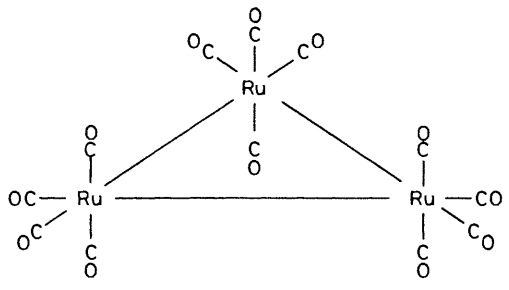
Vibrational Spectrum of $Ru_3(CO)_{12}$; Analogy with the Adsorption System CO/Ru(001)

By Alex Bradshaw

(Fritz-Haber-Institut der Max-Planck-Gesellschaft, 1000 Berlin 33, W. Germany)

Summary The A_2'' vibrational mode of the axial CO ligands in $Ru_3(CO)_{12}$ is found to be identical in character and frequency to that of the collective C–O stretching mode in the adsorption system CO/Ru(001).

It has recently been pointed out that metal cluster compounds might serve as useful models for the understanding of chemisorption processes on metal surfaces.[1] Both photoelectron[2,3] and vibrational[2,4] studies of carbonyl cluster compounds have in fact already revealed considerable similarity between the two systems. This communication is concerned with a unique example of the cluster–surface analogy to be found in the vibrational properties of $Ru_3(CO)_{12}$[5] and CO_{ad}/Ru(001).[6,7]



(1)

The $Ru_3(CO)_{12}$ molecule (1) has D_{3h} symmetry. Because the symmetry operations of the group cannot transform an axial CO into a radial CO, or *vice versa*, the dynamics of the two sets of ligands can be treated independently (to a first approximation). Consideration of the D_{3h} character table shows that the Raman-active A_1' mode[5] at 2127 cm^{-1} corresponds to the in-phase vibration of all six axial CO ligands. In the same way the i.r.-active A_2'' mode at 2062 cm^{-1} [5] corresponds to the three axial ligands on one side of the metal atom plane vibrating in-phase, but being exactly out-of-phase with the three on the other side. Whereas the A_1' mode will mix to a certain extent with the A_1' radial mode, the A_2'' mode is unique in that no radial mode belongs to this representation.

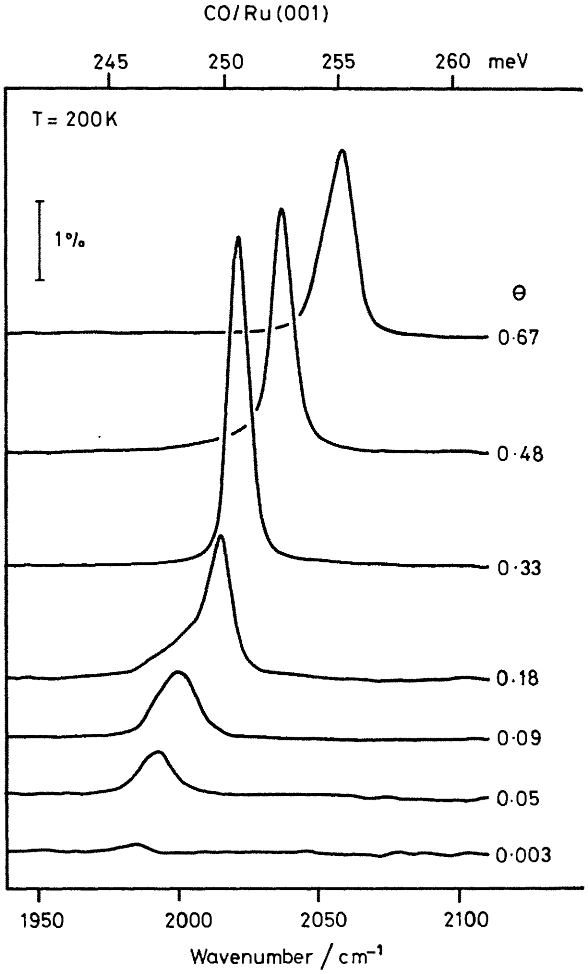


Figure. I.r. absorption band due to the C–O stretch vibration as a function of increasing coverage in the CO/Ru(001) adsorption system. T = 200 K. After Pfnür, *et al.*[7]

Saturation coverage of CO adsorbed on Ru(001) at $T \leqslant 200$ K corresponds to a hexagonal close-packed array of CO molecules out-of-registry with the substrate.[8] Although distinct adsorption sites are not involved, the metal–carbon bond still resembles that of a terminal CO ligand in a metal carbonyl.[7] Indicative of this mode of bonding is a C–O stretch frequency varying from 1984 to 2061 cm^{-1} as a function of coverage, as shown in the Figure.[7] The dynamic dipole moment associated with the C–O stretch is strongly screened by the metallic conduction electrons. The actual field of screening charges induced by the dynamic dipole is exactly equivalent to the field of a virtual image dipole symmetrically situated on the other side of the surface in the metal. The image dipole not only damps the vibration, giving rise to a finite line width in the spectrum, but also changes its frequency. The coverage-dependent frequency shift shown in the Figure can only be explained quantitatively when full account is taken of the image dipoles. For the vibrational spectrum of an ordered array of CO molecules adsorbed terminally on a perfect metal we thus have essentially two arrays of oscillators coupled across the image plane. The instantaneous charge distribution on the image dipoles is, however, in the same sense as the real dipoles *i.e.* the image plane is not equivalent to a symmetry plane. An alternative representation is to consider the image dipoles as being of opposite sense but vibrating 180° out-of-phase with the real dipoles. It is clear that this collective vibration is then exactly analogous to the A_2'' vibration in (**1**). The major differences are that there are only three axial CO ligands (plus their three 'images') in (**1**) and that their mutual separation is 12% lower than in the saturated adsorbate layer. These two effects would appear to compensate, because the adsorbate layer at saturation coverage gives rise to a band at 2061cm^{-1} compared with 2062 cm^{-1} in (**1**). The exact agreement is perhaps accidental but it is nonetheless a clear indication of the validity of this particular cluster–surface analogy.

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