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Cite as: J. Chem. Phys. **94**, 8592 (1991); <https://doi.org/10.1063/1.460041>

Submitted: 01 September 1989 • Accepted: 07 January 1991 • Published Online: 31 August 1998

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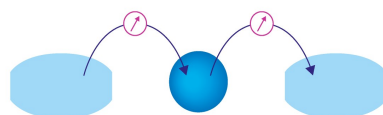
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A photoemission study of the surface carbonate species on Ag{110}

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(Received 1 September 1989; accepted 7 January 1991)

The electronic structure of the surface carbonate species adsorbed on Ag{110} has been studied with angle-resolved photoemission using synchrotron radiation. Despite the low symmetry of the surface complex (C_s) and more than one azimuthal orientation of the vertical symmetry plane, it has been possible to assign the adsorbate-induced levels. Recent semiempirical quantum chemical calculations have proved to be of considerable assistance in this process. The resonant behavior observed for the $3a''$ level is discussed in the context of photoelectron data for the free BF_3 molecule, which is isoelectronic with CO_3^{2-} . The C_s symmetry pertaining in the present experiment is compared with the effective D_{3h} symmetry observed in x-ray-absorption spectroscopy of the same system.

I. INTRODUCTION

Whereas the orientation and electronic structure of diatomic molecules adsorbed on metal surfaces have been thoroughly investigated in recent years, comparatively little is known about more complicated systems. Recent advances in the application of structural techniques which do not require long-range order (e.g., x-ray-absorption spectroscopy and photoelectron diffraction) have shown, however, that molecules and molecular fragments can take up particular, well-defined orientations relative to the substrate. In some cases, the adsorption site can also be directly determined. In such situations the use of selection rules in photoemission experiments can give a complete assignment of the adsorbate-induced features in the spectrum, provided that the point group symmetry is high enough. An example is provided by the surface formate species adsorbed on the Cu{110} surface.¹ Since photoemission, or photoelectron spectroscopy, is still the only effective probe of surface electronic structure available,² this type of experiment can be extremely useful in understanding the nature of the chemisorption bond, in particular in conjunction with appropriate quantum chemical calculations. In this spirit we have remeasured the photoemission spectrum of the adsorbed carbonate species on Ag{110} using synchrotron radiation.

The formation of the surface carbonate species from the reaction of CO_2 with oxygen-precovered silver catalysts was first observed in the infrared absorption experiments of Force and Bell.³ Subsequent investigations by Madix and co-workers revealed that this reaction also occurs on an otherwise atomically clean {110} surface under ultra-high vacuum conditions.⁴⁻⁶ Thermal desorption experiments⁴ using isotopically labeled preadsorbed oxygen were able to show that all three C-O bonds of the surface carbonate are kinetically equivalent, suggesting that all three oxygen atoms are bound directly to the surface. Vibrational spectroscopy of the carbonate species adsorbed on Ag{110},^{6,7} however, favored adsorption through a single oxygen atom, while the infrared measurements of Force and Bell were indicative of both mono- and bidentate adsorption of Ag catalysts.³ This apparent conflict between thermal desorption and vibrational spectroscopy could be resolved by assuming a reversible

interconversion between the two species. Campbell and Paffett⁸ also found an $1s$ XPS peak for carbonate on Ag{110} which was considerably broader than the instrumental resolution, suggesting nonequivalent oxygen atoms.

In fact, only recently has the adsorption geometry of the carbonate species on Ag{110} been determined definitively. Near edge x-ray-absorption investigations by Bader *et al.*⁹ and Madix *et al.*¹⁰ have established that the molecule is adsorbed with the σ_h plane parallel to the surface. The Ag-Ag separation in the $\langle 110 \rangle$ direction of 2.98 Å and the O-O hard sphere outer limit of 4 Å of the carbonate anion means that for steric reasons the observed (1×2) surface structure can only be due to an adsorbate-induced reconstruction.⁹ Oxygen K -edge surface-extended x-ray-absorption fine structure (SEXAFS) data indicated that the oxygen-silver bond length is 2.8 Å.⁹ Since this value could also result from the overlap of several O-Ag bond lengths, neither the exact absorption site nor the nature of the reconstruction could be determined. Figure 1 shows two possible carbonate adsorption sites for the (1×2) surface (assuming a missing row reconstruction) with adsorption sites on the silver ridge

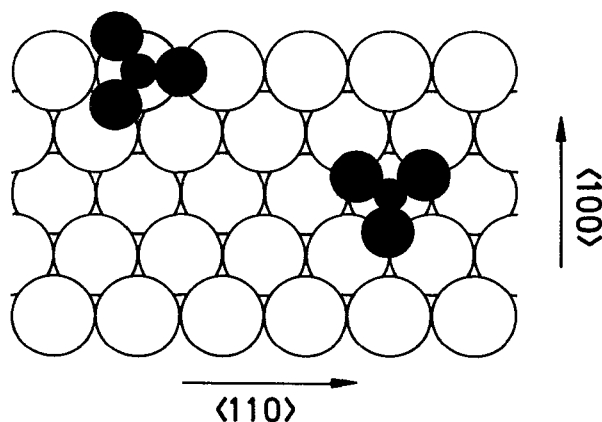


FIG. 1. Possible adsorption sites for the carbonate species adsorbed on the Ag{110} surface (from Ref. 7).

atoms as well as in the troughs. Madix *et al.* were also able to reinterpret the vibrational spectrum and found satisfactory agreement with the parallel adsorption geometry.¹⁰

The near edge absorption spectra of Bader *et al.* revealed additional information concerning the electronic structure of the surface carbonate species.⁹ Firstly, three bands were found at the O *K*-edge which were assigned (in order of increasing absorption energy) to the transitions $1s \rightarrow 2a_2''$, $1s \rightarrow 5a_1'$, and $1s \rightarrow 5e'$.⁹ A schematic molecular orbit diagram for the carbonate species is shown in Fig. 2. Since the $2a_2''$ resonance is the first observed at the absorption edge, the three orbitals $1a_2'$, $1e'$, and $4e'$ must all lie below the Fermi level and are filled. This indicates that (formally at least) the surface carbonate is a dianionic species, CO_3^{2-} . Secondly, at the C-edge the $1s \rightarrow 5a_1'$ absorption band was not observed, indicating that, at least in this experiment, the effective symmetry of the flat-lying carbonate species remains D_{3h} , despite the loss of the σ_h symmetry plane. The effective symmetry in the photoemission experiment is one of the important questions addressed in this paper. Fortunately, quantum chemical cluster calculations have recently been performed for this system by Rodriguez and Campbell¹¹ and give some idea of the extent of the valence level splittings induced by the lower symmetry of the surface species.

Photoemission studies of the adsorbed carbonate species on Ag{110} have previously been carried out by Barteau and Madix,¹² Felter *et al.*,¹³ and Prince *et al.*^{14,15} Apart from some minor differences our spectra resemble theirs, but the

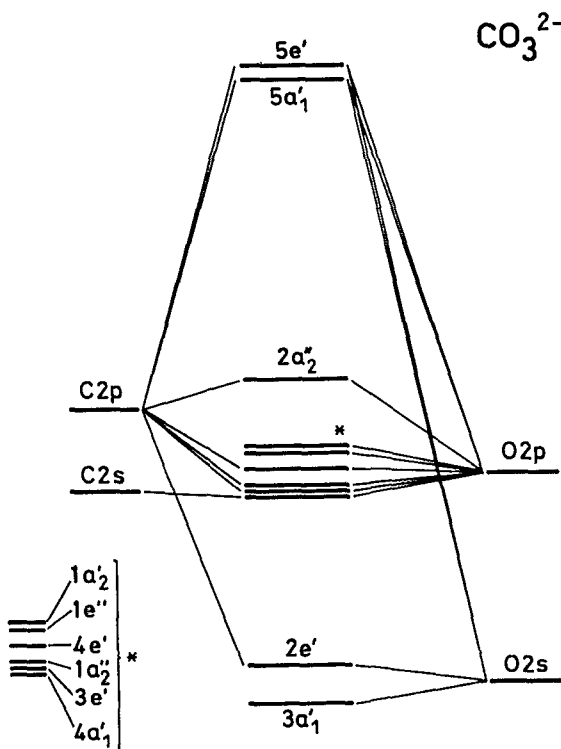


FIG. 2. Schematic molecular orbital energy diagram for the carbonate dianion CO_3^{2-} .

combination of momentum resolution with synchrotron radiation in the present study provides new information leading to a more definitive assignment of the spectral features and—benefitting from the cluster calculations¹¹—more insight into this interesting chemisorption system.

II. EXPERIMENTAL

The experiments were performed in a VG ADES 400 electron spectrometer, equipped with facilities for low-energy electron diffraction (LEED) and Auger-electron spectroscopy (AES). Synchrotron radiation was provided by the electron storage ring BESSY in Berlin using the 1m Seya-Namioka monochromator with a 1200 l/mm grating and a toroidal grating monochromator (TGM3) also with 1200 l/mm grating. The experiments were performed in the photon energy range 20 eV to 50 eV. The overall resolution was ~ 200 meV on the Seya and ~ 350 meV on TGM3. This combination of instruments has a particular advantage: The TGM permits use of an extended photon energy range, whereas the Seya—due to its excellent focusing properties—allows the light to be threaded through a small hole in the electron energy analyzer normally used for alignment purposes without creating scattered light. Thus, it is possible to perform an experiment at normal light incidence and normal photoelectron emission, which is a unique experimental geometry for the application of photoemission selection rules.

The Ag{110} crystal was cleaned *in situ* by argon ion bombardment and annealing to 800 K. The base pressure in the vacuum system was below 1×10^{-10} mbar. The carbonate was prepared by the reaction of preadsorbed oxygen (1.2×10^{-4} mbar.s exposure) with CO_2 (ca. 2×10^{-3} mbar.s exposure) at room temperature. Following preparation of the adsorbate layer, sharp half-order LEED features were observed in the $\langle 100 \rangle$ azimuth, indicative of a (1×2) surface structure.

III. RESULTS AND DISCUSSION

A. The application of photoemission selection rules

Angle-resolved photoemission spectra of Ag{110}(1 \times 2) CO_3 system are shown in Fig. 3. The angle of incidence of the *p*-polarized light ($h\nu = 40$ eV) was 50° in the $\langle 100 \rangle$ azimuth; The spectra at the various polar angles indicated were also measured in this plane. (The corresponding data in the $\langle 110 \rangle$ azimuth are not shown here, but are essentially similar except in the region of the Ag *4d* band.) Four features induced by carbonate formation are observed at 2.2, 3.2, ca. 9.1, and 10.7 eV below the Fermi level, E_F . Since the peak position varies with emission angle, we note that the feature at ca. 9.1 eV definitely contains more than one component. It is provisionally assigned to two features, labeled C and D at 8.9 and 9.3 eV below E_F , respectively. For a photon energy of 40 eV, the peak D is weak at normal emission, giving rise to a maximum in the combined feature at lower binding energy. In general, the spectra agree well with the previous photoemission data^{12–15} although Prince and Paulucci¹⁵ have identified a further feature at 3.7 eV (i.e., on the high binding energy side of peak B). We have not been able

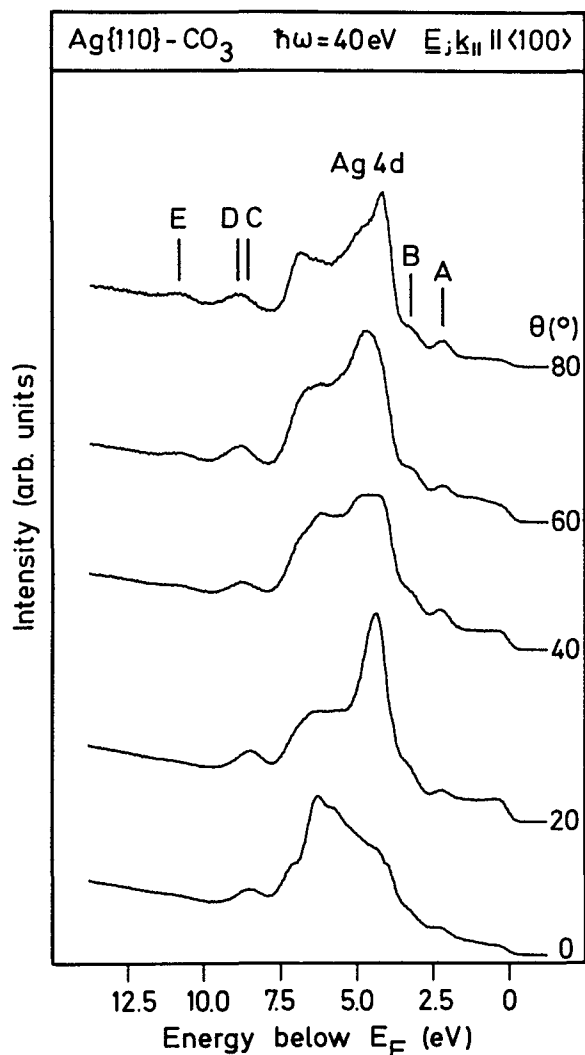


FIG. 3. Photoemission spectra at 40 eV (p -polarized light) as a function of emission angle. The spectra were recorded in the $\langle 100 \rangle$ azimuth. The detection azimuth, the surface normal, and the plane of incidence were coplanar.

to observe this under any of the conditions (photon energy, emission angle, and polarization) used in the present study.

Application of selection rules in angle-resolved photoemission allows an assignment of the symmetry of the adsorbate-induced features.^{16,17} Within the dipole approximation, the photoemission intensity is proportional to the square of the matrix element $\langle f | \mathbf{A} \cdot \mathbf{p} | i \rangle$. When the detector is placed along a symmetry axis or in a mirror plane of the whole system, the final state $\langle f |$ can only be detected if it is symmetric with respect to that symmetry element.^{18,19} Using polarized light, the symmetry of the vector potential \mathbf{A} is fixed in the chosen Cartesian coordinate frame (z usually corresponds to the surface normal). It is then possible to predict which initial states lead to dipole-allowed transitions. For normal emission the final state must be totally symmetric, i.e., it must belong to the totally symmetric representation of the point group. Should the effective symmetry of the carbonate species remain D_{3h} in the photoemission experiment,

the final state would then belong to a_1' . The selection rules would then allow only emission from e' orbitals (with x, y -polarized light) and from a_1' and a_2'' orbitals (with z -polarized light). Table I lists the expected valence molecular orbitals of a dianionic carbonate species (see Fig. 2) and correlates the symmetry and polarization dependence in a normal emission experiment for the point groups D_{3h} , C_{3v} , and C_s . The latter might be expected to pertain for the two adsorption geometries shown in Fig. 1. Normal emission data recorded at a photon energy of 26 eV for various angles of incidence, α , are shown in Fig. 4 for the vector potential in the $\langle 110 \rangle$ azimuth. (Data taken in the $\langle 100 \rangle$ azimuth bear a close resemblance to the spectra presented here.) At least four adsorbate-induced features are observed. According to Table I, four features should be observed in normal emission if the D_{3h} point group pertains but only two in the special normal incidence/normal emission geometry of the top spectrum ($\alpha = 0^\circ$). Moreover, if we assume that the first three levels expected ($1a_2'$, $4e'$, and $1e''$) are above the Ag d band, two features are observed as opposed to the single one predicted by D_{3h} . The obvious conclusion to draw is that a symmetry lowering to C_{3v} or C_s has occurred. If peak A were assigned to the $1a_2'$ level ($1a_2$ in C_{3v} , $6a''$ in C_s), which is the level of lowest ionization potential in inorganic carbonates,²⁰⁻²² the symmetry could only be C_s since it would be forbidden in D_{3h} and C_{3v} . On the other hand, it should then be visible only in one azimuth. The symmetry could still be C_s , however, if peak A were composed of more than one feature, or if there were more than one azimuthal orientation, as shown in Fig. 1.

The so-called α dependence of Fig. 4 can, in principle, provide further information on assignment.¹⁷ Changing the angle of incidence for p -polarized light changes the relative strengths of the vector potential components A_z and A_x (A_y). This in turn gives rise to characteristic plots of intensity vs angle of incidence for normal emission from orbitals of particular symmetry. These depend on the optical constants of the metal surface (via the Fresnel equations) and are independent of the photoemission matrix element, the value of which acts only as a scaling factor. In Fig. 4 we first note that there is no strong α dependence of peak A , suggesting that it is not a'' in C_s . (The characteristic intensi-

TABLE I. Correlation table for the molecular orbitals of the surface carbonate species adsorbed on Ag{110}. The Cartesian components of the vector potential which are effective in exciting normal emission from a particular orbital are shown in brackets. The absence of (x) , (y) , or (z) means that this orbital will not be observed in normal emission. The z axis is in the surface normal.

D_{3h}	C_{3v}	C_s
$1a_2'$	$1a_2$	$6a''(y)$
$1e''$	$4e(x,y)$	$9a' + 4a''(z,x) + (y)$
$4e'(x,y)$	$5e(x,y)$	$10a' + 5a''(z,x) + (y)$
$1a_2''(z)$	$5a_1(z)$	$8a'(z,x)$
$3e'(x,y)$	$3e(x,y)$	$7a' + 3a''(z,x) + (y)$
$4a_1'(z)$	$4a_1(z)$	$6a'(z,x)$

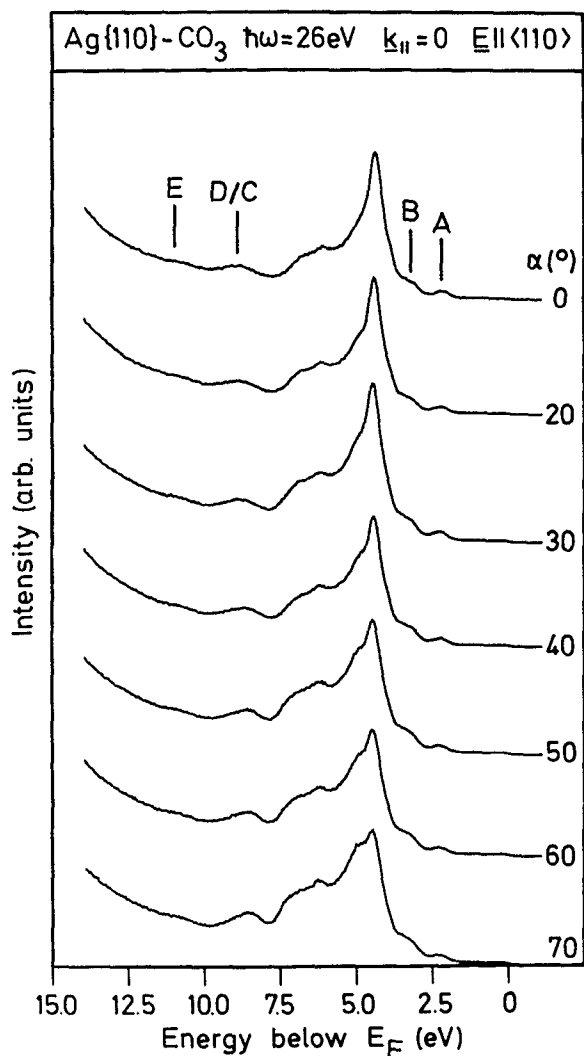


FIG. 4. Normal emission spectra at 26 eV with the E vector in the $\langle 110 \rangle$ azimuth, as a function of incidence angle, α .

ty dependence of a level belonging to a'' would still be observed, even if there were more than one azimuthal orientation.) If C_s symmetry pertains, then it is likely that peak A also contains an a' level. The joint feature C/D exhibits a distinct dependence on the angle of incidence: As α is increased, the maximum shifts to lower binding energy. This indicates that peak C is preferentially excited by the z component of the electric vector, but peak D by the x and/or y components. If the effective point group were C_{3v} , C and D would be assigned to emission from a_1 and e type orbitals. In the case of C_s three levels would be expected (a' and $a' + a''$) in this joint feature (Table I). It is only possible to conclude that peak C corresponds to an a' level and that there is probably a strong a'' component in peak D .

Since the balance of evidence suggests that the symmetry is C_s , it is interesting to consider experimental geometries which can, in principle, determine the azimuth of the one remaining symmetry plane. As was shown recently by Netzer *et al.* for benzene on Pd{110},²³ the symmetry plane can be located in an off-normal emission experiment with s -polarized light in which the electrons are collected in a plane

perpendicular to the vector potential of the light. In this so-called forbidden geometry ($A \perp k_{\parallel}$), emission is only allowed from orbitals which are antisymmetric with respect to the reflection in the symmetry plane. In view of the close proximity of the peaks C and D and the uncertainty of the assignment of features A and B , we will focus our attention on Peak E at 10.7 eV below E_F . Although this feature is observed only very weakly in normal emission spectra and sometimes not at all, it can be reasonably safely assigned to the $4a'_1$ orbital (a_1 in C_{3v} or a' in C_s). This orbital is symmetric with respect to reflection in the vertical symmetry plane and should be observed in an "allowed" geometry when the vector potential of the light and the emission direction are coplanar. As the data of Fig. 5 show, however, the feature E is observed not only in the allowed geometry, but also in the forbidden geometry for electron emission in both principal azimuths. This suggests that there is no unique mirror plane: Either the remaining symmetry planes are parallel to both the $\langle 110 \rangle$ and $\langle 100 \rangle$ azimuths or they are randomly orient-

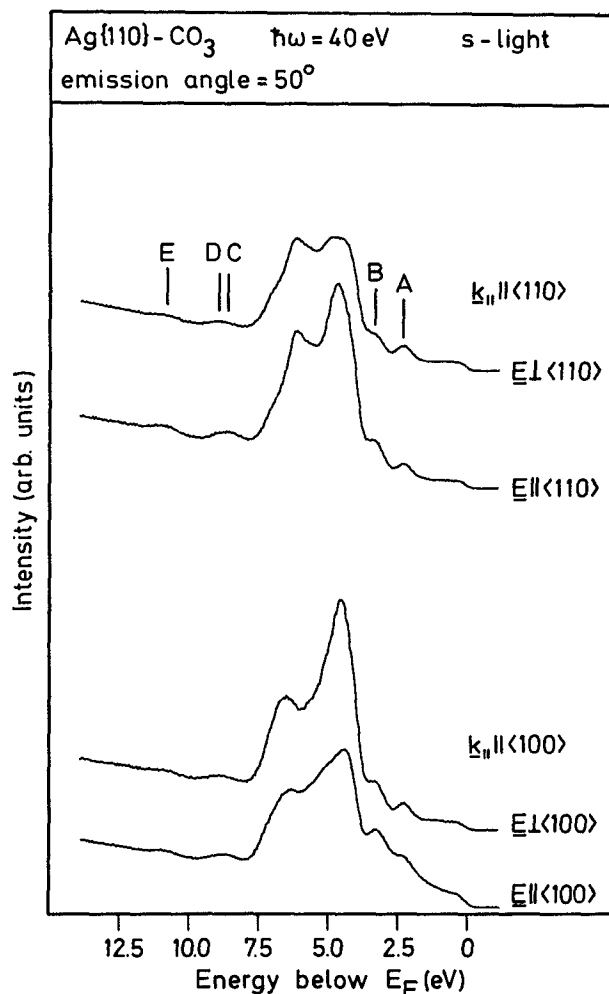


FIG. 5. Photoemission data in the allowed and forbidden geometries at 40 eV photon energy. The two lower spectra on the bottom were recorded with $k_{\parallel} \parallel \langle 100 \rangle$, the two upper spectra with $k_{\parallel} \parallel \langle 110 \rangle$.

ed. Peak *A* does not vanish either, which would be the case in one azimuth for $A \parallel k_{\parallel}$, if it were a'' with only one azimuthal orientation.

Finally, we note that the photoemission data themselves also exclude the vertical bidentate C_{2v} configuration sometimes considered in earlier studies. This is indicated by the normal emission/normal exit spectra in both azimuths and the forbidden geometry experiments in Fig. 5. They also provide an interesting contrast to the corresponding data for the bidentate surface formate species¹ which show how effective the selection rules can be when the symmetry is not too low. We mention this here merely for the sake of completeness: The vertical bidentate geometry is after all completely ruled out by the x-ray-absorption data.^{9,10}

B. Comparison with quantum chemical calculations

The likely presence of two coexisting symmetry planes coupled with the low effective point group (C_s) seems to be the reason why the polarization effects in the photoemission spectra are not very pronounced. The recent INDO/S calculations by Rodriguez and Campbell (RC)¹¹ for the carbonate species adsorbed on silver clusters help to throw some light on this problem. (INDO is the incomplete neglect of differential overlap.) Figure 6 shows a comparison of the experimental ionization energies for the peaks *A–E* from the present work with RC's orbital energy diagram for a cluster configuration similar to that shown on the left of Fig. 1. Also indicated are experimental ionization energies^{20,21} and orbital energy diagrams (SCF²⁰ and INDO/S from RC¹¹) for the inorganic carbonate anion. (We should be mindful here of the dangers involved in comparing experimental binding energies with calculated orbital energies: See for example the

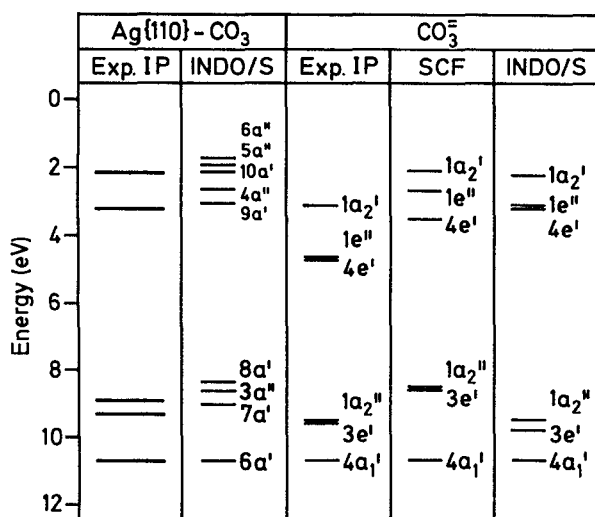


FIG. 6. Schematic comparison of the observed photoemission binding energies for the carbonate species adsorbed on Ag{110} (present paper) with INDO/S orbital energies (Ref. 11) for the free ion and the adsorbed species. Binding energies for the anion in Li_2CO_3 (Refs. 20 and 21) are also shown as well as the corresponding orbital energies from a HF-SCF calculation (Ref. 22). In each case the energy of the $6a'$ (or $4a'$) level has been aligned with Peak *E* in the experimental spectrum.

discussion in Ref. 1). All the data have been aligned at the $4a'_1$ level, which becomes $6a'$ in C_s , and clearly corresponds to peak *E* in the experimental spectra. The orbital energy diagram from the Ag-CO₃ cluster calculation only shows the orbitals of predominantly CO₃ character. If the alternative adsorption geometry is taken, namely, with the carbonate anion still adsorbed over a ridge Ag atom but rotated by 90°, the diagram remains very similar. Only the symmetry labels of the a' and a'' levels derived from the e' and e'' states are swapped over. The calculations clearly show that the splitting due to the reduction in symmetry to C_s is considerable and cannot be neglected in the interpretation of the photoemission data. A plausible assignment of the latter, which is consistent with the angle-resolved experiments reported above, is as follows. Peak *A* contains the $6a''$, $5a''$, and $10a'$ levels and *B* the $4a''$ and $9a'$. The other conceivable possibility would be to include the $5a''$ in peak *B* rather than peak *A*. The assignment of the joint feature *C/D* is somewhat more straightforward: Peak *C* is clearly the $8a'$ level, leaving *D* as the superposition of $3a''$ and $7a'$. The $3a''$ level appears to dominate in the normal incidence/normal emission geometry in Fig. 4 (top spectrum). As already remarked above, peak *E* can be assigned to the $6a'$ level.

As in the case of the surface formate species,¹ semiempirical molecular orbital (m.o.) cluster calculations at this level of approximation appear to explain the photoelectron spectrum of the adsorbed carbonate quite satisfactorily. We can therefore also assume that they provide a reasonable description of the chemisorption bond. RC were able to show that the adsorbed carbonate is bonded to Ag{110} mainly through the oxygen atoms and that all the C-O bonds have a bond order of about one. As far as the substrate is concerned, the chemisorption bond is mostly due to the Ag *s* and *p* orbitals: The *d* orbital contribution is only about 4%. Relative to the free ion the carbonate species is a strong π donor (from the $1a'_2$ and $1e''$ orbitals) and a less strong σ donor.

C. Shape resonance phenomena

With low incidence angles of the light ($\alpha = 20^\circ$) at normal emission, peak *D* exhibits strong resonant behavior. The intensity of this peak as a function of photon energy between 20 and 30 eV shows a maximum at approximately 24 eV, as shown in Fig. 7. The data presented are the integrated intensities of peak *D* as a function of photon energy. The spectra were normalized to the drain current of the last mirror in the beamline. The intensity of peak *D* at a photon energy of 24 eV is approximately one order of magnitude higher than at 30 eV. This behavior indicates that there is an excitation from a bound level ($3a''$ or $7a'$ in peak *D*) into a continuum state. No other adsorbate-induced features show this effect.

Such "shape" resonances have often been observed in valence level photoemission spectra of chemisorbed diatomic molecules.²⁴ Recently, Huber *et al.*²⁵ have also identified a similar resonance on the $2e_{1u}$ level of benzene adsorbed on Ni{111} where, within an effective point group of C_{3v} , the symmetry of the final state was identified as a_1 . In the present data the behavior of peak *D* can also be explained by the

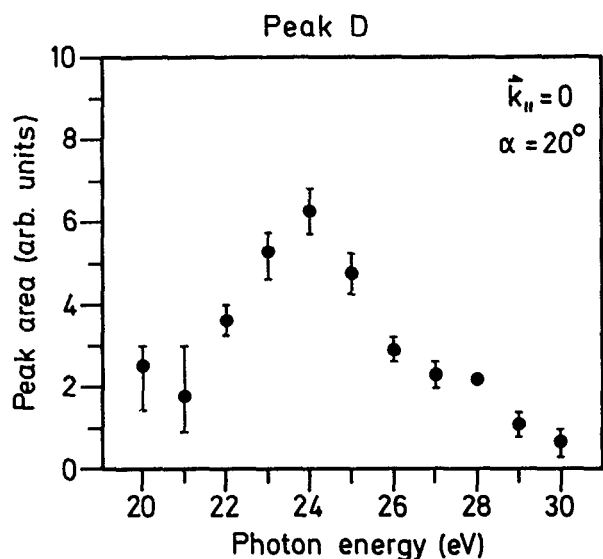


FIG. 7. Intensity of peak *D* (assigned to $3a'$ in C_s) as a function of photon energy in normal emission ($\alpha = 20^\circ$) with the electric vector in the $\langle 110 \rangle$ azimuth. Data recorded in the $\langle 100 \rangle$ azimuth show identical behavior.

presence of a continuum orbital ~ 15 eV above the Fermi edge. In the recent x-ray-absorption experiments of Bader *et al.*,⁹ shape resonances were identified approximately 12 and 16.5 eV above the oxygen $1s$ ionization threshold. These were assigned to transitions into the unoccupied $5a'_1$ and $5e'$ orbitals, respectively, of the carbonate species (see Fig. 2). The excitation into the $2a'_2$ orbital is a bound-to-bound transition giving rise to a characteristically sharp π^* resonance below the photoionization threshold. At the carbon edge only the second σ^* feature ($5e'$) is observed due to the apparent D_{3h} symmetry in the x-ray-absorption experiment. The resonant behavior of peak *D* shown in Fig. 7 could be due to a transition into either of the $5a'_1$ or $5e'$ unoccupied states. Table II shows the dipole-allowed transitions which might contribute to the resonance behavior of peak *D*. (The result for C_{3v} is the same as for D_{3h} .) The normal emission condition requires that the final state electron belongs to the representations: a'_1 and a'_2 in D_{3h} , and a' in C_s . Were the effective symmetry D_{3h} , as in the x-ray-absorption experiment, this resonance could only be due to the $3e' \rightarrow 5a'_1$ transition, which is polarized in the x, y (or surface) plane (see Table

TABLE II. Polarization dependence of the possible transitions giving rise to the resonant behavior of Peak *D*.

Initial state		Final state		Polarization dependence	
D_{3h}	C_s	D_{3h}	C_s	D_{3h}	C_s
$3e'$	$7a', 3a''$	$5e'$	$13a', 7a''$	$(x, y)^a$	$(x, z), (y)$
$3e'$	$7a', 3a''$	$5a'_1$	$12a'$	(x, y)	$(x, z), (y)$
$1a''_2$	$8a'$	$5e'$	$13a', 7a''$		$(x, z), (y)$
$1a''_2$	$8a'$	$5a'_1$	$12a'$	(z)	(x, z)

^aThese transitions can be excited, but not observed, in normal emission.

II). Since the resonance is only observed with near normal incidence of the light, the assignment of the transition therefore appears to be correct. As shown above, however, the effective symmetry of the carbonate species on Ag {110} in the photoemission experiment is C_s and peak *D* is dominated by emission from the $3a''$ orbital in the geometry considered here. Under these circumstances the final state is $12a'$ or $13a'$ (derived from $5a'_1$ and $5e'$, respectively) and, indeed, only the transition from the $3a''$ orbital is expected to be polarized in the y direction. This is still not a watertight assignment since the transition from the $7a'$ level is polarized in the x, z plane and the A_x component could possibly give rise to the observed behavior. However, it is an important result supporting the assignment evidence in Sec. III A.

It is not possible to say whether the transition takes place into the $12a'$ or the $13a'$ state. There are two pieces of evidence which suggest it might be the former. Firstly, in the "free" carbonate ion with D_{3h} symmetry the $3e' \rightarrow 5e'$ transition would not be observed in normal emission. The extent to which the $3a'' \rightarrow 13a'$ transition is observed in C_s will then depend on the extent of the perturbation accompanying the loss of symmetry. This may be a strong effect, but *a priori* we would expect the transition to be weaker than one which is allowed anyway. Secondly, it is known from the comparison of x-ray-absorption and photoemission data in the gas phase that shape resonances tend to undergo a shift to higher kinetic energies of ~ 3 eV on going from an inner shell spectrum to a valence level spectrum.²⁶ Thus, in the present work, the resonance shown in Fig. 7 also occurs at a kinetic energy ~ 3 eV higher than the $5a'_1$ resonance in the x-ray-absorption data of Bader *et al.*⁹ According to this rule of thumb, the $5e'$ resonance (giving rise to the $13a'$ resonance in C_s) would actually come at ~ 30 eV photon energy in the photoemission data.

Further peaks in the spectrum might perhaps be expected to show shape resonance phenomena. Under D_{3h} , for example, the transitions $4e' \rightarrow 5a'_1$ and $1a''_2 \rightarrow 5a'_1$ could also be excited by the (x, y) and z components, respectively, of the electric vector and also be observed in normal emission. Furthermore, all the valence levels, with the exception of $1a''_2$, can couple to the $5e'$ resonance. As stated above, no such resonance effects are seen on other peaks. Similarly, Huber *et al.*²⁵ found a shape resonance only on the $2e_{1u}$ level for benzene adsorbed on Ni{111} even though resonant behavior for other levels would have been dipole allowed. It is interesting in this connection to look at shape resonance phenomena in the molecule BF_3 ²⁶⁻²⁸ which is isoelectronic with the carbonate dianion. The schematic m.o. diagram of Fig. 2 pertains and the ionization energies of BF_3 also exhibit the same ordering as those of CO_3^{2-} . It is notable in the data of Dehmer *et al.*²⁸ that the only photoemission peak which exhibits a strong resonance is the $3e'$ at $h\nu \sim 26$ eV. As far as the energy of the resonance is concerned, there is good agreement with the multiple scattering calculations of Swanson *et al.*,²⁷ although these predict that a similar resonance also occurs in the β parameter and branching ratio of the $4e'$ orbital. The latter is observed neither in the gas phase BF_3 work nor in the CO_3^{2-} data reported here. The feature is described as a composite resonance with significant contri-

butions from shape resonances of both a'_1 and e' symmetry. They are thought to have equivalent intensities, but the e' resonance at somewhat higher energy is predicted to be sharper and thus to determine the position of the combined feature. In the present work on the carbonate species the resonance is clearly in the a'_1 (or a') channel.

Why does only the $3e'$ (or $3a''$) level show resonant behavior when in fact such transitions are dipole allowed for all the valence orbitals? Dehmer *et al.*²⁶ advance interchannel coupling and/or averaging over vibrational motion as effects which might smear out shape resonances. Furthermore, interchannel coupling and vibronic coupling can play a role. Explaining such effects apparently still poses a "major challenge to our understanding of shape resonance phenomena."²⁶

D. Effective symmetry

The photoemission data show that the appropriate point group symmetry in this experiment is C_s . This may be surmised from the application of photoemission selection rules under particular conditions (orientation of the E vector and photoelectron emission direction), as described in Sec. III A. In the x-ray-absorption experiment, however, Bader *et al.*⁹ concluded that the appropriate point group for the adsorbed carbonate species was D_{3h} , since only one σ -type resonance was found at the C K-absorption edge. How significant are these apparently contradictory findings? Clearly the adsorption geometry of Fig. 1 formally gives rise to the point group C_s . In any case, the σ_h symmetry plane is expected to disappear to give at least a symmetry lowering to C_{3v} .¹⁶ The extent to which a symmetry lowering is actually observed depends on the extent of the perturbation of the molecular wave functions by the interaction with the substrate, i.e., on the extent to which they acquire metal character via hybridization with substrate orbitals. The calculations of Rodriguez and Campbell¹¹ indicate that these effects are strong enough to cause splittings and shifts in the valence levels of up to 1 eV. Since the molecular wave functions in the valence region are directly probed in the photoemission experiment, it is not surprising that the observed symmetry is C_s . The problem is therefore one of explaining why the D_{3h} point group is found in the x-ray-absorption experiment. Here we have to refer to an "effective" symmetry, since it is clearly not that expected by the structure model of Fig. 1.

Bader *et al.*⁹ proposed that the D_{3h} like behavior of the σ -type resonances ($5a'_1$ and $5e'$) was actually due to the corresponding bonding molecular orbitals ($3a'_1$ and $2e'$, see Fig. 2) being very low in energy and little affected by the interaction with the substrate. This is unlikely to be correct, because the spatial extent of the continuum wave functions with $5a'_1$ and $5e'$ character is relatively large and they are therefore likely to be strongly affected by the presence of the metal surface. An alternative explanation is based on the localized nature of the excitation. The $1s$ orbital overlaps spatially with the central region of the wave function of the unoccupied level. The perturbation of the latter as a result of the bonding to the metal only affects strongly the outer region.

Thus, the value of the matrix element within the C_s point group may not change significantly compared to that of the corresponding unperturbed level within the D_{3h} point group, i.e., $|\langle \Psi_f(5a'_1) | \tau | \Psi_i(2a'_1) \rangle|$ is still zero, even when it would be formally correct to write $\langle \Psi_f(12a') | \tau | \Psi_i(3a') \rangle$ due to the symmetry lowering.

IV. CONCLUSIONS

In the system Ag{110}-CO₃ five adsorbate-induced features can be clearly identified in the photoemission spectrum at 2.2 (A), 3.2 (B), 8.9 (C), 9.3 (D), and 10.7 (E) below the Fermi level, E_F . No evidence was found for a feature at 3.7 eV as reported previously. The application of photoemission selection rules—possible because of the known orientation of the surface carbonate species—shows that the point group symmetry is C_s . There is no unique symmetry plane, indicating at least two azimuthal orientations of the molecule. There is good agreement (assuming Koopmans' theorem) between the experimental binding energies and the relative orbital energies from a recent semiempirical m.o. cluster calculation. On this basis, we assign peak A to contributions from $6a''$, $5a''$, and $10a'$, peak B to $4a''$ and $9a'$, peak C to $8a'$, peak D to $3a''$ and $7a'$ and peak E to $6a'$. Peak D shows pronounced resonant behavior, peaking strongly at a photon energy of 24 eV. This appears to be due to the $3a''$ component (derived from $3e'$ in D_{3h}); The symmetry of the unoccupied level is a' (probably derived from $5a'_1$ in D_{3h}). Although such resonances are dipole allowed for all valence orbitals, the effect is observed only for the $3a''$ level. The same situation is encountered in the molecule BF₃, which is isoelectronic with CO₃²⁻. The shape resonance is observed only in the $3e'$ branching ratio, the reason for which is at present unknown. That the effective symmetry in the x-ray-absorption spectrum of adsorbed carbonate is D_{3h} rather than C_s , appears to be due to the different nature of the excitation in that experiment.

ACKNOWLEDGMENTS

We thank Professor C. Campbell for useful discussions and for communicating his results prior to publication as well as Professor N. V. Richardson for a critical reading of the manuscript. This work has been supported financially by the Deutsche Forschungsgemeinschaft through the Sonderforschungsbereich 6 and by the German Federal Ministry for Research and Technology under Grant No. 05 490 FXB8.4.

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