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MODEL CALCULATION FOR THE FREQUENCY SHIFT IN CO COADSORBED WITH K ON Cu(001)

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The dramatic frequency shift recently observed for CO coadsorbed with alkali atoms on transition metals is analyzed by calculating the electronic structure of $Cu_{12}K_2CO$ and by comparing it with that of $Cu_{12}CO$, K_2CO, CO^-, and CO at the self-consistent Hartree–Fock model-potential level. The CO vibrational frequency in the coadsorbed system is reproduced by the calculation, and the frequency shift is elucidated: it is brought about by electron redistribution which leads to reduction of the overlap population between the C and O. The electron redistribution is caused mainly by an increase of electron flow into the 2π level due to a downward shift of this level because of direct interaction between CO and K.

1. Introduction

Systems in which carbon monoxide is coadsorbed with alkali atoms such as potassium have been studied extensively both theoretically and experimentally in recent years, to understand how the coadsorption of catalytic promoters affects the electronic structure of reactants [1]. Among the influences of an alkali on coadsorbed CO, the frequency shift of the C–O stretching vibrational frequency is a very dramatic one. The present work has been motivated to investigate this dramatic frequency shift which is reported to amount to more than 500 cm^{-1} [1,2]. The most widely accepted model to understand the CO frequency shift on a metal surface is the Blyholder-type picture of CO bonding [3], i.e., the electron occupation of the antibonding CO 2π level weakens the CO bond and results in a decrease in the C–O stretching frequency. This model may not be applied in the original form and a careful analysis will be needed to understand the large shifts observed upon alkali metal promotion, because the vibrational frequency of CO^-, where one extra electron occupies

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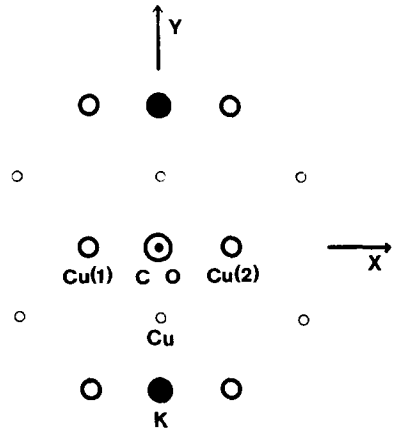

Fig. 1. The geometry of the $Cu_{12}K_2CO$ cluster. Open circle: Cu on the first layer; small open circle: Cu on the second layer; black dot: C; large open circle: O; closed circle: K.

the 2π orbital, has been experimentally observed to be reduced by only ~ 300 cm^{-1} [4]. In this report we will try to elucidate how potassium atoms affect the electronic structure of CO and the CO stretching frequency shift, by calculating the electronic structure of CO coadsorbed with K on a copper surface. We adopt a cluster model, considering that the range of the alkali metal–coadsorbate interaction is primarily short range [5]. The frequency shifts will be analysed in terms of the charge density and molecular orbital contour maps and the gross and overlap population in the CO moiety by comparing them in the cases of $Cu_{12}K_2CO$, $Cu_{12}CO$, K_2CO, CO^-, and CO. The $Cu_{12}K_2CO$ cluster shown in fig. 1 is considered here as a model of the system in which CO is coadsorbed with K on Cu(001), because the most drastic frequency shift has been observed experimentally when the [CO]/[K] ratio reached 0.5 [5]. Among the CO molecular orbitals, the 5σ, 1π and 2π orbitals are the key orbitals to the CO bond change upon adsorption on a metal surface. In this geometry the 5σ orbital belongs to the A_1 irreducible representation of the C_{2v} point group, the $1\pi_x$ and $2\pi_x$ orbitals belong to the B_1 and the $1\pi_y$ and $2\pi_y$ orbitals belong to the B_2. The $1\pi_x$ and $2\pi_x$ orbitals will be subjected to the direct influence of the copper atoms through orbital mixing between CO and Cu(4s), since CO is adsorbed at the bridge site in this model. (A preferential filling of the bridge-bonded site by the CO adsorbate in the presence of the K has been observed experimentally [5,6].) On the other hand, the $1\pi_y$ and $2\pi_y$ orbitals will interact mainly with potassium orbitals. The effects caused by the copper surface and the effects caused by the potassium atoms, therefore, can be distinguished by a separate analysis of the molecular orbitals mainly composed of the CO π_x and π_y orbitals. The effect on the 5σ is estimated by analysing the orbital belonging to the A_1 irreducible representation. The

computational details for this analysis are given in section 2. Section 3 discusses the numerical results.

2. Computational details

We have chosen a $Cu_{12}K_2CO$ cluster as a model to study the interaction of CO with coadsorbed K atoms and the Cu(001) surface. The cluster has C_{2v} symmetry (fig. 1). The section of bulk Cu is represented by the Cu_{12} cluster composed of two layers, each containing six atoms. The Cu–Cu nearest-neighbor distance is taken as 2.56 Å, which is the experimental value for bulk Cu [7]. The CO molecule sits at a bridge site between the central two Cu's (Cu(1) and Cu(2)); the Cu–C distance is fixed to be 2.20 Å. The two K atoms are coadsorbed at bridge sites in such a way that the K–K axis is bisected by the plane which contains Cu(1), Cu(2) and the CO molecule. The Cu–K distance is fixed to be 3.20 Å, which is the sum of the radii of single metallic bonds for the Cu and K [8].

Calculations were performed in the framework of the Hartree–Fock–Roothaan scheme by using the program package JAMOL3 [9]. In order to save computational cost, we utilized a model potential [10] for Cu and K. The model potential for Cu(1) and Cu(2) in the surface layer, to which the CO is bridge-bonded, is the sd-MP set [11]. The sd-MP set represents effects of the electrons except for the outermost 3d and 4s electrons. The model potential for the other ten Cu atoms describes the 28 "core" electrons, and only one electrons (4s) per atom is treated explicitly. We generated the model potential for K, considering 4s and 3p electrons as active electrons. The model potentials, except for the sd-MP set, are determined in the present work in a similar way as in the case of the sd-MP set. All electrons of the C and O atoms are considered as active electrons. The basis sets for C and O are taken from the work of Huzinaga et al. [12]. Basis-set contractions used in this work are as follows in the simple notation (s/p/d):

Cu(1), Cu(2): (5/1*/41),
the other Cu: (5/1*),
K: (41/41*1*),
C, O: (431/211),
where 1* stands for a p-type polarization function [12].

3. Results and discussion

The numerical results are collected in tables 1 and 2. All orbitals and configurations of $Cu_{12}K_2CO$, $Cu_{12}CO$, K_2CO, CO^-, and CO are denoted according to the irreducible representations of C_{2v} so as to make comparison

Table 1
CO stretching frequency ω_e, bond length r_e, force constant κ, overlap population S_{CO} and gross population

	ω_e (cm^{-1})	r_e (Å)	κ ($\times 10^6$ dyne/cm^2)	S_{CO}	Gross population		
					C	O	Sum
CO	2339	1.13	2.21	0.99	5.73	8.27	14.00
$Cu_{12}CO$	1923	1.19	1.49	0.76	6.12	8.33	14.45
CO^-	1752	1.24	1.24	0.38	6.35	8.65	15.00
K_2CO	1673	1.24	1.13	0.24	6.11	8.69	14.80
$Cu_{12}K_2CO$	1393	1.28	0.78	0.17	6.22	8.70	14.92

easy between these five systems. In these calculations the CO stretching frequencies are obtained from potential curves calculated by moving the O atom along the C–O axis.

The C–O stretching frequency ω_e decreases from 2339 cm^{-1} in the gas phase to 1393 cm^{-1} in the $Cu_{12}K_2CO$ cluster, in the sequence of CO, $Cu_{12}CO$, CO^-, K_2CO, and $Cu_{12}K_2CO$. The CO bond distance increases from 1.13 to 1.28 Å in the same sequence. The CO frequency of 1393 cm^{-1} and the CO bond distance of 1.28 Å obtained for $Cu_{12}K_2CO$ compare very well with the experimental values of 1390–1420 cm^{-1} (CO/K/Pt(111)) [5] and 1.27 Å (CO/Na/Pt(111)) [13]. It is worthy to remark here that the red shift in K_2CO is larger than that in $Cu_{12}CO$ (table 1). The red shift of the CO stretching frequency and the lengthening of the CO bond are the reflection of the decrease of the C–O force constant, which is closely related to the decrease of the overlap population as seen in table 1. The red shift of the CO stretching frequency in the presence of coadsorbed K will be interpreted in terms of the decrease of the CO overlap population in the following.

The total gross population of the CO^- molecule is larger by 1.0 compared to that of the CO molecule. The extra one electron in the CO^- occupies the antibonding 2π orbitals resulting in the decrease of the overlap population as shown in table 2. The decrease of the CO overlap population in $Cu_{12}CO$ is due to the occupation of the CO $2\pi_x$ orbital by the back-donated electron from the Cu surface. The back-donation arises through a lowering of the $2\pi_x$ level

Table 2
CO overlap population

	$1\pi_x$	$1\pi_y$	$2\pi_x$	$2\pi_y$
CO	0.38	0.38	0	0
$Cu_{12}CO$	0.35	0.40	−0.39	−0.02
CO^-	0.34	0.34	−0.25	−0.25
K_2CO	0.33	0.27	0	−0.44
$Cu_{12}K_2CO$	0.31	0.28	−0.20	−0.43

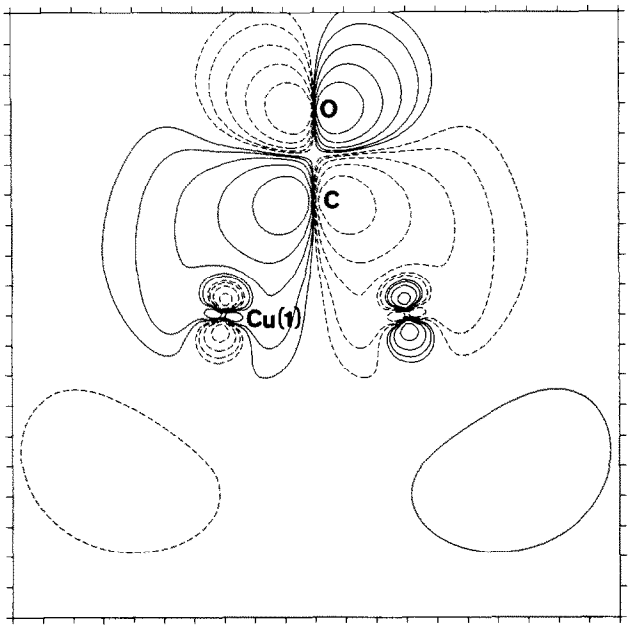

Fig. 2. The contour map of $2\pi_x$ orbital in $Cu_{12}CO$ in the $x-z$ plane.

which is caused by a mixing of this orbital with the metal orbitals. As the metal orbitals participating in the mixing are those mainly composed of Cu(1) and Cu(2), the change of the overlap population occurs in the $2\pi_x$ level (table 2). On the other hand, the decrease of the overlap population occurs in the $2\pi_y$ level in the case of K_2CO (table 2), because the excess electron is transferred from the potassium atoms. The electron flows from K to CO through a level lowering due to mixing of the $2\pi_y$ orbital and the potassium orbitals. Table 1 shows that the effect of K on the overlap population is larger than that of the substrate. The effect of the substrate in the case of $Cu_{12}CO$ and the effect of the coadsorbed K in the case of K_2CO are additive in $Cu_{12}K_2CO$ as seen in table 2 as far as the overlap population is concerned. This additive character of the effects of Cu and K is also seen by comparing the 2π orbitals in $Cu_{12}CO$ (fig. 2) and K_2CO (fig. 3) with those in $Cu_{12}K_2CO$ (figs. 4 and 5). Almost the same amount of decrease of the overlap population of the $2\pi_y$ orbitals is seen in both cases of K_2CO and $Cu_{12}K_2CO$ (table 2). This suggests that the electron is transferred directly from K rather than through the surface, by a direct interaction between K and CO [14].

The Mulliken population analysis indicates a 1.4 electron transfer to the CO 2π level and a backward transfer of 0.5 electrons through the 5σ level. The σ and π electron transfer, although they are directionally opposed,

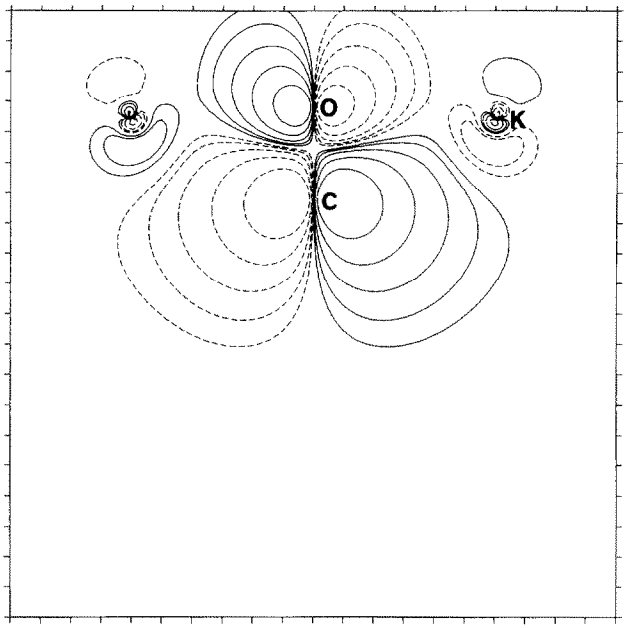

Fig. 3. The contour map of $2\pi_y$ orbital in K_2CO in the $y-z$ plane.

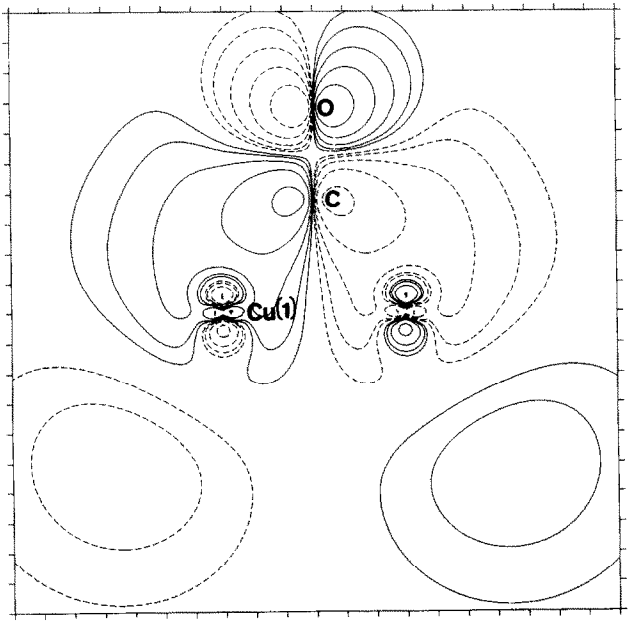

Fig. 4. The contour map of $2\pi_x$ orbital in $Cu_{12}K_2CO$ in the $x-z$ plane.

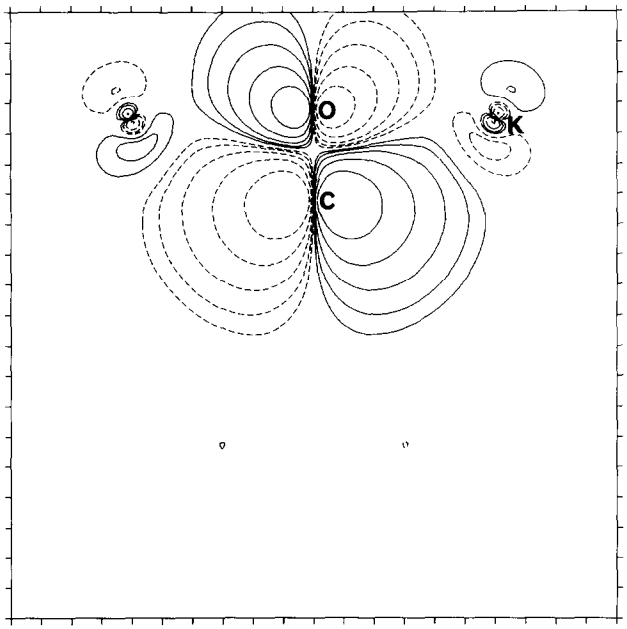

Fig. 5. The contour map of $2\pi_y$ orbital in $Cu_{12}K_2CO$ in the $y-z$ plane.

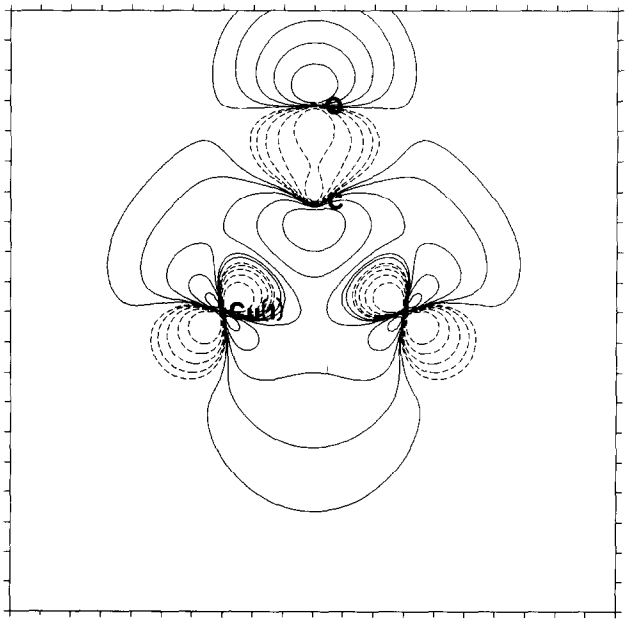

Fig. 6. The contour map of 5σ orbital in $Cu_{12}K_2CO$ in the $x-z$ plane.

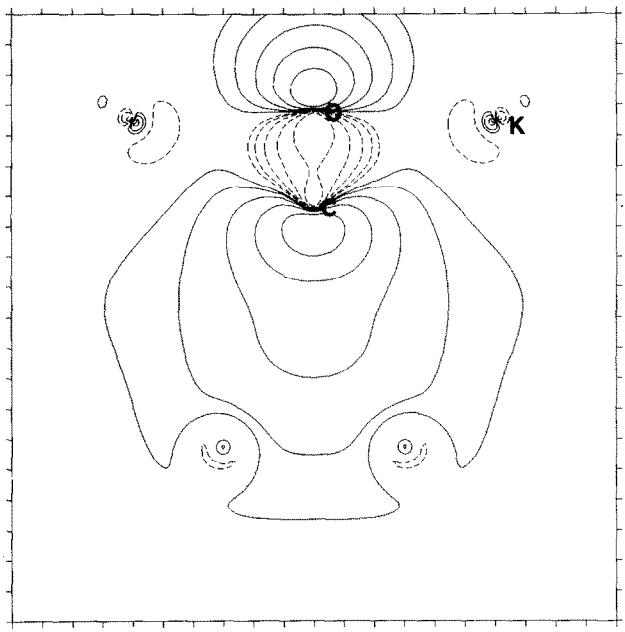

Fig. 7. The contour map of 5σ orbital in $Cu_{12}K_2CO$ in the $y-z$ plane.

contributes to a weakening of the CO bond [15], since the 2π orbital is of antibonding character between C and O as is already discussed and the 5σ orbital is of bonding character as shown in figs. 6 and 7. This electron flow explains why the CO overlap population in $Cu_{12}K_2CO$ is reduced more than that in CO^-, although the total gross population (14.9) in the CO moiety in $Cu_{12}K_2CO$ is smaller than that (15.0) in CO^- (table 1). The excess reduction of the CO overlap population results in a larger frequency shift in the coadsorption system than in CO^-.

The change of the overlap population due to the 1π orbitals is very small compared to the drastic change due to the 2π orbital. The 1π orbital becomes polarized a little towards the O end of the CO molecule, as we can see by comparing the orbital in $Cu_{12}CO$ (fig. 8) with the orbitals in K_2CO (fig. 9) and $Cu_{12}K_2CO$ (figs. 10 and 11). This polarization of the 1π orbital may drive further occupation of the 2π level which weighs on the carbon end as originally suggested by Heskett et al. [16]. We cannot deny the possibility, however, that the occupation of the 2π orbital might have caused the 1π polarization.

As we have seen above, the frequency shift is brought about by electron redistribution which leads to reduction of the overlap population between C and O. The difference of the electron density between $Cu_{12}K_2CO$ and the

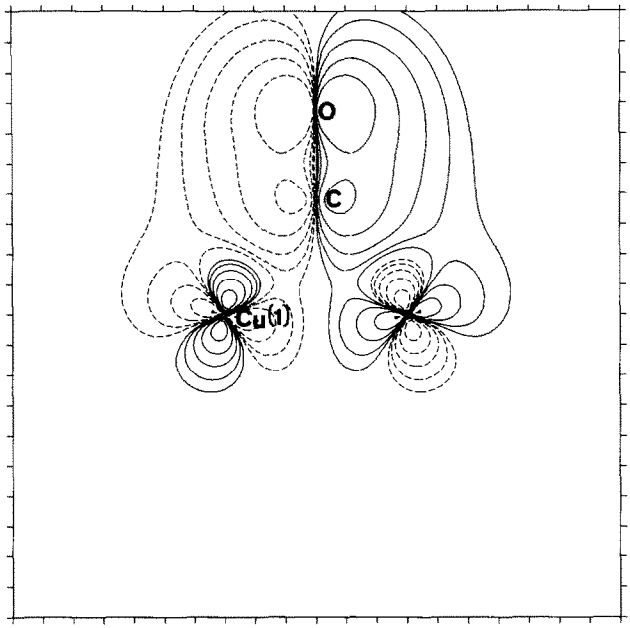

Fig. 8. The contour map of $1\pi_x$ orbital in $Cu_{12}CO$ in the $x-z$ plane.

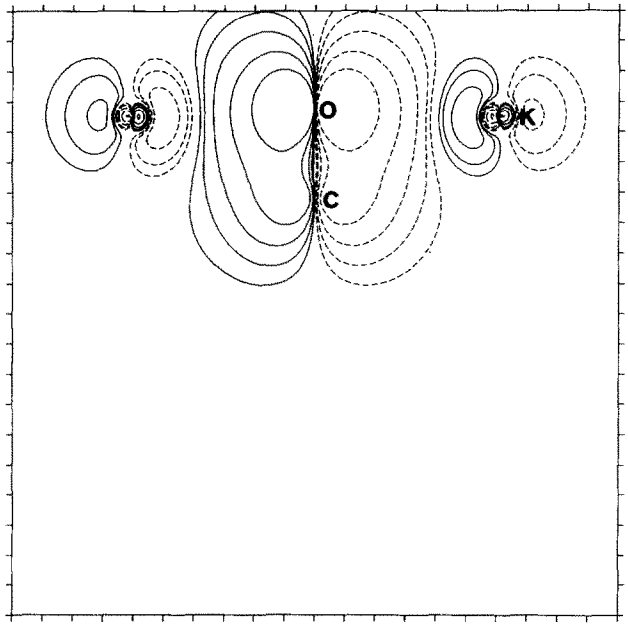

Fig. 9. The contour map of $1\pi_y$ orbital in K_2CO in the $y-z$ plane.

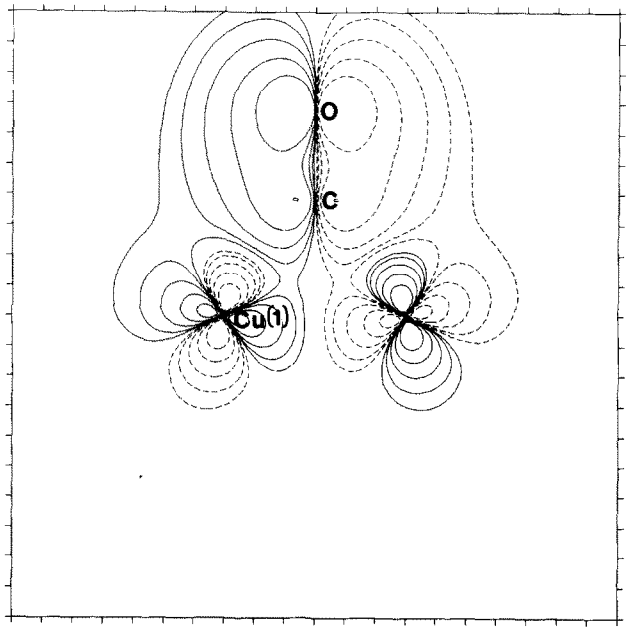

Fig. 10. The contour map of $1\pi_x$ orbitals in $Cu_{12}K_2CO$ in the $x-z$ plane.

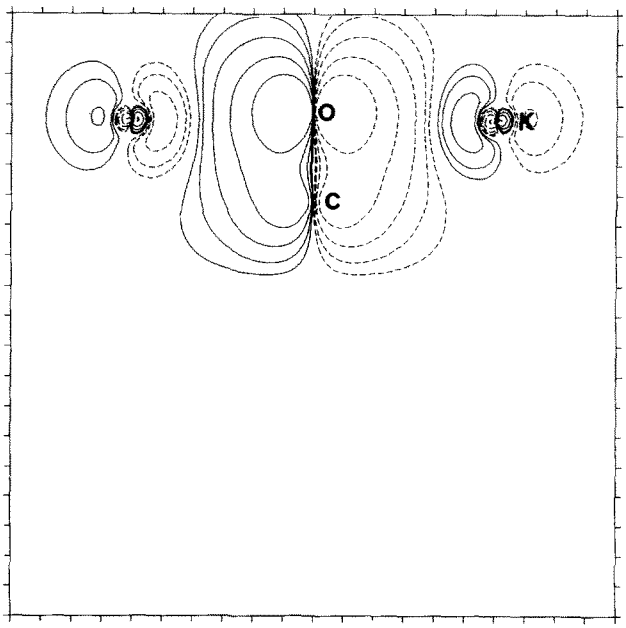

Fig. 11. The contour map of $1\pi_y$ orbitals in $Cu_{12}K_2CO$ in the $y-z$ plane.

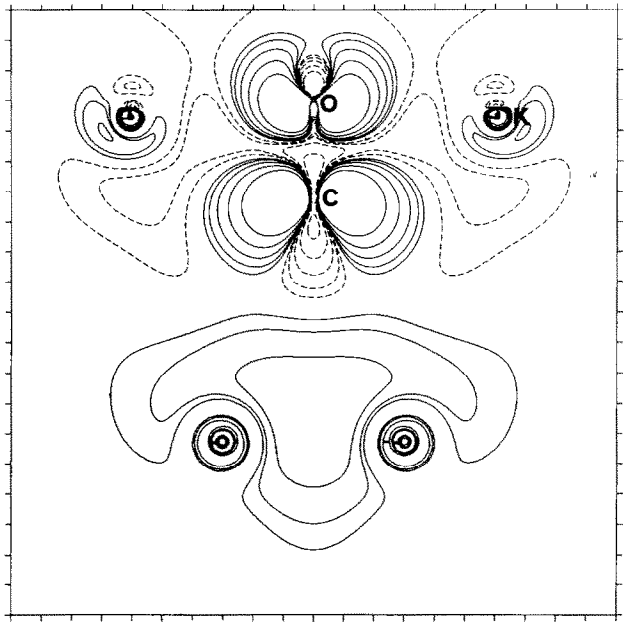

Fig. 12. The electron-density difference $\rho(Cu_{12}K_2CO) - \rho(Cu_{12}CO) - \rho(K_2)$ in the $y-z$ plane.

system $Cu_{12}CO + K_2$ is depicted in fig. 12. The density difference is obtained by subtracting the density in $Cu_{12}CO$ and K_2 from the density in $Cu_{12}K_2CO$. Fig. 12 shows how the electron density of $Cu_{12}CO$ is rearranged under the influence of the coadsorbed potassium atoms: the electron redistribution is seen to be caused mainly by the charge density increases in the $2\pi_y$ orbital.

In summary the drastic red shift of the CO stretching frequency has been shown to be due to the electron flow into the 2π level (1.4 electrons) from the substrate and coadsorbed potassium atoms, and to the electron flow into the substrate (0.5 electrons) through the 5σ level. The effect of K is larger than that of the substrate and the interaction between CO and K is direct rather than indirect through the substrate.

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References

[1] H.P. Bonzel, Surface Sci. Rept. 8 (1987) 43.
[2] D. Hesket, Surface Sci. 199 (1988) 67.
[3] G. Blyholder, J. Phys. Chem. 68 (1964) 2772.
[4] H. Ehrhardt, L. Langhans, F. Linder and H.S. Taylor, Phys. Rev. 173 (1968) 222.
[5] G. Pirug and H.P. Bonzel, Surface Sci. 199 (1988) 371.
[6] J.E. Crowell, E.L. Garfunkel and G.A. Somorjai, Surface Sci. 121 (1982) 303.
[7] R.W.G. Wycoff, Crystal Structures, 2nd ed., Vol. 1 (Wiley, New York, 1965).
[8] L. Pauling, The Nature of the Chemical Bond (Cornell Univ. Press, New York, 1960).
[9] H. Kashiwagi, T. Takada, E. Miyoshi, S. Obara and F. Sasaki, A program package JAMOL3 for SCF-MO calculations.
[10] Y. Sakai, J. Chem. Phys. 75 (1981) 1303;
Y. Sakai and S. Huzinaga, J. Chem. Phys. 76 (1982) 2537, 2552.
[11] Y. Sakai, E. Miyoshi, M. Klobukowski and S. Huzinaga, J. Comput. Chem. 8 (1987) 226.
[12] S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai and H. Tatewaki, Gaussian Basis Sets for Molecular Calculations (Elsevier, Amsterdam, 1984).
[13] F. Sette, J. Stohr, E.B. Kollin, D.J. Dwyer, J.L. Gland, J.L. Robbins and A.L. Johnson, Phys. Rev. Letters 54 (1985) 935.
[14] P.A. Schulz, C.H. Patterson and R.P. Messmer, J. Vacuum Sci. Technol. A 5 (1987) 1061.
[15] B. Silvi, O. Ayed and W.B. Person, J. Am. Chem. Soc. 108 (1986) 8148.
[16] D. Heskett, I. Strathy, E.W. Plummer and R.A. de Paola, Phys. Rev. B 32 (1985) 6222.