

IDENTIFICATION OF PRECURSOR STATES IN THE DISSOCIATION OF ADSORBED BENZENE ON Os(0001): A HREELS STUDY

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Received 18 October 1989

Applying high-resolution electron energy loss spectroscopy we identify two precursor states, i.e. adsorbed phenyl (C_6H_5) and benzyne (C_6H_4) in line with a recent photoemission and temperature-programmed desorption study. Dipole selection rules are used to deduce information on the adsorbate geometries of the species. Both intermediate species are proposed to be bonded to the substrate with the six-membered ring plane inclined with respect to the surface plane. The inclination angle of the phenyl species is smaller than that of the benzyne species.

In a recent study of benzene adsorption and reaction on Os(0001) applying angle-resolved photoemission and thermal desorption spectroscopy a reaction pathway starting from adsorbed benzene at low temperature towards a carbon overlayer at high temperature has been proposed [1]. Thermal desorption spectroscopy (TDS) showed that in the reaction firstly one, and then two hydrogen atoms dissociate from the ring indicating that the first step may be the formation of a phenyl, the second step the formation of a benzyne species. Angle-resolved photoelectron spectroscopy revealed considerable changes in the electronic structure of the system when the adsorbate was heated across the transformation temperatures determined in TDS [1] for the successive losses of two hydrogen atoms. Variations in the observed ionization potentials were found, and, even more characteristically, the angular dependences of the line intensities showed pronounced changes. While the emission from the a_{1g} ion state, which is a σ -frame ion state, peaked in normal direction in the benzene adsorbate phase, the corresponding ion state of the hydrogen deficient species, namely phenyl and benzyne, showed a pronounced maximum in off-normal emission. In fact, the off-normal emission

maximum shifted from 15° to 45° when going from phenyl to benzyne. The combined information led us to the conclusion that the molecular plane in the hydrogen deficient species is tilted with respect to the surface plane by 15° in the phenyl adsorbate and by 45° in the benzyne adsorbate. In order to put the conclusions drawn in the study mentioned above on ring inclination on a more solid footing we have now studied the same system with another surface sensitive technique. We present in this Letter the results of a high-resolution electron energy loss investigation. The results of the present study basically corroborate the conclusions discussed above.

Fig. 1 shows a series of HREEL spectra taken in the specular direction with a Leybold ELS 22 system integrated into a μ -metal shielded ultrahigh vacuum system containing additional facilities for LEED, AES, and residual gas analysis. The resolution was typically 50 cm^{-1} . The preparation of the adsorbate was performed as reported before but without using a dosing system [1]. Spectrum (a) shows the data of a benzene adsorbate phase at $T=273 \text{ K}$. This adsorbate gives rise to a $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ LEED pattern [1]. The HREEL spectrum in specular scattering is dominated by one transition which can be

Table 1
Observed energy losses and assignment for C_6H_6 , C_6H_5 , C_6H_4 and C_nH_n adsorbates

Assignment	Symmetry	C_6H_6 (gas) ref. [12]	$C_6H_6/Rh(111)$ $T=300$ K ref. [4]	$C_6H_6/Pt(111)$ $T=300$ K ref. [2]	$C_6H_6/Ni(111)$ $T=310$ K ref. [2]
ν_{C-H}	$A_{1g}, B_{1u},$ E_{1u}, E_{2g}	3047–3062	3000	3000	3000
ν_{C-C}	E_{2g} E_{1u}	1595 1479	1420	1420	1430
δ_{C-H}	A_{2g}	1346			
ν_{C-C}	B_{2u}	1309	1320		
δ_{C-H}	E_{2g} B_{2u}	1177 1146	1130	1130	1130
δ_{C-C}	E_{1u} B_{1u}	1035 1010			
γ_{C-H}	A_{1g} B_{2g}	993 991			
	E_{2u} E_{1g}	969 846	880 810	920 830	830
γ_{C-C}	B_{2g}	707			720
γ_{C-H}	A_{2u}	675			
δ_{C-C}	E_{2g}	607			
γ_{C-C}	E_{2u}	404			
ν_{C-H}	A_{2u}		550 345	570 360	320

^{a)} Ref. [21]. ^{b)} Ref. [23]. ^{c)} Ref. [20]. ^{d)} Refs. [22,23].

assigned by comparison with similar spectra on other benzene adsorbate systems [2–13], as shown in table 1, where we have listed the known vibrational frequencies and their assignment to normal modes of gaseous and adsorbed benzene. A comparison of specular and 5° off-specular spectra of adsorbed benzene is given in fig. 2. This comparison basically reveals the fact that dipole selection rules determine the dominant C_6H_6 vibration at 810 cm^{-1} . According to table 1, the strong band at 810 cm^{-1} in specular scattering geometry has to be assigned to a C–H wagging (γ) mode. These modes lead to strong dynamic dipoles perpendicular to the metal surface, if the molecular plane is oriented parallel to the Os surface. Other vibrational modes show negligible intensities in the specular scattering direction (fig. 1), but gain intensity off specular (fig. 2). All studies presented so far conclude from such behaviour that chemisorbed benzene lies flat on metal surfaces at room temperature. The small peak at 1885 cm^{-1} is probably due to residual CO. We only note that at

even lower temperature ($T=80\text{ K}$) we find the growth of benzene multilayers, as indicated in the EEL spectra (not shown) by additional lines similar to those reported by Jakob and Menzel for $C_6H_6/Ru(0001)$ [13].

Upon elevating the temperature to $T=325\text{ K}$ (spectrum (b)), which is equivalent to the temperature, where the system loses the first hydrogen atom [1], the wagging mode shifts to lower values, namely 760 cm^{-1} . Simultaneously, a sharp band at 400 cm^{-1} in the C–C wagging region gains intensity, while the region of C–H vibrations above 3000 cm^{-1} only shows a slight intensity, considerably more though than for the flat-lying benzene adsorbate. However, C–H bending modes at 1110 and 1390 cm^{-1} are detectable. For C_6H_6 on Os(0001) the vibrational frequencies for the various substrate temperatures above room temperature and for specular electron detection are compiled in table 1.

Further increase of the temperature to a value ($T=382\text{ K}$), where the second hydrogen atom is lost

$C_6H_6/Ru(001)$ $T=130\text{ K}$ ref. [12]	$C_6H_6/Os(0001)$ $T=273\text{ K}$ this work	$C_6H_5/Os(0001)$ $T=325\text{ K}$ this work	Symmetry	C_6H_4 (matrix) ^{d)}	$C_6H_4/Os(0001)$ $T=382\text{ K}$ this work	$C_nH_n/Os(0001)$ $T=737\text{ K}$ this work
3020	2900	3010	a_1	3088 ^{a)}	3020	
			a_1	2082 ^{b)}	2565	
			b_2	1627 ^{c)}	2000	
			a_1	1607 ^{c)}		
1410			b_2	1451 ^{c)}		
			a_1	1395 ^{b)}		
1320	1355	1390	b_2	1355 ^{b)}	1395	
1260					1290	
1110					1155	
1110		1110	a_1	1055 ^{b)}		
1010	1050		b_1	1038 ^{b)}		
960						
860						
		850	b_1	848 ^{b)}	980	
860	790					
		760	b_1	739 ^{b)}	780	
750						
570	450–520		b_2	470 ^{b)}		
		520			580	635
290		400			465	515

leads to several further changes in the EEL spectrum (spectrum (c) in fig. 1): firstly, the intensity of the elastic peak decreases by orders of magnitude, indicating a pronounced disordering of the adsorbate layer; secondly, several modes in the region of C–C frame vibrations between 465 and 700 cm^{-1} , as well as in the region of C–H bending modes between 980 and 1400 cm^{-1} grow in (table 1). Most pronounced, however, is the considerable intensity in the region of the C–H stretching modes above 3000 cm^{-1} . Note that the observed vibrational frequencies are only slightly shifted with respect to those observed for the benzene moiety. For a definite assignment it would be desirable to compare the observed frequencies with those of the benzyne–Os₃ cluster compounds for which X-ray structure determinations are reported showing an inclined C₆H₄ ring with respect to the Os₃ cluster plane [14–19]. Unfortunately, the vibrational spectra of these compounds in the hydrocarbon region have not been reported. However,

the vibrational spectrum of matrix-isolated benzyne has been determined and assigned on the basis of a normal mode analysis [20–23]. The experimentally observed infrared active bands as well as their symmetry is given in table 1. A comparison with the benzene spectrum shows that except for one vibration, i.e. the ν_{C-C} mode at 2082 cm^{-1} , the benzyne vibrational energies are in the neighbourhood of those of C₆H₆. For the adsorbed benzyne we find the indication of loss at 2000 and 2565 cm^{-1} , which may be due to the ring vibration. The other observed vibrational losses are in the range of those for benzene. The band at 2000 cm^{-1} can also be due to co-adsorbed CO. On the other hand the changes of the loss intensities in going from benzene to adsorbed benzyne are most characteristic and consistent with a pronounced geometrical change of the adsorbed species as shall be alluded to in the following.

The simplest way to explain the observed changes of intensities is to consider a molecular plane which

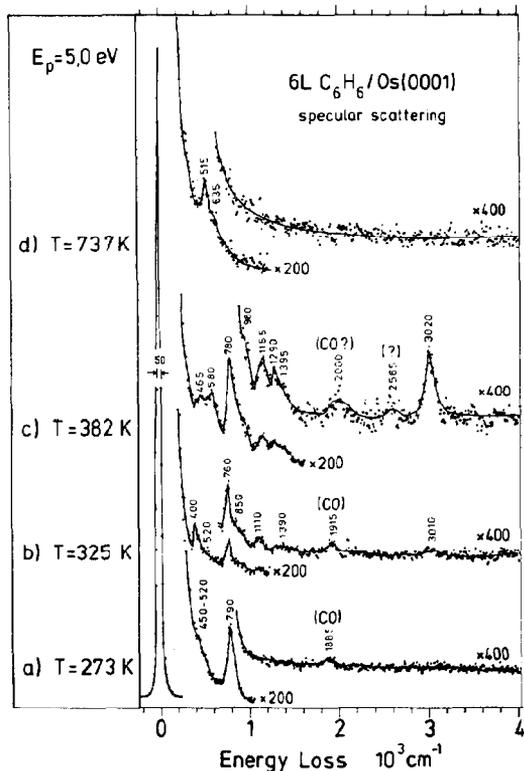


Fig. 1. HREEL spectra of a benzene adsorbate at various substrate temperatures. All spectra are taken in specular scattering geometry. The spectra have been normalized with respect to the maximum of the elastic peak.

is no longer parallel to the surface plane but rather tilted to a certain angle. It is very hard to estimate the tilt angle quantitatively. Jakob and Menzel [13] qualitatively estimate the tilt of the molecular plane by forming the ratio (R_i) of the vibrational loss intensities of the C-H stretch modes above 3000 cm^{-1} with respect to the C-H wagging mode ($\nu_{\text{C-H}}$) below 1000 cm^{-1} under specular scattering conditions. These authors find R_i values of 2×10^{-2} for flat lying C_6H_6 and 12×10^{-2} for C_6H_6 , where the molecular plane is inclined in a physisorbed C_6H_6 layer. We find values of 1×10^{-2} for adsorbed C_6H_6 , 4×10^{-2} for the phenyl phase, and 30×10^{-2} for adsorbed C_6H_4 . Since we know that the C-H framework in phenyl and benzyne stays coplanar within a few degrees in the cluster compound – as it is in gaseous benzene – we may draw the conclusion from the change of R_i as a function of temperature that the tilt angle with

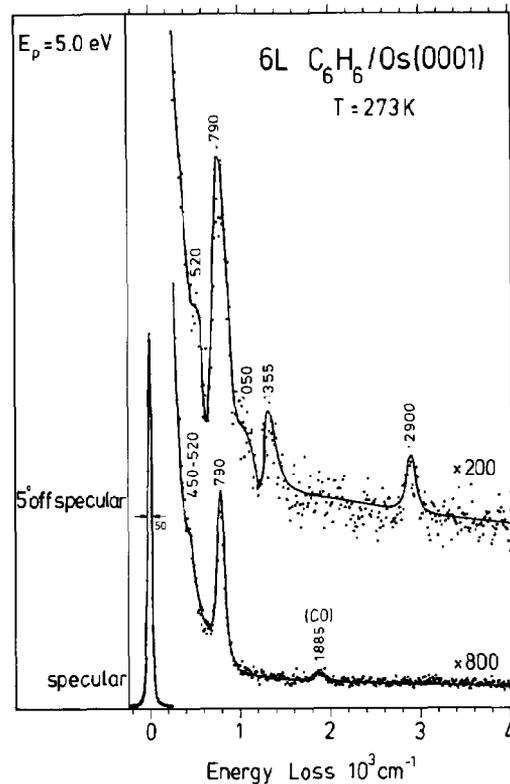


Fig. 2. HREEL spectra of a benzene adsorbate at room temperature. The spectrum taken in specular scattering geometry is compared with the spectrum at 5° off-specular scattering. The spectra have been normalized with respect to the maximum of the elastic peak.

respect to the surface normal decreases from 90° in the C_6H_6 adsorbate to a value comparable or even larger than C_6H_6 physisorbed on $\text{Ru}(0001)$. A reasonable value for the physisorbed phase is 45° , so that we can expect a tilt angle in the neighbourhood of this value for the benzyne species on $\text{Os}(0001)$. Our previous photoemission study is compatible with these findings. Also, as a result of the photoemission study we concluded that in the phenyl adsorbate the tilt angle of the molecular plane increases only slightly with respect to the benzene adsorbate. Our present HREELS data corroborate this finding as well. Upon heating the surface above 400 K the spectra continuously change and, at temperatures above $T = 500\text{ K}$, the vibrational wagging modes, characteristic of the existence of a six-membered ring, have disappeared. This is compatible with the conclusions based on the

TDS data [1] that above this temperature the ring structure breaks up. We have not studied this latter temperature region in detail with HREELS and leave this for future studies.

The present paper provides further experimental evidence to support a reaction channel of adsorbed benzene proposed in an earlier study [1], namely a successive loss of hydrogen accompanied by the formation of at least two intermediate species which we believe to be a phenyl and a benzyne species, before the six-membered ring structure starts to break up, and finally leads to the formation of a carbon overlayer on the Os(0001) surface. To our knowledge there is only one other study reported in the literature where the authors find experimental indications of an adsorbed benzene moiety on a solid surface. Liu and Friend [24] have published XPS and NEX-AFS data for the system $C_6H_6/Mo(110)$. By comparison with reference data (gained via decomposition of C_6H_5SH on $Mo(110)$) [24] they deduce the presence of a benzyne species on the surface. Evidence from vibrational spectroscopy has so far not been reported. The present study represents the first experimental indication via HREELS for the existence of a benzyne precursor for benzene dissociation.

We thank the Deutsche Forschungsgemeinschaft and the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, as well as the Fonds der Chemischen Industrie for financial support.

References

- [1] H.H. Graen, M. Neuber, M. Neumann, G. Illing, H.-J. Freund and F.P. Netzer, *Surface Sci.*, submitted for publication.
- [2] S. Lehwald, H. Ibach and J.E. Demuth, *Surface Sci.* 78 (1978) 577.
- [3] J.C. Bertolini and J. Rousseau, *Surface Sci.* 89 (1979) 467.
- [4] B.E. Koel, J.E. Crowell, C.M. Mate and G.A. Somorjai, *J. Phys. Chem.* 88 (1984) 1988.
- [5] M. Abon, J.C. Bertolini, J. Billy, J. Massadier and B. Tardy, *Surface Sci.* 162 (1985) 395.
- [6] G.D. Waddill and L.L. Kesmodel, *Phys. Rev. B* 31 (1985) 4940.
- [7] B.E. Koel, J.E. Crowell, B.E. Bent, C.M. Mate and G.A. Somorjai, *J. Phys. Chem.* 90 (1986) 2949.
- [8] B. Tardy, J.C. Bertolini and R. Ducros, *Bull. Soc. Chim.* 3 (1985) 313.
- [9] V.H. Grassian and E.L. Muettterties, *J. Phys. Chem.* 91 (1987) 389.
- [10] M. Surman, S.R. Bare, P. Hofmann and D.A. King, *Surface Sci.* 179 (1987) 243.
- [11] P. Jakob, A. Cassuto and D. Menzel, *Surface Sci.* 187 (1987) 407.
- [12] P. Jakob and D. Menzel, *Surface Sci.* 201 (1988) 503.
- [13] P. Jakob and D. Menzel, *Surface Sci.*, submitted for publication.
- [14] S.C. Brown, J. Evans and L.E. Smart, *J. Chem. Soc. Chem. Commun.* (1980) 1021.
- [15] C.W. Bradford, R.S. Nyholm, G.J. Gainsford, J.M. Guss, P.R. Ireland and R. Mason, *J. Chem. Soc. Chem. Commun.* (1972) 87.
- [16] F.H. Köhler, *Chem. i. u. Zeit* 6 (1977).
- [17] A.J. Deeming, J.P. Rothwell, M.B. Hursthouse and J.D.J. Backer-Dirks, *J. Chem. Soc. Dalton Trans.* (1973) 1879.
- [18] M.A. Gallop, B.F.G. Johnson, J. Lewis, A. McCamley and R.N. Perutz, *J. Chem. Soc. Chem. Commun.* (1988) 1071.
- [19] R.J. Goudsmit, B.F.G. Johnson, J. Lewis, P.R. Raitby and M.J. Rosales, *J. Chem. Soc. Dalton Trans.* (1983) 2257.
- [20] O.L. Chapman, K. Mattes, C.L. McIntosh, J. Pacansky, G.V. Calder and G. Orr, *J. Am. Chem. Soc.* 95 (1973) 6134; O.L. Chapman, C.-C. Chang, J. Kolc, N.R. Rosenquist and H. Tomioka, *J. Am. Chem. Soc.* 97 (1975) 6586.
- [21] I.R. Dunkin and J.G. MacDonald, *J. Chem. Soc. Chem. Commun.* (1979) 772.
- [22] H.-H. Nam and G.E. Leroi, *Spectrochim. Acta* 41A (1985) 67.
- [23] H.-H. Nam and G.E. Leroi, *J. Mol. Struct.* 157 (1987) 301.
- [24] A.C. Liu and C.M. Friend, *J. Chem. Phys.* 89 (1988) 4396.