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ACTIVATION OF CARBON MONOXIDE ON SODIUM CLUSTERS CNDO CALCULATIONS

By

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Abstract

The 'on-top' adsorption of CO on the hollow site of Na₅[4,1] cluster has been shown to be the probable mode of adsorption. The optimum distances for Na₅-CO as well as Na₅C-O bonds have been deduced from the variation of total energy as a function of these distances. The existence of an inverse linear relationship between M-CO (where M=Na₅, Cu₅, Ni₅) bond distance and the experimental heat of adsorption of CO is also shown.

Introduction

In recent times with the advent of modern surface analytical tools which can directly probe the changes in molecular levels, there is an urgent need for rationalizing the observed electronic structure of molecules by virtue of activation on surfaces. Among the various available molecular species, carbon monoxide is one of the adsorbates, whose molecular level changes as a result of adsorption has been investigated extensively both by theoretical calculations¹⁻³⁾ as well as by experimental techniques⁴⁻⁷⁾ like UPS, EELS, IR and XPS. The reasons for the choice of CO as a prototype are:

1) It can act both as a σ -base and π -acid so that in one and the same adsorbed species one can ascertain both bonding as well as backbonding characteristics of the metal, which will indirectly reflect on the density of states of the metal.

2) The knowledge of activation of CO on metals both as molecular or as dissociated species have relevance for *a priori* selection or formulation of catalysts for important reactions like Fischer-Tropsch and methanation reactions.

3) The extent of back donation of electrons from the metal to the antibonding 2π level of CO can be expected to cause further weakening of the

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C-O bond and can thus lead to dissociative adsorption and hence at the same time represent as a model for treating dissociative adsorption.

In this context, the adsorption of CO on alkali metals can be relevant to estimate the extent of back donation as their valence 's' electrons can participate in back bonding similar to transition metal 'd' electrons. However, the experimental studies of adsorption of CO on metals other than transition metals are rare.

Method

The present communication, therefore, deals with the results obtained on the activation of CO on sodium clusters treated within the framework of CNDO calculations. Though it may be desirable to consider many atom clusters for realistic estimate of the parameters, the calculations have been restricted to a five atom cluster in the present calculations. The parameter variations considered in these calculations include i) the configurations of the adsorbed CO species itself, ii) the CO-cluster distance and of the C-O distance for 'on-top' adsorption of CO on the hollow site with its molecular axis parallel to the surface normal with carbon closest to the surface.

The CNDO/2 version calculations have been adopted for the calculation of the molecular energy levels as well as the total energy of the system. The binding energy of each mode of adsorption is calculated by finding the difference between the total energy of the system and the sum of the atomic energies of individual atoms. Details of the CNDO/2 calculation procedures are available elsewhere^{8,9}.

Results and Discussion

1. Geometry of the Five Atom Cluster :

Calculations^{10,11} on sodium clusters available predict that for Na_x ($x=2$ to 8) species, the equilibrium geometries are configurations resembling to those of corresponding Van der Waal's molecules. But Baetzold *et al.*¹² have performed CNDO calculations and have shown that linear structures are more stable than planar or three dimensional configurations for Na_x ($x=2$ to 8) clusters. Linear structures may not represent the real situation on the surface. So, a five atom cluster has been chosen with four atoms in a plane and a single atom lying below the plane (in the notation of ref. (13), $\text{Na}_5 [4, 1]$) to represent the (100) plane of the bcc lattice of the metal.

2. Configuration of Adsorption :

To our knowledge there are no experimental studies available on chemi-

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TABLE 1 Energy values for various modes of adsorption of carbon monoxide on sodium clusters

Mode of adsorption	Total energy ¹ a. u	Binding energy ¹ a. u	Total energy ² a. u	Binding energy ² a. u
CO adsorbed on Na ₅ [4, 1] cluster horizontally	-20.212	5.023	-20.327	4.908
CO adsorbed on Na ₅ [4, 1] cluster vertically through oxygen	-27.373	-2.165	-27.440	-2.205
CO adsorbed on Na ₅ [4, 1] cluster in a bridged configuration	φ	φ	-27.488	-2.252
CO adsorbed on Na ₅ [4, 1] cluster vertically through carbon	-27.453	-2.217	-27.503	-2.267

1—Calculated using the values for Na₅-CO and Na₅C-O distances assumed as sum of the covalent radii.

2—Calculated using the equilibrium distances obtained by geometrical optimization of vertical mode of adsorption. Na₅-CO=2.468 Å Na₅C-O=1.201 Å.

φ —Calculation not carried out due to difficulties in convergence.

sorption of CO over pure sodium metal. Few studies made on adsorption of CO on Na-A zeolites¹⁴⁾ are also not detailed enough to give exact configuration of CO over sodium in the adsorbed state. For various modes of adsorption considered the energies were computed using the Na₅C-O and Na₅-CO distances as equal to the sum of covalent radii. The results of these calculations showed that the vertical adsorption of CO through carbon atom is the stablest mode of adsorption. Therefore geometrical optimization was carried out for this configuration. After finding the geometrically optimized equilibrium distances, again these equilibrium distances for Na₅-CO and Na₅C-O bonds were used and the energies were calculated for various modes of adsorption. The results obtained are summarised in Table 1. The total energies for the horizontal mode of adsorption in which the carbon and oxygen atoms are simultaneously approaching the surface with the molecular axis of CO parallel to the surface (binding energy is unrealistically

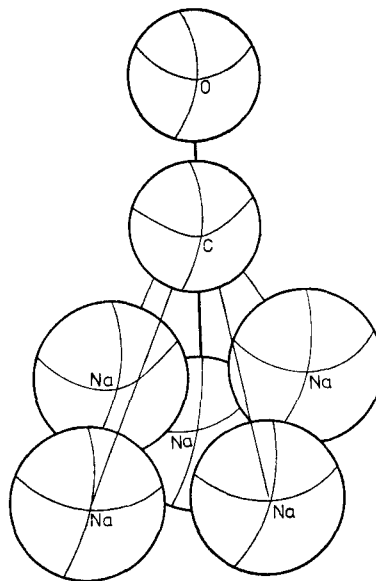


Fig. 1. Vertical mode of adsorption of CO on Na₅ cluster through the carbon atom.

positive) and for the vertical on-site adsorption of CO on Na_5 through the oxygen atom are higher than the vertical on-site adsorption through carbon atom. Though the difference between the binding energy of CO adsorption on Na_5 in a bridged configuration and the binding energy of vertical adsorption of CO through carbon atom is small, the vertical mode of adsorption always has a higher binding energy. Based on this, it is concluded that the vertical adsorption through carbon atom is the most probable form of adsorption and is therefore, chosen to study the adsorption of CO on sodium metal. The schematic representation of adsorption of CO over Na_5 cluster through carbon atom is shown in Fig. 1.

3. Molecular Energy-level Diagram :

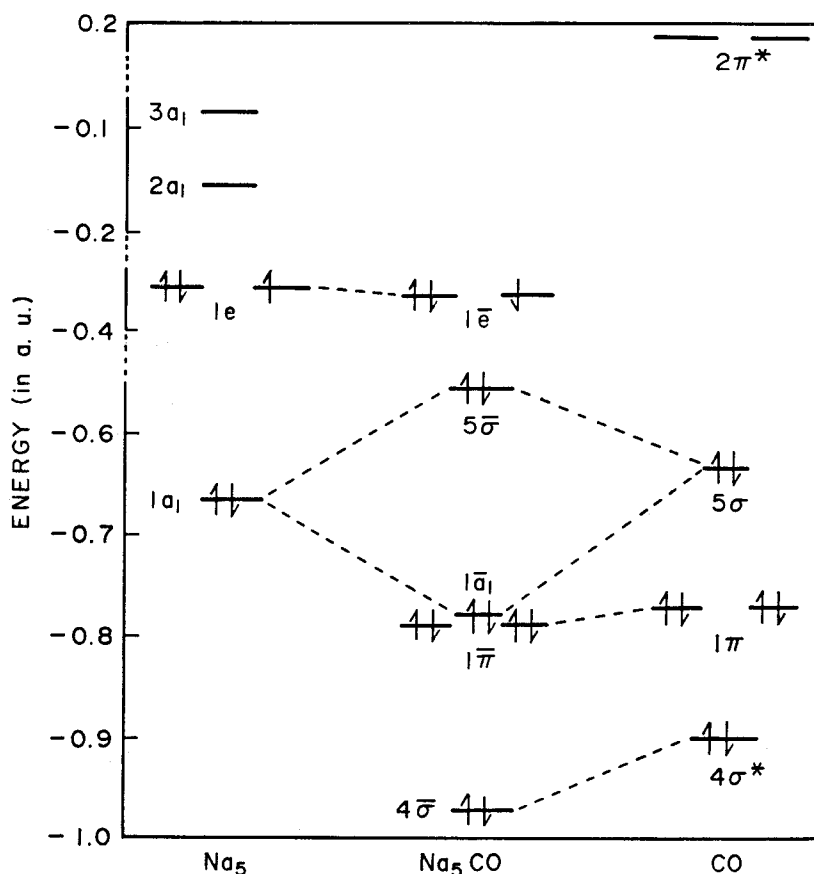


Fig. 2. MO diagram showing the valence level interactions between Na_5 cluster and CO.

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The molecular energy levels of Na_5 cluster, CO and Na_5CO species were computed. The valence energy levels that are undergoing interaction are shown in the molecular energy level diagram (Fig. 2). The $1 a_1$, $1 e$, $2 a_1$ and $3 a_1$ levels of the Na_5 cluster are energetically well above the 3σ and 4σ levels of CO. So the 3σ and 4σ levels have very small interaction with the a_1 level of Na_5 cluster and they are slightly stabilized. The 2π antibonding level of CO is well above the occupied $1 e$ level of the Na_5 cluster and practically there is no interaction between them. This indicates that there is no transfer of metal electron to the antibonding 2π level of CO unlike the back donation of $d\pi$ electrons in the case of transition metals^{15,16}, or donation of $1 e$ electrons from the metal to 2π level of CO as in the case of Li clusters¹⁷. The $1 a_1$ level of Na_5 and 5σ level of CO interact to give

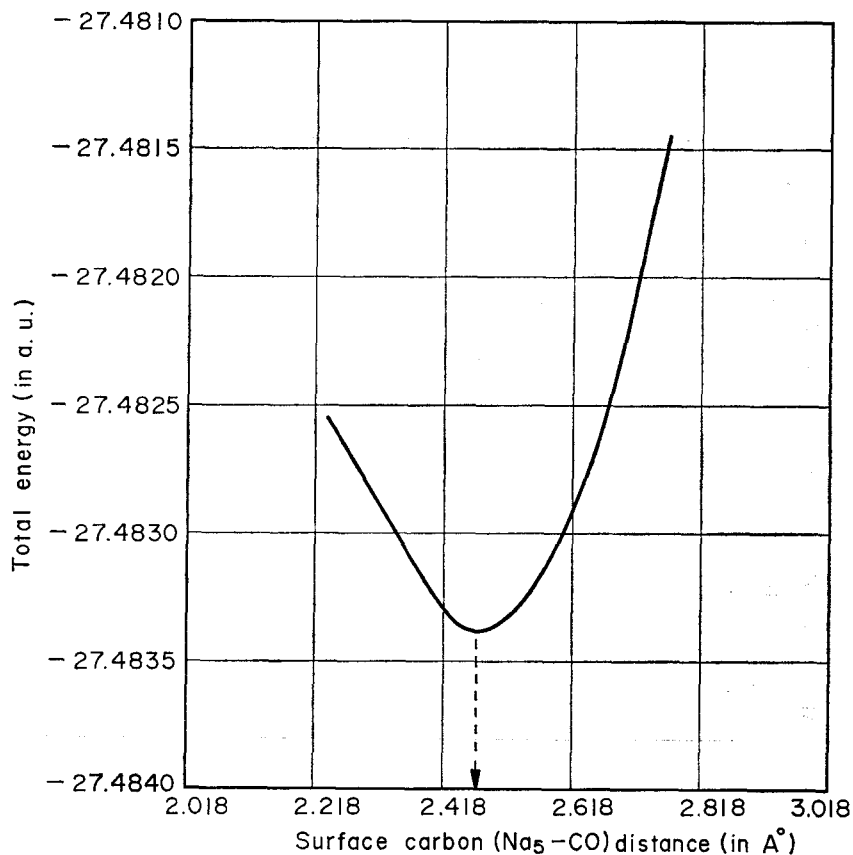


Fig. 3. The variation of the total energy of the Na_5CO species as a function of $\text{Na}_5\text{-CO}$ distance.

stabilized $1 \bar{a}_1$ level and the destabilized $5 \bar{\sigma}$ level and their variations with respect to distance are discussed in the following section.

4. Variation of Surface-Carbon Distance :

Calculations were carried out for various Na_5 -CO distances keeping the C-O distance constant at the value in gaseous state (*i.e.* 1.131 Å). The variation of the total energy of the Na_5CO species as a function of Na_5 -CO distance is shown in Fig. 3. The distance corresponding to the minimum in energy is 2.468 Å. In the adsorbed state the Ni_5 -CO distance (1.588 Å) and Cu_5 -CO distance (1.985 Å) have been reported for the minimum energy configurations and these bond distances are comparatively smaller than the Na_5 -CO distance (2.468 Å) obtained in these calculations. The experimentally determined heats of chemisorption for the adsorption of CO on sodium¹⁴, copper¹⁵, and nickel¹⁶ metals show that the heat of adsorption of CO on sodium is minimum. Fig. 4. gives the plot of the M-CO (where $M = \text{Na}_5$, Cu_5 , and Ni_5) distance against the heat of chemisorption of CO on these

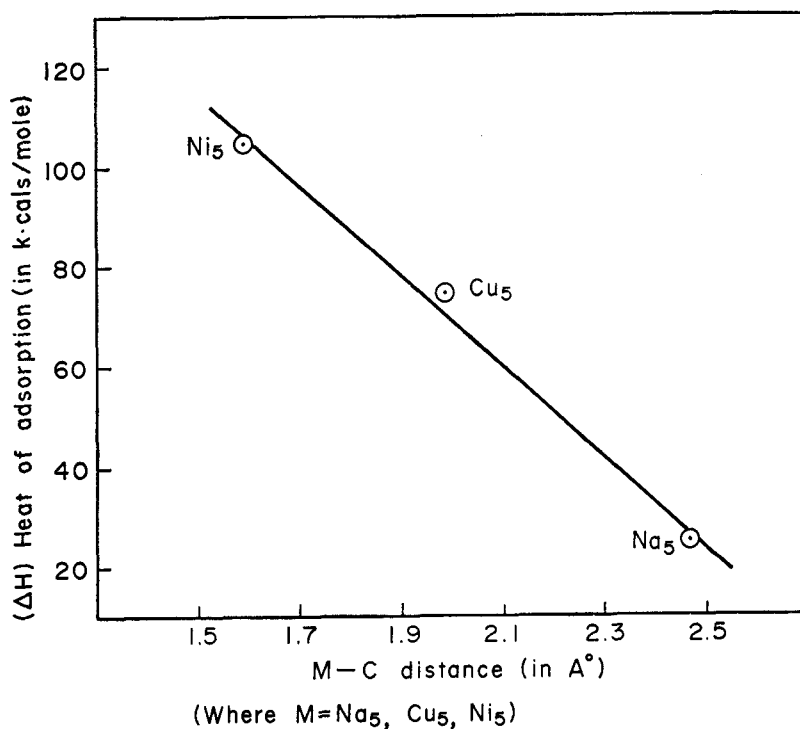


Fig. 4. Correlation between M-CO (where $M = \text{Na}_5, \text{Cu}_5, \text{Ni}_5$) distance and the experimental heats of adsorption.

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metals. There is an inverse linear relationship between M-CO distance (or in other words M-C bond order) and the heat of chemisorption. It is therefore, a natural consequence that the calculated $\text{Na}_5\text{-CO}$ distance is comparatively greater because of the low heat of chemisorption. This weak binding of CO to Na_5 is probably acceptable due to the absence of transfer of 1 e electrons of sodium to 2π level of CO while in transition metals it is known that the $d\pi$ electrons populate the 2π level of CO due to back donation, leading to a strong bond between $\text{Ni}_5\text{-C}$ or $\text{Cu}_5\text{-C}$ and in some cases even cause the dissociation of CO. In Na_5CO system $1\bar{a}_1$ is the bonding combination of $1a_1$ of Na_5 and 5σ of CO, and so when the $\text{Na}_5\text{-CO}$ distance is increased the $1\bar{a}_1$ level is destabilized and in turn the antibonding combination $5\bar{\sigma}$ is getting stabilized. The other levels are not affected much by the

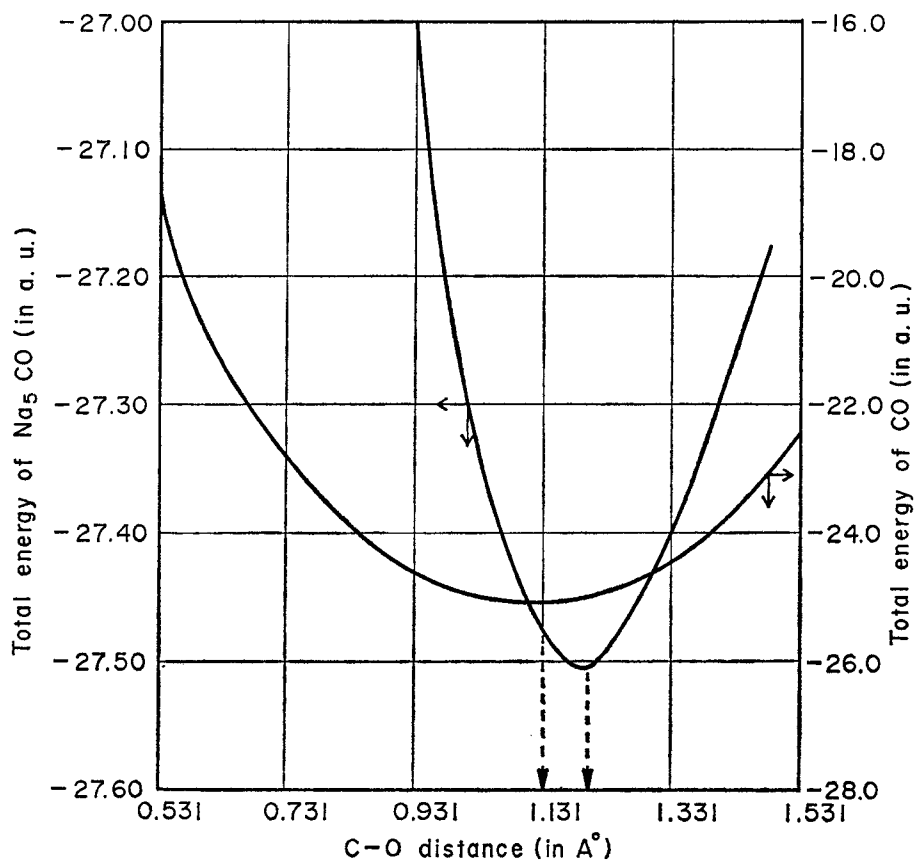


Fig. 5. The variation of the total energy of the Na_5CO system and that of CO molecule as a function of C-O distance.

variation of the $\text{Na}_5\text{-CO}$ distance showing that they exhibit only a small interaction.

5. *Variation of the $\text{Na}_5\text{C-O}$ Distance :*

For the same configuration considered in the previous section, the calculations have been carried out by varying the C-O distances keeping the $\text{Na}_5\text{-CO}$ distance at the equilibrium value namely 2.468 Å. The variation of the total energy of CO and Na_5CO as a function of C-O distance is shown in Fig. 5. The equilibrium distance for free CO was 1.131 Å which agrees with the reported C-O distance, while in the adsorbed state it is stretched and the equilibrium distance deduced is 1.201 Å. This shows that the C-O bond is weakened due to chemisorption. The dissociative chemisorption of CO may not be probable since the binding energies calculated for Na_5C and Na_5O species are positive. Further, stretching of C-O bond causes the stabilization of $1\bar{e}$ energy level indicating it as a antibonding combination of $\text{Na}_5 1e$ and CO 1π levels. Since the frontier orbital is getting stabilized due to stretching, it is less probable that CO may be dissociated.

Conclusions

The CNDO/2 calculations carried out on the interaction of CO on Na_5 cluster show that the adsorption of CO on sodium metal is weak and the calculated equilibrium distance for the M-C bond correlates with observed heat of adsorption. The absence of backbonding in the case of sodium metal and CO acting as a σ -base alone are the causes for the weak adsorption bond of CO on sodium metal.

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