² at $\omega = 2000 \text{ cm}^{-1}$. In Eq. (6) the minus signs occur due to the fact that the CO molecule is inclined to the substrate in the direction of motion of the particular normal mode. The sign of the interaction of a dipole with its image when the dipole is parallel to the substrate has opposite sign to the interaction of a dipole perpendicular to the substrate. A linear term in θ_b and θ_c has been left out of the $(g_a + g_b + g_c)$ term since it averages to zero (as will all odd powers of θ) and does not contribute to the final result. The new frequencies due to the coupling to the substrate are

$$\begin{aligned} \omega_{\pm}^2 = \omega_0^2 - \frac{q^2\delta}{md^3} [0.282(1 + 1.17\theta_a^2 - 0.557\theta_b^2 - 0.279\theta_c^2) \\ \mp 0.222(1 + 0.508\theta_a^2 + 0.938\theta_b^2)], \end{aligned} \quad (9)$$

where ω_{0+} and ω_{0-} are the symmetric and antisymmetric vibrational modes of the pair of molecules excluding interactions through the substrate.

Experimentally, one observes an approximately equal decrease in frequency of both symmetric and antisymmetric modes with increase of temperature. In order for this to occur, the wagging mode (b) of the librational motion must have a much smaller amplitude than the a rocking mode. There is also an unequal contribution to the frequency shift of the symmetric and antisymmetric CO modes from mode (a). However, the difference in shift for the two modes is about one third that of the absolute shift and would not have been detected experimentally.

The librational motion may be represented by the Hamiltonian

$$H = \frac{\hbar^2}{2I_a} \frac{d^2}{d\theta_a^2} + \frac{1}{2} I_a \Omega_a^2 \theta_a^2. \quad (10)$$

To find the temperature variation of the vibrational frequencies we have to take a thermodynamic average of the expectation values of θ_a^2 and θ_b^2 using the harmonic oscillator wave functions. Then

$$\langle \langle \omega_{\pm}^2 \rangle \rangle = \omega_{0\pm}^2 - \frac{a\hbar}{2I_a \Omega_a} \coth \frac{\hbar \Omega_a}{2kT} + \frac{a'\hbar}{2I_c \Omega_c} \coth \frac{\hbar \Omega_c}{2kT}, \quad (11)$$

TABLE I. Parameters in reference to Fig. 3 used in the calculation.

CO bond length = 1.15 Å
Rh atomic radius = 1.34 Å
Rh-C bond length = 1.83 Å
$d_a = 2.40$ Å
$d_s = 1.34$ Å
$d = 3.48$ Å
C-Rh-C angle = 90°

where

$$a = \frac{q^2 \delta}{m d^3} (0.330 \pm 0.113), \quad a' = \frac{q^2 \delta}{m d^3} (0.0787),$$

and $\bar{\omega}_{0+}$ and $\bar{\omega}_{0-}$ are the symmetric and antisymmetric vibrational modes, respectively, including the temperature independent interactions with the substrate. We have ignored the side to side wagging mode (b) as mentioned previously. Finally, the shift of the CO stretch as a function of temperature is

$$\Delta \omega_{\pm} = \frac{-a \hbar}{4 I_a \Omega_a \bar{\omega}_{0\pm}} \coth \frac{\hbar \Omega_a}{2 k T} + \frac{a' \hbar}{4 I_c \Omega_c \bar{\omega}_{0\pm}} \coth \frac{\hbar \Omega_c}{2 k T}. \quad (12)$$

For the system in question, $kT \gg \hbar \Omega$; consequently,

$$\Delta \omega_{\pm} = \frac{-a k T}{2 \bar{\omega}_{0\pm} I_a \Omega_a^2} + \frac{a' k T}{2 \bar{\omega}_{0\pm} I_c \Omega_c^2}. \quad (13)$$

The measured temperature dependence of the shift of the symmetric stretch frequency $\Delta \omega_{+}$ is shown in Fig. 2. Using the physical constants tabulated in Table I, we evaluate the frequency shift. The contribution of the CO scissor motion (c) is negligible. The experimental curves of Fig. 2 are reproduced if we use $\Omega_a = 4.5 \text{ cm}^{-1}$ as the rocking frequency of the whole $\text{Rh}(\text{CO})_2$ complex. This corresponds to an angular excursion of about 45° from the normal. For comparison, the rotational frequency of a hypothetical $\text{Rh}(\text{CO})_2$ gas phase molecule with an equivalent moment of inertia is $4.6 \times 10^{-2} \text{ cm}^{-1}$, suggesting that 4.5 cm^{-1} is not an unreasonable frequency for this hindered rotational motion. Recently, ^{13}C -NMR studies of CO chemisorbed on Rh surfaces identical to this sample have detected low frequency motion in the adsorbed CO species.¹³ This may be due to fluxional or ligand exchange processes or to restricted diffusion over small metal particles. The frequency of motion seen by NMR is several orders of magnitude smaller than the rocking frequency of the $\text{Rh}(\text{CO})_2$ complex detected here.

We conclude therefore that it may be reasonably expected that the observed vibrational frequency decrease

with increasing temperature is caused by the increase of the electrodynamic coupling between the dynamic dipole moment of the adsorbed complex and the Al_2O_3 substrate due to the rocking motion of the $\text{Rh}(\text{CO})_2$ complex.

SUMMARY

An electrodynamic model of the coupling of the vibrational normal modes of a $\text{Rh}(\text{CO})_2$ complex with the Al_2O_3 substrate is presented. It is found that the experimentally observed temperature dependent shift in the vibrational frequency of the CO molecules may be accounted for by the change in the excursion amplitude of rocking motion of the $\text{Rh}(\text{CO})_2$ complex as a function of temperature. As the temperature decreases the excursion amplitude decreases in turn, decreasing the coupling with the substrate which leads to an increase in the vibrational frequency of the CO normal modes.

It should be mentioned that the direction of shift in frequency as a function of temperature is a significant result of the theory. The direction of the frequency shift and order of magnitude of the results make the model presented plausible.

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