A discussion on the assignment of the C-O vibration bands of metal hexacarbonyl derivatives

Vibration studies conducted simultaneously in many laboratories on varied homologous series of derivatives of the type $M(CO)_{6-n}L_n$ (M = Cr, Mo, W; L = molecule containing a ligand atom of the group V B) have been recently treated in several papers. Some of our measurements and conclusions on the C–O vibrations of these derivatives having been the object of interesting discussions, namely in the papers of Cotton and Kraihanzel[3,5], and following the recent publication of a paper[6] on the same subject, we wish to discuss a certain number of points.

It is well known that the assignment of the observed vibration frequencies can be made by several methods: thus in the series of $M(CO)_{6-n}L_n$ derivatives, we have used[2] methods of comparison of IR and Raman activities, considered the polarisation states of Raman bands, IR and Raman intensities, and used at last the notions of mode correlations and frequency filiations. Orgel, from a qualitative point of view[1], and Cotton and Kaihanzel[3,5,6] from a semi-quantitative point of view, tried to select the correct assignments of frequencies by deductions from valence theory as to the relative magnitude of force constants. We shall not discuss here the rigor of this last procedure; indeed, it often leads to assignments in good agreement with ours which we based on experimental measurements; this shows how their suppositions and approximations are justified *a posteriori*.

Certain cases, however, deserve some comment: mainly those of the *trans*-$M(CO)_3L_3$ derivatives (L = phosphite and phosphine), and of the amine derivatives.

(1). Concerning the *trans*-$M(CO)_3L_3$ derivatives, let us reconsider the case of *trans*-$M(CO)_3[P(OC_2H_5)_3]_3$. The following assignments were suggested:

1988 cm^{-1}	weak	A_1		A_1	
1909 cm^{-1}	medium	A_1	(ref. 2)	B_1	(ref. 6)*
1883 cm^{-1}	strong**	B_1		A_1	

The figure shows the IR and Raman spectra of this compound which had already been isolated. The assignment of the highly polarised band at 1988 cm^{-1} to one of the A_1 modes leaves no doubt; also the strong IR and the weak Raman intensities of the band at 1883 cm^{-1} lead us to assign it to the B_1 mode without further discussion. One problem, however, remains to be solved. It is known that spectra of $M(CO)_{m-n}L_n$ derivatives (m = 4, 5, 6; M = Ni, Fe, Cr), where L are ligands of the type $P(OR)_3$, show several anomalies. Thus it can be seen on the spectrum of *trans*-$Mo(CO)_3[P(OC_2H_5)_3]_3$ that the B_1 band presents a distinct shoulder situated at 1890 cm^{-1}; at last one has to admit the existence of four absorption bands in the C–O stretching region. Out of these bands, only three can be related to C–O fundamental vibrations. Since the assignment of the bands at 1988 cm^{-1} and 1883 cm^{-1} to C–O stretching modes (A_1 and B_1) is without ambiguity, it remains to be seen which of the two bands at 1909 and 1890 cm^{-1} respectively is the third expected C–O stretching frequency (A_1). It is noteworthy that the homologue derivatives $M(CO)_3[P(OR)_3]_3$

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* As a matter of fact, Cotton uses here the average of our IR and Raman measurements (namely $\nu(A_1)$ = 1989 cm^{-1}; $\nu(A_1)$ = 1877 cm^{-1}; $\nu(B_1)$ = 1912 cm^{-1}). We prefer to use the IR frequencies because of the good precision obtained in their measurement.
** And not "medium", as mentioned by Cotton, ref. 6, p. 704.

where M = Cr, Mo, W and R = CH_3, C_2H_5, C_4H_9 present very similar spectra. The only argument for the assignment we have retained is finally the one bearing on the relative band intensities. In spite of the proximity of the bands at 1883 cm^{-1} and 1890 cm^{-1} we have been able to determine comparatively the intensity ratio of the B_1 band (1883 cm^{-1}) to either of the sum of the intensities of the bands at 1988 and 1890 cm^{-1} and at 1988 and 1909 cm^{-1}: the first ratio is approximatively 2, and the second is about 3.3. Since the expected ratio[7] is 2, we can conclude that the second band A_1 must be situated at 1890 cm^{-1}.

In short, the assignment proposed by COTTON is to be rejected. Although the argument based on intensity ratios is not an absolute one, we retain finally the following assignments: A_1: 1988 cm^{-1}; A_1: 1890 cm^{-1}; B_1: 1883 cm^{-1}, which we prefer to the assignments suggested previously[2]. It differs only in the frequency of the intermediate band A_1.

This being said, the band at 1909 cm^{-1} appears as an anomaly which will be discussed later[8].

(2). For the trans-$Mo(CO)_2[P(C_2H_5)_3]_3$ the following assignments were suggested successively:

$$\left.\begin{array}{l} A_1 \quad 1952 \text{ cm}^{-1} \\ \left.\begin{array}{l} A_1 \\ B_1 \end{array}\right\} 1846 \text{ cm}^{-1} \end{array}\right\} \text{(ref. 2)} \qquad \left.\begin{array}{l} 1952 \text{ cm}^{-1} \\ 1887 \text{ cm}^{-1} \\ 1846 \text{ cm}^{-1} \end{array}\right\} \text{(ref. 6)}$$

In fact, on the spectra we have published (Fig. 3-C3 of ref. 2), Cotton thought that he could take into account the band at 1887 cm^{-1}. Actually, this band was due to the presence of a small quantity of trans-$Mo(CO)_4[P(C_2H_5)_3]_2$, and it disappears completely in the spectrum of the well-purified samples[7].

Finally, if we take into account the asymmetry of the B_1 band, and if we compare the intensities of its components, we have to reject Cotton's assignments and retain the following: A_1: 1954 cm^{-1}; A_1: 1841 cm^{-1}; B_1: 1846 cm^{-1}.
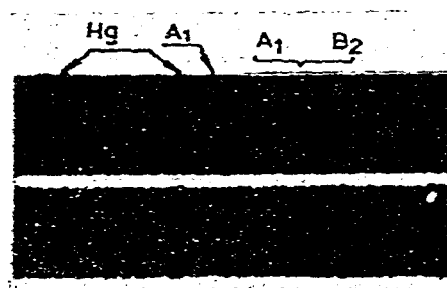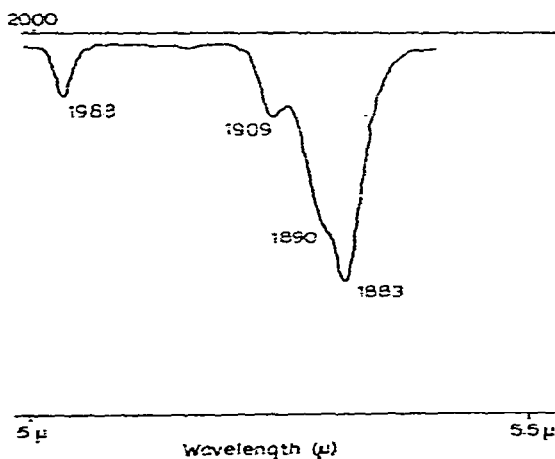

Fig. 1. IR spectrum of trans-$Mo(CO)_3[(P(OC_2H_5)_3]_3$ in n-hexadecane.

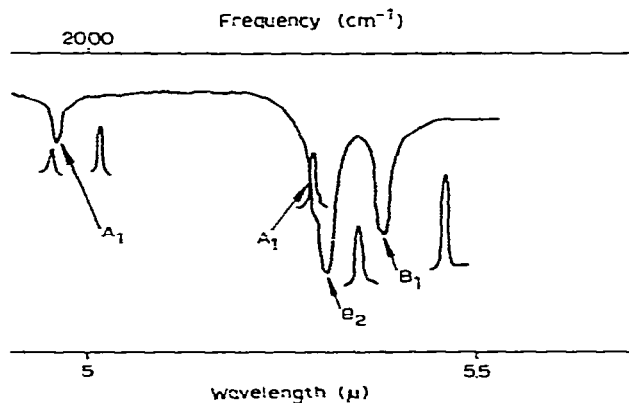Fig. 2. Raman spectrum (C–O region) of trans-$Mo(CO)_3[P(OC_2H_5)_3]_3$ in cyclohexane.

Fig. 3. IR spectrum of $Mo(CO)_4(CH_3)_4$-en in heptane.

(3). Cotton found questionable as well the assignments of the bands of *trans*-$Mo(CO)_3\cdot P(OC_6H_5)_3]_3$. We may point out that the solution is provided for by the band intensities of the spectrum of this compound (monoclinic, $2/m$): A_1: 2017 cm^{-1}; A_1: 1924 cm^{-1}; B_1: 1932 cm^{-1}.

(4). The second case we would like to treat in our discussion is related to the validity of the frequencies retained for the $M(CO)_{6-n}L_n$ derivatives, where L are ligands with amine groups. From this point of view, we know[2,4,10,11] that it is the non-polar solvents which cause the least perturbation. The case of the $M(CO)_5L$ monosubstituted derivatives raises no difficulty since most of these compounds are very soluble in non-polar solvents such as saturated hydrocarbons.

The case of the disubstituted *cis*-$Mo(CO)_4L_2$ brings up the problem of choice of the solvent. One might think that some divergence exists among the proposed assignments for two very close derivatives:

cis-$Mo(CO)_4(CH_3)_4$-en[4]	*cis*-$Mo(CO)_4$en[5]	en = ethylenediamine
A_1 2014 cm^{-1}	2015 cm^{-1}	$(CH_3)_4$-en = tetramethylethylene-
A_1 1888 cm^{-1}	1864 cm^{-1}	diamine
$B_2{}^*$ 1881 cm^{-1}	1890 cm^{-1}	
$B_1{}^*$ 1856 cm^{-1}	1818 cm^{-1}	

The increase in solubility through the introduction of four methyl groups has permitted us to observe the first complex in solution in n-hexadecane. The assignments are reported on Figs. 3 and 4. It can be seen that, in order to pass from the spectrum of type I (fig. 3) to that of type II (fig. 4), we need only suppose a shift of the pair A_1, $B_1(CO^{(C-L)})$ towards the low frequencies in relation to the pair A_1, $B_2(CO^{(C-C)})$. We were able to show that such a shift can be realised indeed on the $M(CO)_4(CH_3)_4$-en derivatives when solvents more polar than hydrocarbons are used[4]. Consequently, one can be sure that the en-derivatives will show a spectrum of the type I if they are examined in a non-polar solvent.

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* The designations B_1 and B_2 depend on the choice of the designation of the planes of symmetry, and no wonder that they vary with the authors. Here we call B_2 the vibration relative to 2 colinear CO groups (CO$^{(C-C)}$) and B_1 the vibration of the two other groups (CO$^{(C-L)}$).

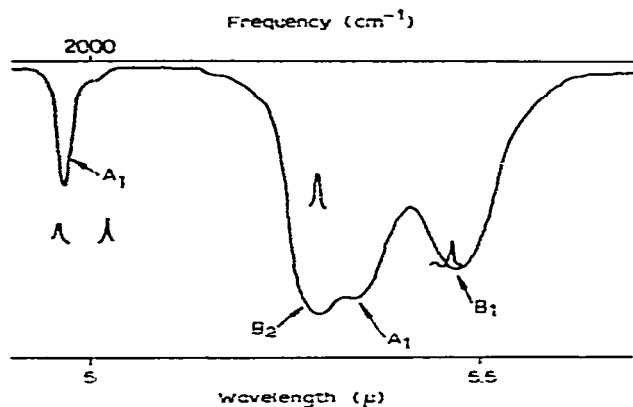Fig. 4. IR spectrum of $Mo(CO)_4(CH_3)_4$-en in chloroform. This spectrum is of the same type as that of $Mo(CO)_4$-en (ref. 5. Fig. 2). Only, the bands are broader.

These observations lead us to admit that the two $CO^{(C-C)}$ groups are less polarisable through solvent effect than the $CO^{(C-L)}$ groups. A similar phenomenon has already been observed on the $M(CO)_4(PR_3)_2$ derivatives when examined in the solid state[2].

(5). As to the cis-trisubstituted derivatives, the introduction of carbon chains on the usual ligands such as diethylenetriamine does not lead to a good solubility in hydrocarbons solvents. However, we were able to obtain the spectrum of a solution of $Mo(CO)_3(CH_3)_5$-dien[9]. In 1,2-dichloroethane, we found $v(A_1) = 1908$ cm^{-1}, $v(E) = 1764$ cm^{-1} (split into 1772 and 1756). If we refer to a similar case, that of cis-$Mo(CO)_3$-$[P(CH_3)_3]_3$, it will be seen that the variations of the frequencies measured in 1,2-dichloroethane and in n-hexadecane can attain about 15 cm^{-1} for the A_1 mode, and about 30 cm^{-1} for the E mode. This correction makes the frequencies of A_1 and E modes of $Mo(CO)_3(CH_3)_5$-dien to be situated at 1923 and 1793 cm^{-1} respectively, in a non-polar solvent. These values are therefore quite different from those admitted by Cotton and Kraihanzel (1898 and 1758 cm^{-1}) for the $Mo(CO)_3$dien derivative, and compare to the values retained for the phosphine homologue derivatives (approx. 1940 and 1840 cm^{-1}).

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