JOURNAL OF CATALYSIS 33, 57–61 (1974)

# Surface Coverage Effects on Adsorption Heat, IR Spectral Position, and Surface Potential Change for Chemisorbed Carbon Monoxide by Simple LCAO-MO Calculations

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Received September 7, 1973

Theoretical correlations among the differential heat of adsorption, the infrared spectral position for C–O bond, and the surface potential change with surface coverage ($\theta$) are derived for carbon monoxide chemisorbed on metal by applying simple molecular orbital theory to $\pi$-system of metal–carbon–oxygen bonds. The effects of the surface coverage on these quantities are generally expressed by $\xi\theta/(1 + \omega\theta)$ where $\xi$ and $\omega$ are constants, i.e., asymptotic behaviors are found to approach $\xi\theta$ for small $\theta$ and a constant for large $\omega\theta$. Qualitative comparisons of these quantities with available experimental data are given.

## INTRODUCTION

An understanding of the adsorption of carbon monoxide on solid surfaces contains many fundamental problems concerning the interactions between the gas phase and solid surfaces. The stable nature of the surface complexes of the carbon monoxide on many transition metals is attributed to a "back donation" or the interaction between $d\pi$-orbital of the metal and $p\pi^*$-antibonding orbital of the carbon monoxide by an analogy to the metal carbonyl complexes. This concept has applied to the interpretation of the position and intensity changes of the infrared band for C-O (*1*, *2*) and also to the surface potential changes (*3*), which occur due to the chemisorbed carbon monoxide. The simple molecular orbital models proposed by Blyholder (*4*, *5*) have successfully accounted for the experimental data on infrared spectra for carbon monoxide adsorbed on metallic surfaces. It is assumed in his one metal atom or metal cluster model that the extent of filling energetically higher orbitals (produced by $d\pi$–$p\pi^*$ interactions) with electrons depends on the competition between these orbitals and the orbitals on surrounding metal atoms for charge. The filling is, therefore, affected by the configuration of surrounding atoms, an increase in surface coverage, addition of other gases, alloying, etc.

Recently, additional experimental results have been published by French workers (*6*, *7*) concerning the interactions between chemisorbed carbon monoxide and other gases such as electron-donor or acceptor compounds adsorbed on platinum (*6*, *7*) and other transition metals (*6*). They concluded that electron transfer may take place through the metal surface atoms between different species simultaneously chemisorbed, in other words, the extent of the electron available for the back-donation could be affected by "long distance" (*7*) effects between absorbates. These experimental results stimulated the author to formulate the effects of such "long distance" or "indirect" interactions between chemisorbed carbon monoxide on several characteristic surface quantities.

In this paper the author presents a

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theoretical correlation between the surface coverage and the surface quantities (differential heat of adsorption, surface potential change, and infrared spectral position) for chemisorbed carbon monoxide and presents a qualitative comparison with the available experiments.

## THEORY

Calculations were made by simple Hückel molecular orbital technique (HMO) which has been found to be at least qualitatively useful not only in organic chemistry (*8*) but also in chemisorption calculations (*9*). The HMO for $\pi$-system was applied to the linear carbon monoxide where the molecule is linked to only one metal atom (i.e., M–C–O; M is surface metal atom), since this is the most extensively accepted structure among the several feasible structures for chemisorbed carbon monoxide (*10*).

Solving the secular equation $\mathrm{Det}(H_{rs} - ES_{rs}) = 0$ by HMO method, the energy ($E_j$) of the $j$th molecular orbital, which is the linear combination of metal ($\phi_M$), carbon ($\phi_C$), and oxygen ($\phi_O$) atom orbitals, and the corresponding molecular orbital function ($\Psi_j$) are obtained as

$$E_1 = \alpha + 2.73\beta \quad (1)$$

$$E_2 = \alpha + \beta \quad (2)$$

$$E_3 = \alpha - 0.73\beta \quad (3)$$

$$\Psi_1 = 0.21\phi_M + 0.58\phi_C + 0.79\phi_O, \quad (1)'$$

$$\Psi_2 = 0.58\phi_M + 0.58\phi_C - 0.58\phi_O, \quad (2)'$$

$$\Psi_3 = 0.79\phi_M - 0.58\phi_C + 0.21\phi_O. \quad (3)'$$

The Coulomb energy of atom $r(H_{rr})$ and the exchange or the overlap energy between atom $r$ and atom $s(H_{rs}$ or $ES_{rs})$ were fixed as follows

$$H_{MM} = \alpha(<0), H_{CC} = \alpha + \beta, H_{OO} = \alpha + 2\beta, H_{MC} = H_{CO} = \beta(<0), S_{rr} = 1 \text{ and } S_{rs} = 0\ (r \neq s),$$

where Coulomb energies have been chosen after the concept based on the electronegativity of the atom involved. The choice of exchange energies is somewhat arbitrary; however, a different choice does not give significant different answers for the results shown in the present work. The lowest molecular orbital ($\Psi_1$) which has a positive sign for all the coefficients is filled with two electrons. Further electrons go into the $\Psi_2$ orbital which is bonding for the M–C bond and antibonding for the C–O bond. We now represent the extent of the electron which could go into $\Psi_2$ by $\delta$. Therefore, $\delta$ is regarded as a quantity indicating the availability of the $d$-orbital or corresponding to the magnitude of the "back donation." Hence, $\delta$ may depend on the types of surface sites (i.e., adsorbent atoms located at the edges, corners, planes and at dislocations, coordination number of the surface atom, etc.) and on the other gases preadsorbed on the surface and their coverages as well as the carbon monoxide chemisorbed. In this paper, we are concerned with the latter effects of $\delta$ where surface is assumed to be homogeneous.

We define the differential heat of adsorption ($Q$) as the nonlocalized energy in M + CO → M–C–O,* from Eqs. (1) and (2) we obtain

$$-Q = 2(0.23 + \delta)\beta, \quad (4)$$

where the factor 2 in front of the bracket comes from the degeneracy of the $\pi$-orbital. Further, the $\pi$-bond order† ($P_{C-O}$) and charge density‡ ($\eta_{CO}$) of the adsorbed carbon monoxide are given from Eqs. (1) and (2)′ as a linear function of $\delta$ by

$$\eta_{CO} = 2(0.09 - 0.67\delta) \quad (5)$$

$$P_{C-O} = 2(0.91 - 0.33\delta), \quad (6)$$

respectively. $\eta_{CO}$ is charged negatively if $\delta > 0.14$ and the quantity is found to increase with an increase in $\delta$.

It has been observed that as the surface coverage of carbon monoxide increases the vibrational frequency of the band for C–O shifts to higher values (*2, 7, 11, 12*). This will be explained by assuming that $\delta$ decreases with the increase in the coverage,

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* $-Q = \Sigma n_j E_j - (E_{CO} + E_M)$ where $n$ is the number of electrons and $E_{CO}$ and $E_M$ are the energies of $\pi$-system of CO and M, respectively.

† $P_{rs} = n_j C_{jr} C_{js}$ where $C_{jr}$ ($C_{js}$) is the coefficient associated with atom $r(s)$ in the $j$th molecular orbital.

‡ $\eta_r = 1 - q_r$ where $q_r = n_j C^2_{jr}$.

because the bond order $P_{C-O}$ which appears to be proportional to the frequency of the band as described later, increases with the decrease in $\delta$ from Eq. (6). In addition, electron-donor compounds, such as water, ammonia, pyridine, and trimethylamine, simultaneously adsorbed shift the band for C–O to lower frequencies (*6*, *7*). Further the extent of the shift was shown to be proportional to the amount of pyridine adsorbed, and also increases as the first ionization potential of the compounds decreases (*7*). However, when electron-acceptor compounds such as hydrogen chloride or another carbon monoxide is added, the C–O band is shifted to higher frequency (*7*).

These results suggest that $\delta$ is associated with not only surface coverages ($\theta$) but also the sign of charge and charge density of simultaneously chemisorbed species through the surface metal atoms. Therefore, $\delta$ is expected as a first approximation to be proportional to the "net flow" of charge from metal to absorbates ($m$) or vice versa. Hence, the value of $\delta$ is given by

$$\delta = \delta_0 + \sum_m \lambda'_m \eta_m \theta_m \qquad (7)$$

where $\delta_0$ is the initial value at $\theta_m = 0$, and $\lambda'_m$ is a positive proportionality constant. Now considering the effects of chemisorbed carbon monoxide alone on $\delta$, Eq. (7) becomes

$$\delta = \delta_0 + \lambda' \eta_{CO} \theta_{CO} \qquad (8)$$

Substituting Eq. (5) into Eq. (8), one can obtain

$$\delta = (\delta_0 + 0.09\lambda\delta)/(1 + 0.67\lambda\theta) \qquad (9)$$

where $\lambda = 2\lambda'$ and $\theta = \theta_{CO}$.

Using Eq. (9) and rearranging, Q, $\eta_{CO}$, and $P_{C-O}$ are given as a function of $\theta$ by

$$Q = Q_0 - \frac{a\theta}{1 + 0.67\lambda\theta} \qquad (10)$$

$$P_{C-O} = P_0 + \frac{b\theta}{1 + 0.67\lambda\theta} \qquad (11)$$

$$\eta_{CO} = \frac{\eta_0}{1 + 0.67\lambda\theta} \qquad (12)$$

where $Q_0$, $\eta_0$, and $P_0$ are initial values at $\theta = 0$. Here $a$ and $b$ are positive constants, $\eta_0\lambda\beta$ and $-0.33\eta_0\lambda$, respectively, since $\eta_0$ for most transition metals is expected to be negative (i.e., $\delta_0 > 0.14$) from the experimental results on surface potential change (*13*).

## Results and Discussion

The curve represented by Eq. (10) is one of the typical curves (*14*) giving the relation between $Q$ and $\theta$, and it is seen that this curve is initially concave. When $\lambda\theta \ll 1$ (i.e., $\lambda$ or $\theta \simeq 0$) in Eq. (10) the conventional linear relation between $Q$ and $\theta$ is recovered.

Barthier *et al.* (*15*) found a direct linear relationship between $\pi$-bond order defined above and vibrational frequency ($\nu$) for C–O in carbonyl compounds. Assuming a similar relation for the present system, one can obtain from Eq. (11)

$$\nu = \nu_0 + \frac{c\theta}{1 + 0.67\lambda\theta} \qquad (13)$$

where $\nu_0$ is the initial frequency (cm$^{-1}$) at $\theta = 0$ and $c$ is a positive constant since $b > 0$. Equation (13) shows that the frequency should shift to a higher value with an increase in surface coverage.

If the change in surface potential ($\Delta V$), which is induced by molecular adsorption, is considered to be due to an adsorbed species of dipole moment $L$ ($= l\eta$, $l$ is a distance between the surface and the adsorbed molecule); $\Delta V$ is proportional to the total dipole moment of the adsorbates ($\propto Lh\theta$, where $h$ is the number of sites per unit area). Hence, for the present system $\Delta V$ can be expressed as a function of $\theta$ from Eq. (12) by

$$\Delta V = \frac{d\theta}{1 + 0.67\lambda\theta} \qquad (14)$$

where $d$ is a constant ($\propto l\eta_0$) if $l$ is taken to be a constant. The form of Eq. (14) is the same as those derived by the electrostatic method (*16*) or by assuming the existence of direct interactions between the adsorbates (*17*). Here, it has been derived by the molecular orbital method. Hence, the effects of the surface coverage on differential heat of adsorption, IR spectral positions for C–O and surface potential change are generally expressed by $\xi\theta/(1+\omega\theta)$ where $\xi$ and $\omega$ are constants; i.e., asymptotic behaviors of the quantity are found to approach $\xi\theta$ for small $\theta$ and a constant for large $\omega\theta$. Similar behavior has been seen in much of experimental data for the carbon monoxide adsorption on metals; e.g., by Beebe *et al.* (*18*) where the differential heat of adsorption on iron decrease from 18 kcal/mole to around 5 kcal/mole with increasing $\theta$, by Culver *et al.* (*13*) where the surface potential change on nickel approach to saturation value of around $-1.3$ V as $\theta \rightarrow 1$ or by Eisinger *et al.* (*19*), Gomer *et al.* (*20*), and Estrup *et al.* (*21*) where work functions on tungsten or Ni (110) single crystals initially increase with good linearity but tend to a constant value for large $\theta$.

The experimental results have also been explained to some extent by assuming direct interactions between adsorbates or a priori heterogeneity of surface or by surface rearrangement during adsorption (*21*). The present work shows that the asymptotic behavior of the quantities for large $\theta$ can be also interpreted by the "indirect" interactions between adsorbates without the postulations mentioned above.

A quantitative comparison of the model with the experimental data would not be enlighting, since a detailed knowledge of $\lambda$, $\beta$, etc., is not available. An additional problem in interpreting experimental results is the difficulty of obtaining the correct value of the surface coverage corresponding to a definite adsorbed state, since several different adsorbed states may be possible for chemisorbed carbon monoxide on single crystals (*22*) or on polycrystals (*2*, *12*).

The contribution of $\sigma$-bond between the surface metal atom and carbon atom in the carbon monoxide adsorbed has not been considered in the above calculations. It seems reasonable to expect the $\sigma$-bonding to remain approximately constant* and also the $\sigma$- and $\pi$-bonds to be separable, then $Q_0$ and $d_\sigma\theta$ due to $\sigma$-bonding should be added as the extra terms to the right side of the Eqs. (10) and (14), respectively. The constant $d_\sigma(\propto l\eta_\sigma)$ should be positive since $\sigma$-bonding is believed to take place by the donation of the lone pair on the carbon atom (i.e., 5 $\sigma$ doublet) to the metal. This suggests the possibility of a maximum value in surface potential change as a function of surface coverage, at $\theta$ max $= (\sqrt{-d/d_\sigma} - 1)/0.167\lambda$; this phenomenon has been observed experimentally, though other explanations have been offered to explain it (*23*).

Presently it seems very hard to make a quantitative estimation of the contribution of "back donation" to the chemisorption of carbon monoxide. The calculation by Grimley (*24*) suggests that on nickel surface about 84% of the binding energy is contributed by "back donation" into the $\pi^*$ orbital. For metal carbonyl molecules some workers (*25*) for $Ni(CO)_4$ obtained the results showing a significant role of "back donation" by using SCF-MO calculation, while others (*26*) obtained the different results for $Cr(CO)_6$, $Mn^+(CO)_6$, etc.

The present calculations have been done using the simple Hückel-MO method which might be criticized as an oversimplification. The calculation using a more rigorous MO-model (e.g., SCF-MO) as used for metal carbonyl molecules would be more acceptable. However, it is still very difficult and not particularly rewarding for the present problem, since we presently have only a limited knowledge concerning the orbitals of the surface atom of the metals due to diminution of the symmetry. Additionally a limited comparison between SCF-MO and simple Hückel-MO was carried out by Blyholder (*27*) for a six-linear-chain model where it was shown that the latter model gives a reasonably good description of the orbital change with the energy change of an end atom. Hence, we expect the present calculations to give a good description of the behavior of the physical quantities though a more detailed description using a more realistic model would be desirable.

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* For instance, when electrons concerned with $\sigma$-bonding are strongly localized at each surface complex.

## ACKNOWLEDGMENTS

The author wishes to thank Professors D. Lichtman and D. E. Beck for reading the manuscript and for valuable suggestions.

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