$[Os_2(CO)_8(\mu_2\text{-}\eta^2\text{-}C_2H_4)]$ as a Vibrational Model for 1,2-di-σ Chemisorbed Ethylene on Metal Surfaces

Christopher E. Anson,[a] Brian F. G. Johnson,[a] Jack Lewis,[a] Donald B. Powell,[b] Norman Sheppard,[b] Ashok K. Bhattacharyya,[c] Bruce R. Bender,[d] R. Morris Bullock,[d] Robert T. Hembre,[d] and Jack R. Norton.[d]

[a] *University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW, U.K.*
[b] *School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.*
[c] *Department of Engineering, University of Warwick, Coventry CV4 7AL, U.K.*
[d] *Department of Chemistry, Colorado State University, Fort Collins, CO 80523, U.S.A.*

A vibrational assignment has been made for $[Os_2(CO)_8(\mu_2\text{-}\eta^2\text{-}C_2H_4)]$ and its deuteriated and ^{13}C analogues: this complex is shown to be a vibrational model for molecular ethylene chemisorption, confirming the (1,2-di-σ) bonding mode.

The chemisorption of ethylene onto metal surfaces has been the subject of a large number of vibrational spectroscopic and other studies. Although at ambient and higher temperatures many different dissociatively adsorbed hydrocarbon species have been identified, at low temperatures (generally $T \leqslant 200$ K) it has been found that the ethylene molecule is adsorbed intact onto the metal surface. Studies of this molecular chemisorption by electron energy loss spectroscopy (EELS) have been reviewed by Sheppard,[1] who pointed out that the EEL spectra obtained can be divided into three basic types, designated Types I, I′, and II. Spectra of Type II have been assigned[2] to a π-bonded ethylene species lying parallel to the surface, by comparison of the observed vibrational frequencies and intensities with those found for Zeise's salt, $K^+[Pt(\pi\text{-}C_2H_4)Cl_3]^-$.[3]

Spectra of Type I have been assigned[2] to a species in which each carbon atom is σ-bonded to a surface metal atom, such that the C–C bond is approximately single. The *gauche* conformer of 1,2-dibromoethane[4] has been used as a vibrational model for this species, but is clearly not ideal for this purpose. The binuclear complex $[Os_2(CO)_8(\mu_2\text{-}\eta^2\text{-}C_2H_4)]$[5] (**1a**) is much more suitable as a model, since the 'diosmacyclobutane' core has a structure closely analogous to the proposed surface species, with the C–C bond length of 1.53 Å[5a] and the scalar couplings (J_{CC} 34.0 Hz; J_{CH} 135.3 Hz)[5d] implying full sp^3 hybridisation at the carbon atoms. Accordingly a detailed vibrational study of the complex was carried out. The structure of the complex is shown schematically in Figure 1.

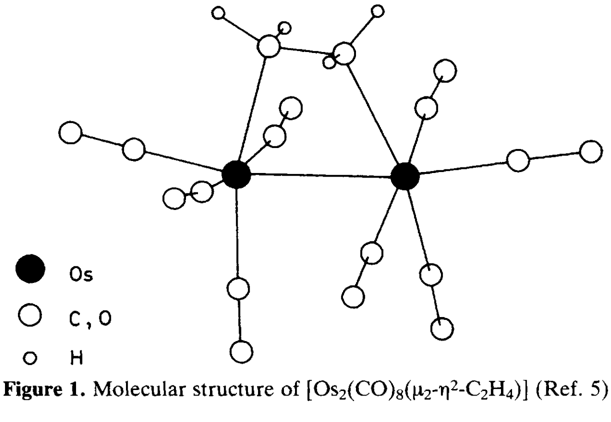

Figure 1. Molecular structure of $[Os_2(CO)_8(\mu_2\text{-}\eta^2\text{-}C_2H_4)]$ (Ref. 5).

Table 1. Vibrational assignment for $[Os_2(CO)_8(C_2H_4)]$ and comparison with surface species[a,b]

		$[Os_2(CO)_8(C_2H_4)]$					$C_2H_4/Pt(111)$ at 92 K[7]			Mean frequencies for type I spectra[1]		
		$(^{12}C_2H_4)$		$(^{13}C_2H_4)$	(C_2D_4)							
Mode[c]		I.r.	Raman	I.r.	I.r.	H/D	C_2H_4 EELS	C_2D_4	H/D	C_2H_4 EELS	C_2D_4	H/D
ν_{CH_2}	b_2/b	2936m	2939w	2926m	2206m	1.33	3000sh	2250w	1.33			
ν_{CH_2}	a_2/a	2917w	n.o.	2907vw	2196w	1.33						
ν_{CH_2}	a_1/a	2910m	2914ms	2900m	2139mw	1.36	2930m	2150m	1.36	2960m	2200m	1.35
ν_{CH_2}	b_1/b	2843m	2843m	2835m	2110m	1.35						
$2\delta_{CH_2}$	B_1/B	2902sh	n.o.	2887sh	n.o.	—						
$2\delta_{CH_2}$	A_1/A	2879vw	2883w	2870sh	2243vw	1.28						
$2\delta_{CH_2}$	A_1/A	2840sh	n.o.	2846mw	2102vw	1.36						
δ_{CH_2}[d]	a_1/a	1445w	n.o.	1439w	1121w	1.28	1430m	1150s	1.24	1420m	1200s	1.18
δ_{CH_2}	b_1/b	1434m	n.o.	1430m	1058m	1.36						
ω_{CH_2}	b_1/b	1225m	n.o.	1216m	913m	1.34	1230[e]	n.o.	—	1220[e]	n.o.	—
ω_{CH_2}[d]	a_1/a	1144vs	n.o.	1134vs	964s	1.18	1060s	900s	1.18	1130vs	920ms	1.20
τ_{CH_2}	a_2/a	1083m	n.o.	1075m	757m	1.43						
τ_{CH_2}	b_2/b	1012mw	n.o.	1011mw	732sh	1.39						
ν_{CC}[d]	a_1/a	981w	n.o.	953w	724vs	1.35	980msh	740m	1.32	900m	730m	1.23
ρ_{CH_2}	a_2/a	837vw	n.o.	830vw	592wsh	1.41	790w	600w	1.32	800[e]	n.o.	—
ρ_{CH_2}	b_2/b	754mw	n.o.	748m	525m	1.44	660w?	n.o.	—			
ν_{OsC}	b_1/b	560ms	556w	552ms	547s	1.07	560[e]	n.o.	—	600[e]	n.o.	—
ν_{OsC}	a_1/a	496m	498vs	492m	487m	1.02	470s	450s	1.04	425s	420s	1.01
$\delta_{Os_2C_2}$	b_1/b	266m	267m	259m	249m	1.07	240[e]	n.o.	—			
ν_{OsOs}	a_1/a	n.o.	146vs	n.o.	n.o.	—						

[a] All frequencies in cm^{-1}; infrared and Raman spectra recorded at 100 K. [b] ν bond stretching mode; δ angle deformation; ω wag; τ twist; ρ rock; s strong; m medium; w weak; v very; sh shoulder; n.o. not observed. [c] Mode symmetries are given according to both C_{2v} and C_2 molecular symmetries. [d] These a_1/a modes are significantly mixed; this mixing seems to be particularly severe in the C_2D_4 species. [e] These weak EELS losses have been observed in a few cases, usually in off-specular spectra, implying probable non-totally symmetrical modes. Underlined EELS losses weaken markedly in off-specular spectra, implying assignment to totally symmetrical modes.

The cluster symmetry is reduced from C_{2v} to C_2 by a rotation ($\simeq 25°$) of the ethylene ligand about the molecular two-fold axis relative to the Os–Os bond.[5a]

Infrared spectra of (**1a**) and its (C_2D_4) and $(^{13}C_2H_4)$ analogues [(**1b**) and (**1c**), respectively] in CsI discs were recorded at 100 K. A Raman spectrum of (**1a**) was also recorded, but fluorescence problems precluded the observation of bands corresponding to modes of the complex in the 1800—700 cm^{-1} region. The assignments for *gauche*-$BrCH_2CH_2Br$[4] and the 'aliphatic half' of cyclobutene[6] were used as rough guides in making the assignments here.

Comparison of the spectra of (**1a**) and (**1c**) enables assignment of considerable ν_{CC} character to a weak band at 981 cm^{-1}; it is shifted by 28 cm^{-1} to 953 cm^{-1} on ^{13}C labelling, whereas the other bands in the 1500—1700 cm^{-1} region are shifted by 10 cm^{-1} or less. Two bands among the low-frequency carbonyl modes, at 560 and 496 cm^{-1}, are also shifted, and can be assigned to the two osmium–carbon stretching modes. The mode at 496 cm^{-1} is considerably the more intense in the Raman spectrum, and is assigned to the symmetric ν_{OsC} mode. The two ν_{OsC} modes show coupling to several of the carbonyl deformation modes, which results in isotopic shifts for the ν_{OsC} modes that are smaller than expected. The band at 266 cm^{-1} is assigned to the antisymmetric in-plane $\delta_{Os_2C_2}$ mode or 'frustrated translation' of the ethylene ligand parallel to the Os–Os bond.

In *gauche*-$BrCH_2CH_2Br$[4], the CH_2 deformation modes occur in a/b pairs, in the frequency order $\delta > \omega > \tau > \rho$. Under the C_2 symmetry of the complex, each of the modes of a symmetry can couple to the ν_{CC} mode, and thus show a rather larger shift to low frequency on ^{13}C substitution than the corresponding b mode. Accordingly, bands at 1445 and 1434 cm^{-1} are assigned to the δ_{CH_2} modes of a and b symmetries, respectively, since they are found at 1439 (−6) and 1430 (−4) cm^{-1} in the spectrum of (**1c**). Similarly, bands at 1225 and 1144 cm^{-1} are assigned to the b and a CH_2 wagging modes, while those at 1083 and 1012 cm^{-1} are assigned to the a and b twisting modes. The intensity of the a twist, higher than expected, may result from its proximity to the very strong wagging mode at 1144 cm^{-1}, to which it can couple under C_2 symmetry. The two rocking modes at 837 and 754 cm^{-1} cannot be distinguished by their shifts on ^{13}C labelling. However, the a mode is expected to be very weak, and is assigned to the band at 837 cm^{-1} on intensity grounds, with the b mode assigned to the medium intensity band at 754 cm^{-1}.

The relative frequencies and intensities observed for the ν_{CH_2} modes in (**1a**) are similar to those observed for the aliphatic ν_{CH_2} modes in cyclobutene,[6] and so these modes are assigned in the same frequency order.

Assignment of the ethylenic modes in (**1b**) is complicated by the strong coupling between the ν_{CC}, ω_{CH_2}, and δ_{CH_2} modes of a (a_1 under C_{2v}) symmetry, which varies from the C_2H_4 to the C_2D_4 complex. This leads to substantial changes in the relative intensities of the bands and to isotopic ratios intermediate between the expected values of near unity for a pure ν_{CC} mode and 1.35—1.42 for pure CH_2 modes. The product of the isotopic shifts for these three mixed modes is 2.07, close to the expected value (2.00). The effects of this coupling are very similar to what was observed for the corresponding modes in the aliphatic C_2H_4 fragment of cyclobutene;[6] bands at 1443 (medium), 1180 (strong), and 966 (weak) cm^{-1} were replaced by bands at 1135 (weak), 955 (medium), and 722 (strong) cm^{-1} on deuteriation.

The assignments for the isotopomers of (**1**) are listed in Table 1, where they are compared with mean EEL frequencies from Type I spectra from C_2H_4 and C_2D_4 adsorption on a range of metal surfaces.[1] Data for Pt(111) are listed separately, since this spectrum lies at an extreme of the Type I series, with somewhat different frequencies. It should be noted that most of the EEL spectra were recorded with specular reflection; the metal surface selection rule then results in the spectra being dominated by losses resulting from totally symmetric a_1/a modes. Modes of other symmetries are active off-specular through impact scattering.

There are small differences between the EEL spectra and those of the model compound, such as the relative mean wavenumbers of the dominant bands in the EEL spectra of C_2H_4 (1130) and C_2D_4 (1200); the corresponding frequencies in (**1a**) (1144) and (**1b**) (1121) are the other way round. These may reflect a differing extent of distortion from C_{2v} symmetry for the adsorbed species compared to (**1**), or the electronic difference between the $[Os_2(CO)_8]$ fragment and the bulk metal surface. Overall, however, the agreement between the spectra of the adsorbed species and of (**1a**) and (**1b**) is very good, thus confirming the identification of Type I spectra with (1,2-di-σ) chemisorbed ethylene species. Comparison with the Pt(111) data suggests that on this surface the ethylene carbon atoms show essentially complete rehybridisation to sp^3, as the frequency agreement (with the sole exception of the 1144/1060 cm^{-1} mode) is very close.

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References

1 N. Sheppard, *J. Electron Spectr. Rel. Phenom.*, 1986, **38**, 175, and references therein.

2 B. J. Bandy, M. A. Chesters, D. I. James, G. S. McDougall, M. E. Pemble, and N. Sheppard, *Phil. Trans. R. Soc. London A*, 1986, **318**, 141.

3 J. Hiraishi, *Spectrochim. Acta, Part A*, 1969, **25**, 749.

4 J. K. Brown and N. Sheppard, *Trans. Faraday Soc.*, 1952, **48**, 128; J. T. Neu and W. D. Gwinn, *J. Chem. Phys.*, 1950, **18**, 1642.

5 (a) K. M. Motyl, J. R. Norton, C. K. Schauer, and O. P. Anderson, *J. Am. Chem. Soc.*, 1982, **104**, 7325; (b) M. R. Burke, J. Takats, F. W. Grevels, and J. G. A. Reuvers, *ibid.*, 1983, **105**, 4092; (c) R. T. Hembre, C. P. Scott, and J. R. Norton, *ibid.*, 1987, **109**, 3468; (d) B. R. Bender, R. Bertoncello, M. R. Burke, M. Casarin, G. Granozzi, J. R. Norton, and J. Takats, *Organometallics*, submitted for publication.

6 L. M. Sverdlov and E. P. Krainov, *Opt. i. Spektr.*, 1962, **13**, 169, quoted in: L. M. Sverdlov, M. A. Kovner, and E. P. Krainov, 'Vibrational Spectra of Polyatomic Molecules,' John Wiley, New York, 1974, p. 278.

7 H. Steininger, H. Ibach, and S. Lehwald, *Surf. Sci.*, 1982, **117**, 685.