Single-crystal I.R.-reflectance Evidence for the ν(CO) Assignment of Molybdenum Hexacarbonyl

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Single-crystal i.r.-reflectance spectroscopy in polarised light has been used to arrive at a definitive assignment of solid $Mo(CO)_6$ in the ν(CO) region.

Solid compounds having a large number of metal-carbonyl groups in the unit cell yield notoriously bad i.r. spectra when in mull and KBr disc form. Molybdenum hexacarbonyl is among the worst of these cases, the ν(CO) absorption extending over a very wide range, relieved only by a few prominent features which are not very easy to measure. Consequently, although very detailed single-crystal and other information is available from Raman studies of $Mo(CO)_6$,[1,2] some aspects of the interpretation are still in doubt because the corresponding i.r. frequencies have never been determined.

We report the results of experiments in which we have measured the i.r.-reflectance in polarised light from oriented single-crystals, Figure 1. The crystals were held at *ca.* 100 K to prevent evaporation in the focused i.r. beam.

A reflectance band is bounded at its low-frequency side by the crystal transverse optic (t.o.) mode and at high frequency by the longitudinal optic (l.o.) mode.[3,4] The object of the experiment is to determine the t.o. mode frequencies as these correspond to the modes usually seen in absorption. The t.o. (and l.o.) mode positions are usually obtained from a Kramers–Krönig analysis of the reflectance data. However, this procedure is unreliable when several oscillators are in close proximity, as in the present case. Accordingly we have estimated these mode positions visually, which is easy for $Mo(CO)_6$ as the reflectance bands are of nearly classical shape. The values thus obtained are believed to be accurate to within ± 3 cm^{-1}, except for T_2. In the B_{1u} spectrum (b) two of the three bands expected are nearly confluent and the error in estimating the L_1 and T_2 positions is correspondingly greater. The minor features not discussed here originate in [ν(CO) + lattice mode] combinations: full details are given elsewhere.[6]

The molecular ν(CO) modes of $Mo(CO)_6$ are modified in the crystal by the site and the correlation fields, as indicated in Table 1. The strong Raman mode $ν_1$ was too weak to appear in the reflectance spectra, which are entirely generated by components of $ν_3$ and $ν_6$. The B_{1u} spectrum, selectively excited with $E||c$, should have three components (one from $ν_3$, two from $ν_6$), and the B_{3u} spectrum likewise, whereas only two (one each from $ν_3$ and $ν_6$) should be present for $E||b(B_{2u})$. The results are in complete agreement with these predictions. Averaging the observed Raman[1] and i.r. components shows that $ν_3$, E_g drops 11.8 cm^{-1} and $ν_6$, T_{1u} 29.2 cm^{-1} from their values in CCl_4 solution[5] on entering the solid state.

The main features of the disc spectrum can be understood in terms of the observed components. In particular, the prominent peak at 1950 cm^{-1} is seen to be due to the B_{2u} component of $ν_6$, T_{1u}, and those at *ca.* 1968 and *ca.* 1961 cm^{-1} to its B_{3u} and B_{1u} parts respectively.

Our i.r. results help to clarify two unsettled features of the Raman assignment of solid $Mo(CO)_6$. Firstly, the presence of i.r. factor group components near 1965 cm^{-1} confirms a suggestion[2] that the weak Raman band at this frequency is of $ν_6$, T_{1u} origin. Secondly, the almost nil i.r. factor group splitting of $ν_3$, E_g suggests that the B_{3g} Raman band at
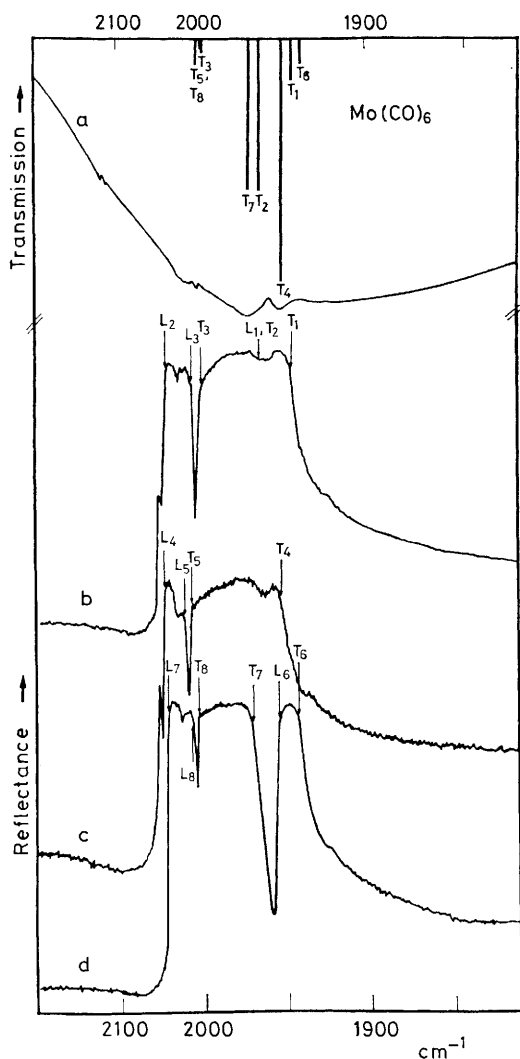

Figure 1. I.r. spectra of $Mo(CO)_6$ in the ν(CO) region at *ca.* 100 K (a) KBr disc, the stick diagram gives approximate relative intensities on the basis of ν(l.o.) — ν(t.o.) values. (b), (c), and (d) show single-crystal reflectance spectra corresponding to $E||c$ (B_{1u} species), $E||b$ (B_{2u}), and $E||a$ (B_{3u}) respectively. Positions of l.o. and t.o. modes are indicated. (Note change of scale at 2000 cm^{-1}.)

Table 1. ν(CO) I.r.-reflectance data and assignments for $Mo(CO)_6$.

Molecule, $O_h \rightarrow$ Site, $C_s \xrightarrow{x4}$ Crystal, D_{2h}^{16}

$ν_1$, A_{1g} (Raman) (2116.7 cm^{-1})[a]	A'	(Components not observed in reflectance)
$ν_3$, E_g (Raman) (2018.8 cm^{-1})	$\begin{cases} A' \\ A'' \end{cases}$	B_{1u} (1998, T_3) + B_{3u} (2004, T_2) A_u (inact.) + B_{2u} (2005, T_5)
$ν_6$, T_{1u} (i.r.) (1986.1 cm^{-1})	$\begin{cases} A' \\ A' \\ A'' \end{cases}$	B_{1u} (1944, T_1) + B_{3u} (1940, T_6) B_{1u} (1964, T_2) + B_{3u} (1969, T_7) A_u (inact.) + B_{2u} (1950, T_4)

[a] Solution values, ref. 5.

2025.5 cm^{-1}, and two other weak ones which accompany it at 2019 and 2034 cm^{-1}, are not components of ν_3.

These results illustrate the power of low temperature i.r.-reflectance spectroscopy for molecular solids: it is a technique which could be used widely. We have also obtained i.r.-reflectance data for $Cr(CO)_6$, $W(CO)_6$, $Fe_2(CO)_9$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Ru_3(CO)_{12}$, in each case being enabled to improve significantly on extant assignments.[6]

References

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