

Solvent Effects on the Infrared Spectra of Chromium,
Molybdenum and Tungsten Hexacarbonyls.*

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The effects of solvents on the infrared spectra of chromium, molybdenum and tungsten hexacarbonyls have been investigated in the 70-2100 cm^{-1} regions for twelve solvents. For all three hexacarbonyls, the CO stretching vibration is lower in solution than in the vapour state, $\nu_{\text{vap}}-\nu_{\text{soln}}$ ranging from 7.6 to 21.5 for chromium, 11.8 to 23.7 for molybdenum and 9.3 to 24.3 cm^{-1} for tungsten. These frequency shifts are discussed in terms of the theory of Drickamer and coworkers. The MCO bending vibrations are almost solvent independent, the average values of $\nu_{\text{vap}}-\nu_{\text{soln}}$ being $+4.6 \pm 1.8$, -2.9 ± 3.2 and -1.0 ± 1.7 for $M=\text{Cr}$, Mo and W respectively. Similarly the MC stretching vibrations are almost solvent independent (except in the case of chromium), the average values of $\nu_{\text{vap}}-\nu_{\text{soln}}$ being -4.5 ± 2.9 , $+5.0 \pm 1.2$ and $+6.0 \pm 1.4$ for $M=\text{Cr}$, Mo and W respectively. Although the CMC bending vibrations have been located for nujol mulls of the metal carbonyls, the instrument proved to be insufficiently sensitive to locate these bands accurately in solution.

Introduction

The study of the solvent sensitivity of molecular vibrational frequencies has given rise to an extensive literature as far as organic compounds are concerned, but only in the last few years has similar interest been shown in inorganic compounds. Barraclough, Lewis and Nyholm¹ have already shown from a study of solvent effects on carbonyl stretching vibrations that useful information can be obtained concerning the electron distribution in metal carbonyls and their derivatives. Further information in this regard has been given by Adams² and by Bellamy,³ and discussed in terms of π -bond formation between the d orbitals of the metal and the π -antibonding orbitals of the carbonyl groups. Accurate data on the solvent sensitivity of the t_2 (ν_3) CO stretching vibration of nickel tetracarbonyl have been given by Bor.⁴

In the present investigation, three of the four infrared-active fundamentals of chromium, molybdenum and tungsten hexacarbonyls (all of t_{1u} symmetry) have been studied in twelve solvents in order to ascertain the effect of polar and non-polar media on these vibrations. The CO stretching frequencies have been determined in all twelve solvents, but owing to solvent interference in certain cases, the MCO bending frequencies and MC stretching frequencies could only be located in six-ten solvents. Although the CMC bending vibrations have been located for nujol mulls of the complexes near to 100 cm^{-1} , the instrument proved to be insufficiently sensitive to locate these bands accurately in solution. These bands have also been located at liquid nitrogen temperatures, in which case resolution of the triple degeneracy occurs.

Experimental Section

The spectra have been recorded using a Unicam SP100 spectrophotometer in the ranges 2100-1900 and 700-400 cm^{-1} , and Grubb-Parsons DM2 and GM3 spectrophotometers in the ranges 400-200 and 200-70 cm^{-1} respectively. The instruments were calibrated by reference to the spectra of DCI^5 in the range 2100-1900 cm^{-1} , of indene⁵ in the range 700-400 cm^{-1} and of water vapour in the range 400-70 cm^{-1} .⁶ The accuracy of the data is believed to lie between ± 0.5 cm^{-1} and ± 1 cm^{-1} over the whole range.

In the low frequency range, special cells with polythene windows were used, but in the other ranges variable thickness cells with KBr windows were used. In the CO stretching region, carbonyl concentrations of $\sim 10^{-3}$ M and path lengths of 1 mm. were used. With polythene cells, the path lengths could not be determined accurately.

The solvents employed were of «spectroscopic» purity or Analar grade, and not purified further. The metal hexacarbonyls were commercial products.

A minimum of four and in some cases up to eight independent measurements of the frequency of each absorption band were made, and the results averaged. The maximum deviation of any individual measurement from the average was 1 cm^{-1} . Each spectrum was

(*) Discussed in part at the Molecular Spectroscopy Meeting of the Italian Research Council, Rome, 23-25 January, 1967.

(**) On leave from the University of Padua, Italy.

(1) C. G. Barraclough, J. Lewis and R. S. Nyholm. *J. Chem. Soc.*, 2582 (1961).

(2) D. M. Adams, *Proc. Chem. Soc.*, 431 (1961); Spectroscopy, Proceedings of the Petroleum Hydrocarbon Research Group, Third Conference, London (1962). The Institute of Petroleum, London, p. 265 (1962).

(3) L. J. Bellamy, «The Infrared spectra of Complex Molecules», 2nd Edn., Methuen and Co. Ltd., London (1958).

(4) G. Bor, *Spectrochim. Acta*, 18, 817 (1962).

(5) Tables of Wavenumbers for the calibration of Infrared Spectrometers, I.U.P.A.C., Butterworths, London (1962).

(6) L. R. Blaine, E. K. Plyer and W. S. Benedict, *J. Res. Nat. Bur. Stand.*, 66A, 223 (1962).

recorded immediately the solution was prepared in order to minimise the effect of any possible reactions between the carbonyls and the solvents.

The CO stretching frequencies have been recorded as a function of time in acetonitrile (the solvent in which decomposition of the carbonyl appeared to be the most rapid). For $\text{Cr}(\text{CO})_6$, there is no variation of ν_6 with time; for $\text{Mo}(\text{CO})_6$, ν_6 decreases by 1 cm^{-1} in a period of four hours and for $\text{W}(\text{CO})_6$, ν_6 decreases by 1 cm^{-1} after a period of two hours. No significant error therefore arises from this cause. Spectra on the GM3 instrument were recorded at liquid nitrogen

temperatures using a specially constructed cell. The precise temperature of the sample in the cell was not known.

Results and Discussion

The results of the investigation are summarised in Tables I-III and for more ready appreciation, are graphed in Figures 1-4. It is convenient to discuss the solvent effects on the four infrared-active modes separately.

Table I. Effect of Solvents on the Frequency of the $\nu_6(t_{1u})\text{CO}$ Fundamental

| Solvent | $\text{Cr}(\text{CO})_6$ | | $\text{Mo}(\text{CO})_6$ | | $\text{W}(\text{CO})_6$ | |
|----------------------|--------------------------|-------------------------------------|--------------------------|-------------------------------------|-------------------------|-------------------------------------|
| | ν_{CO} | $\nu_{\text{vap}}-\nu_{\text{sol}}$ | ν_{CO} | $\nu_{\text{vap}}-\nu_{\text{sol}}$ | ν_{CO} | $\nu_{\text{vap}}-\nu_{\text{sol}}$ |
| Vapour (ref. 4) | 2000.1 | — | 2002.6 | — | 1997.5 | — |
| n-hexane | 1991.0 | 9.1 | 1990.8 | 11.8 | 1987.5 | 10.0 |
| cyclohexane | 1992.5 | 7.6 | 1990.6 | 12.0 | 1985.5 | 12.0 |
| benzene | 1992.2 | 7.9 | 1990.2 | 12.4 | 1988.2 | 9.3 |
| carbon tetrachloride | 1988.0 | 12.1 | 1989.0 | 13.6 | 1982.3 | 15.2 |
| chloroform | 1986.3 | 13.8 | 1985.7 | 16.9 | 1980.3 | 17.2 |
| acetone | 1982.3 | 17.8 | 1985.1 | 17.5 | 1980.1 | 17.4 |
| toluene | 1984.0 | 16.1 | 1984.9 | 17.7 | 1980.2 | 17.3 |
| acetonitrile | 1982.4 | 17.7 | 1983.5 | 19.1 | 1978.4 | 19.1 |
| dichloromethane | 1984.1 | 16.0 | 1983.2 | 19.4 | 1978.8 | 18.7 |
| iodomethane | 1980.5 | 19.6 | 1981.1 | 21.5 | 1975.4 | 22.1 |
| bromoform | 1978.6 | 21.5 | 1979.8 | 22.8 | 1973.4 | 24.1 |
| dibromomethane | 1979.3 | 20.8 | 1978.9 | 23.7 | 1973.2 | 24.3 |

Table II. Effect of Solvents on the Frequency of the $\nu_7(t_{1u})\text{MCO}$ Bending Fundamental

| Solvent | $\text{Cr}(\text{CO})_6$ | | $\text{Mo}(\text{CO})_6$ | | $\text{W}(\text{CO})_6$ | |
|----------------------|--------------------------|-------------------------------------|--------------------------|-------------------------------------|-------------------------|-------------------------------------|
| | δ_{CrCO} | $\nu_{\text{vap}}-\nu_{\text{sol}}$ | δ_{MoCO} | $\nu_{\text{vap}}-\nu_{\text{sol}}$ | δ_{WCO} | $\nu_{\text{vap}}-\nu_{\text{sol}}$ |
| Vapour** | 668 | — | 593 | — | 585 | — |
| n-hexane | 663.8 | + 4.2 | 594.8 | — 1.8 | 586.0 | — 1.0 |
| cyclohexane | 662.1 | + 5.9 | 594.3 | — 1.3 | 585.2 | — 0.2 |
| benzene | * | — | 596.4 | — 3.4 | 586.0 | — 1.0 |
| carbon tetrachloride | 662.0 | + 6.0 | 593.7 | — 0.7 | 585.7 | — 0.7 |
| chloroform | * | — | 596.3 | — 3.3 | 586.3 | — 1.3 |
| acetone | 663.6 | + 4.4 | 599.1 | — 6.1 | 587.7 | — 2.7 |
| toluene | * | — | 594.0 | — 1.0 | 585.8 | — 0.8 |
| acetonitrile | 665.2 | + 2.8 | 598.7 | — 5.7 | 586.3 | — 1.3 |
| dichloromethane | * | — | 596.3 | — 3.3 | 585.6 | — 0.6 |
| iodomethane | 663.6 | + 4.4 | 595.0 | — 2.0 | 585.6 | — 0.6 |
| bromoform | * | — | * | — | * | — |
| dibromomethane | * | — | * | — | * | — |

* Solvent absorption. ** L. H. Jones, *Spectrochim. Acta*, 19, 329 (1963).

Table III. Effect of Solvents on the Frequency of the $\nu_8(t_{1u})\text{MC}$ Stretching Fundamental

| Solvent | $\text{Cr}(\text{CO})_6$ | | $\text{Mo}(\text{CO})_6$ | | $\text{W}(\text{CO})_6$ | |
|----------------------|--------------------------|-------------------------------------|--------------------------|-------------------------------------|-------------------------|-------------------------------------|
| | ν_{CrC} | $\nu_{\text{vap}}-\nu_{\text{sol}}$ | ν_{MoC} | $\nu_{\text{vap}}-\nu_{\text{sol}}$ | ν_{WC} | $\nu_{\text{vap}}-\nu_{\text{sol}}$ |
| Vapour** | 441 | — | 368 | — | 374 | — |
| n-hexane | 442.6 | — 1.6 | 364.0 | + 4.0 | 368.5 | + 5.5 |
| cyclohexane | 444.1 | — 3.1 | 364.0 | + 4.0 | 368.5 | + 5.5 |
| benzene | 445.4 | — 4.4 | 362.0 | + 6.0 | 366.6 | + 7.4 |
| carbon tetrachloride | 447.0 | — 6.0 | 364.0 | + 4.0 | 369.0 | + 5.0 |
| chloroform | 444.1 | — 3.1 | * | — | * | — |
| acetone | 447.2 | — 6.2 | * | — | * | — |
| toluene | * | — | 363.5 | + 4.5 | 368.0 | + 6.0 |
| acetonitrile | 448.0 | — 7.0 | * | — | * | — |
| dichloromethane | 446.1 | — 5.1 | 361.8 | + 6.2 | 367.4 | + 6.6 |
| iodomethane | 444.8 | — 3.8 | 362.5 | + 5.5 | 368.0 | + 6.0 |
| bromoform | * | — | 362.5 | + 5.5 | 368.0 | + 6.0 |
| dibromomethane | * | — | 363.0 | + 5.0 | 368.0 | + 6.0 |

* Solvent absorption. ** L. H. Jones, *Spectrochim. Acta*, 19, 329 (1963).

CO Stretching Fundamentals. From the data in Table I and Figure 1 it is clear that the solvent effect on all three hexacarbonyls is very similar in the CO stretching region. In all cases, the CO stretching frequency is lower in solution than in the vapour state, these latter data being taken from the work of Bor.⁴

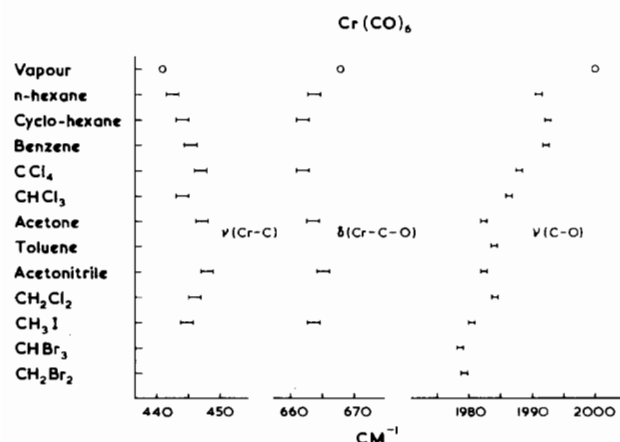


Figure 1. Solvent effects on the Vibrational Spectra of $\text{Cr}(\text{CO})_6$.

The solvent shifts, $\nu_{\text{vap}} - \nu_{\text{soln}}$, range from 7.6 to 21.5 cm^{-1} for $\text{Cr}(\text{CO})_6$, from 11.8 to 23.7 cm^{-1} for $\text{Mo}(\text{CO})_6$ and from 9.3 to 24.3 cm^{-1} for $\text{W}(\text{CO})_6$. The solvent shifts are greater in more polar and in halogeno solvents than in non-polar ones, but all attempts to correlate the shifts with those predicted on the basis of dielectric constant theories⁷ were unsuccessful, presumably because these theories neglect too many types of solute-solvent interactions.

It appears that solvent shifts are more realistically represented by the theory developed by Drickamer and coworkers.^{8,9} According to this theory, the solvent shift for a diatomic molecule having only one vibrational degree of freedom is given by the following expression:

$$\nu_{\text{vap}} - \nu_{\text{soln}} = (8\pi^2 c^2 m_r \nu_{\text{soln}})^{-1} \left[3 \frac{k_A}{k_H} \left(\frac{\delta E_{12}}{\delta r_1} \right) - \left(\frac{\delta^2 E_{12}}{\delta r_1^2} \right) \right]_{r_1=r_e} \quad (1)$$

where m_r is the reduced mass of the oscillator, k_H and k_A are the harmonic and first anharmonic force constants, E_{12} is the interaction energy between the solute bond and the solvent and r_1 is the distance between the nuclei of the diatomic molecule. The above expression may also be applied to localised stretching vibrations of polyatomic molecules, such as the CO stretching vibrations of metal carbonyls. This theory has been applied by Horrocks and Mann to solvent effects on the CN stretching frequency of isonitriles,¹⁰ and carbonyls.¹¹

(7) Discussion Meeting, *Proc. Roy. Soc., A* 255, 1-81 (1960); A. D. Buckingham, *ibid.*, 248, 169 (1958); *Trans. Faraday Soc.*, 56, 753 (1960); A. D. E. Pullin, *Spectrochim. Acta*, 13, 125 (1958); *ibid.*, 16, 12 (1960).

(8) A. M. Benson and H. G. Drickamer, *J. Chem. Phys.*, 27, 1164 (1957).

(9) R. R. Wiederkehr and H. G. Drickamer, *ibid.*, 28, 311 (1958).

(10) W. D. Horrocks and R. H. Mann, *Spectrochim. Acta*, 19, 1375 (1963).

(11) *Idem. ibid.*, 21, 399 (1965).

These authors⁸⁻¹¹ have shown that one of the most important factors determining the direction of solvent shifts in the above expressions is the sign of $\delta u_1 / \delta r_1$, where u_1 is the dipole moment of the solute bond. If $\delta u_1 / \delta r_1$ is negative, then $\nu_{\text{vap}} - \nu_{\text{soln}}$ is negative (as for nitriles) whereas the reverse is true if $\delta u_1 / \delta r_1$ is positive (as for organic carbonyls). Because the experimental data indicate in all cases that $\nu_{\text{vap}} - \nu_{\text{soln}}$ is positive for metal carbonyls it follows from the arguments of Horrocks and Mann¹⁰ that the sign of $\delta u_1 / \delta r_1$ is positive in these molecules.

The larger solvent shifts with solvents of high dipole moment, and with bromo- and iodo-containing solvents is also understandable in terms of the theory of Drickamer *et al.*^{8,9} The solute-solvent interaction energy (E_{12}) is expressed as the sum of four interaction energies between the solute bond and the solvent bond as follows:⁹

$$e_i^{\text{dis}} = - \frac{3}{2} \frac{I_i \alpha_i}{(1 + I_i) R_i^6} \quad e_i^{\text{el}} = \frac{\mu_i^2}{R_i^3} f_i^{\text{el}}$$

$$e_i^{\text{ind}} = \frac{\mu^2 \alpha_i}{R_i^6} f_i^{\text{ind}} \quad e_i^{\text{rep}} = \frac{C_i}{R_i^{12}}$$

where e_i^{dis} is the dispersion energy, e_i^{el} is the electrostatic energy of dipolar orientation, e_i^{ind} is the energy of the dipole, induced-dipole interaction and e_i^{rep} is the intermolecular repulsion energy; α , μ and I are the polarisability, dipole moment, and ionisation energy of the solute bond; R_i is the distance between the solute bond and the i^{th} solvent bond; f_i^{ind} and f_i^{el} are orientation factors and C_i is an empirical parameter. The solvent shifts are determined, as indicated in equation (1), by the energy derivative terms, and the shift in solution is to lower energies if $\delta E_{12} / \delta r_1$ is negative since the factor k_A / k_H is negative.⁸⁻¹⁰ From a consideration of all the energy derivative terms, it is concluded that the solvent shift is expected to be larger the higher the solvent dipole moment and the higher the solvent polarisability. The importance of the latter factor is seen in Figures 1-3 (in which the order of the

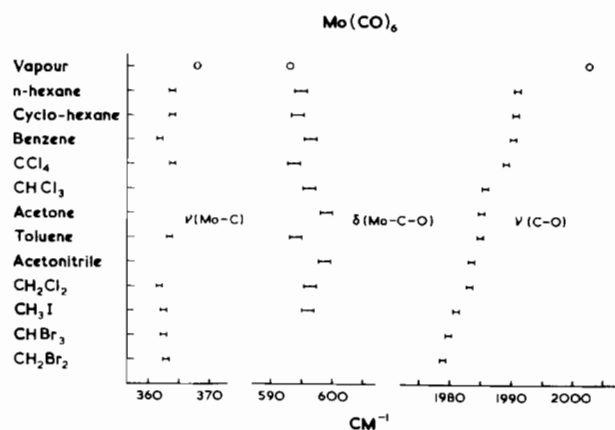


Figure 2. Solvent effects on the Vibrational Spectra of $\text{Mo}(\text{CO})_6$.

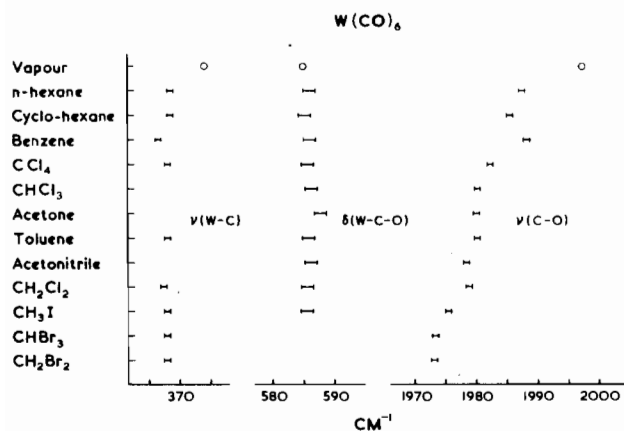


Figure 3. Solvent Effects on the Vibrational Spectra of $W(CO)_6$.

solvents is empirical) because bromo- and iodo-substituted methanes give rise to the largest solvent shifts, despite the fact that C-Br and C-I bond dipole moments are lower than that for a C-Cl bond.

The induction energy, E_{ind} , representing the interaction between the solute dipole and the solvent polarisability can be calculated from dielectric theory and forms the basis for the earlier dielectric constant theories of solvent shifts. Clearly these theories will be appropriate where the dipole moment and the polarisability of the solvent bonds are low, as in the case of many hydrocarbon solvents, i.e. where E_{dis} and E_{or} can be ignored. However, this is not the case with halogeno solvents, particularly with regard to bond polarisabilities; these increase from 0.65 for the CH bond in $CHCl_3$, to 2.61 for the CCl bonds in CCl_4 to 3.60 for the CBr bonds in CH_2Br_2 . In these and related solvents, these dispersion forces make important contributions to the decrease in solute bond stretching frequencies. The present data confirm this, because the CO solvent shifts in the various halogeno solvents lie in the order n-hexane \sim cyclohexane \sim benzene $<$ CH_nCl_{4-n} $<$ CH_nBr_{4-n} i.e. the order of increasing bond polarisabilities. Differences between the CCl bond dipole moments then account for the generally smaller differences between the solvent shifts found in the different chloro-methanes. The CCl bond dipole moments of CCl_4 , $CHCl_3$ and CH_2Cl_2 are 0.5, 0.7 and 1.0 Debye respectively,^{8,7} in agreement with the observed order of CO solvent shifts, which is $CCl_4 < CHCl_3 < CH_2Cl_2$. The solvent shifts reported herein for $Mo(CO)_6$ are slightly less than those reported previously for several solvents.¹¹

In Figures 4, 5 the relative shifts $\Delta\nu/\nu$ for the CO stretching frequencies of $Cr(CO)_6$ and $W(CO)_6$ in the various solvents are plotted against the corresponding values for $Mo(CO)_6$. Linear plots were obtained in both cases, the (least squares) slopes being 0.86 and 0.85 respectively and the r.m.s. σ values being 0.13 and 0.10 respectively. Hence the solvent dependence of the CO stretching vibrations of $Cr(CO)_6$ and $W(CO)_6$ are identical, and slightly greater than that of $Mo(CO)_6$.

MCO Bending Fundamentals. The MCO bending fundamentals of the three hexacarbonyls are almost solvent independent. However, rather surprisingly,

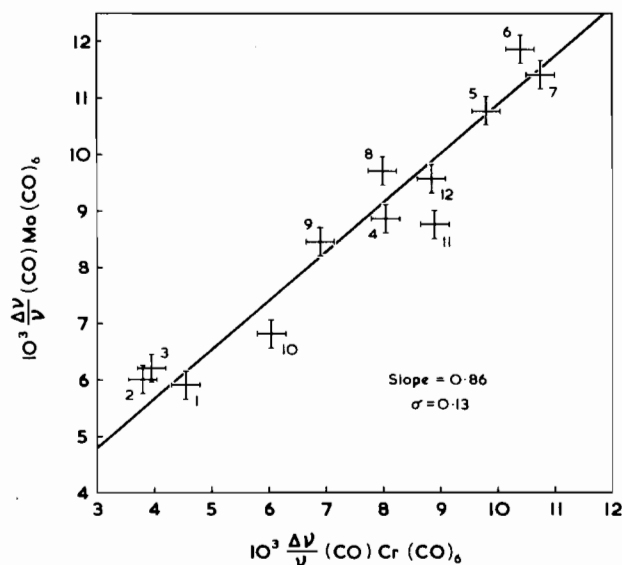


Figure 4. Plot of $\Delta\nu/\nu$ for $Mo(CO)_6$ versus $\Delta\nu/\nu$ for $Cr(CO)_6$. 1, n-hexane; 2, cyclohexane; 3, benzene; 4, toluene; 5, iodo-methane; 6, dibromomethane; 7, bromoform; 8, dichloro-methane; 9, chloroform; 10, carbon tetrachloride; 11, acetone; 12, acetonitrile.

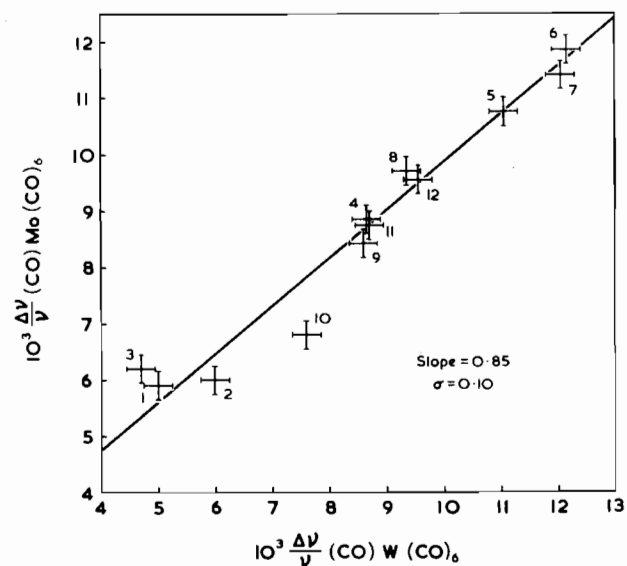


Figure 5. Plot of $\Delta\nu/\nu$ for $Mo(CO)_6$ versus $\Delta\nu/\nu$ for $W(CO)_6$. Solvent order is for Figure 4.

whereas the CrCO bending frequency is lower in solution than in the vapour state, the MoCO and WCO bending frequencies are higher in solution, than in the vapour state. The average values of $\nu_{vap} - \nu_{soln}$ for all solvents measured is $+4.6 \pm 1.8$ (Cr), -2.9 ± 3.2 (Mo) and -1.0 ± 1.8 (W) cm^{-1} . (The \pm values define the limits within which all the solvent shifts lie — not the accuracy of the measurements, which is 0.5-1.0 cm^{-1} as indicated in the experimental section).

MC Stretching Fundamentals. The MC stretching frequencies of $Mo(CO)_6$ and $W(CO)_6$ are solvent independent, the values of $\nu_{vap} - \nu_{soln}$ being $+5.0 \pm 1.2$

and $+6.0 \pm 1.4 \text{ cm}^{-1}$ respectively. However, again $\text{Cr}(\text{CO})_6$ behaves in a different way from the other two carbonyls; $\nu_{\text{vap}} - \nu_{\text{soln}}$ is always negative, with an average value of $-4.5 \pm 2.9 \text{ cm}^{-1}$. Moreover, it is solvent dependent, the MC stretching frequency increasing with increasing dipole moment and polarisability of the solvent from 442.6 cm^{-1} for n-hexane to 448 cm^{-1} for acetonitrile. Its solvent dependence is thus the opposite to that of the CO stretching frequencies, as might have been anticipated from current theories of π -bonding in metal carbonyls.

It is not obvious why the solvent shifts from the vapour state values in this region for $\text{Cr}(\text{CO})_6$ are different in direction from those of the other two carbonyls, although the relative degrees of σ - and π -bonding are doubtless not the same in all these cases. However, electron diffraction data^{12,13} (Table IV) indicate that whereas the CO bond lengths of all three

Table IV. Bond Length Data for the Metal Hexacarbonyls

| Carbonyl | MC (Å) | CO (Å) | Ref. |
|--------------------------|--------|--------|------|
| $\text{Cr}(\text{CO})_6$ | 1.92 | 1.16 | 11 |
| $\text{Mo}(\text{CO})_6$ | 2.063 | 1.145 | 12 |
| $\text{W}(\text{CO})_6$ | 2.059 | 1.148 | 12 |

carbonyls are equal ($\sim 1.15 \text{ Å}$), the MC bond length of $\text{Cr}(\text{CO})_6$ is much ($\sim 0.14 \text{ Å}$) shorter than those of the other two carbonyls. This may imply a different electron distribution in the M-C-O systems for $\text{Cr}(\text{CO})_6$ than for the other hexacarbonyls. This point cannot be discussed further without a full molecular orbital calculation on the three carbonyls and a comparison of the electron populations on each atom.

CMC Bending Fundamentals. The CMC bending fundamentals have been studied at room temperature and at liquid nitrogen temperature as nujol mulls and the results are given in Table V, together with the vapour state values of McDowell and Jones.¹⁴ These

Table V. Values of ν_{1u} $\delta(\text{C}-\text{M}-\text{C})$ Bending Fundamental in Nujol Mulls

| | $\text{Cr}(\text{CO})_6$ | $\text{Mo}(\text{CO})_6$ | $\text{W}(\text{CO})_6$ |
|-----------------------------|--------------------------|--------------------------|-------------------------|
| Room temperature | 109 s, br | 82 w; 92.5 s; 101 m, sh | 92.5 m |
| Liquid Nitrogen temperature | 105 m, sh; 112 s; 119 m | 82 w; 94.5 s; 107 m, br | 82.5 w; 95 m; 108 w, br |

modes lie near to 100 cm^{-1} in each case, the frequency order being $\text{Cr} > \text{Mo} > \text{W}$, and nujol mull (77°K) $>$ nujol mull (298°K) $>$ vapour state value. In all three cases, the $\nu_9(t_{1u})$ absorption band shows more structure at

(12) L. O. Brockway, R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

(13) S. P. Arnesen and H. M. Seip, *Acta Chem. Scand.*, **20**, 2711 (1966).

(14) R. S. McDowell and L. H. Jones, *J. Chem. Phys.*, **36**, 3321 (1962).

liquid nitrogen temperatures than at room temperatures. This is particularly obvious for $\text{Cr}(\text{CO})_6$, for which ν_9 occurs as a single band at 109 cm^{-1} at room temperature, but as a triple band at liquid nitrogen temperatures, centred at 112 cm^{-1} with satellite bands $\pm 7 \text{ cm}^{-1}$ from the band centre (Figure 6). It seems

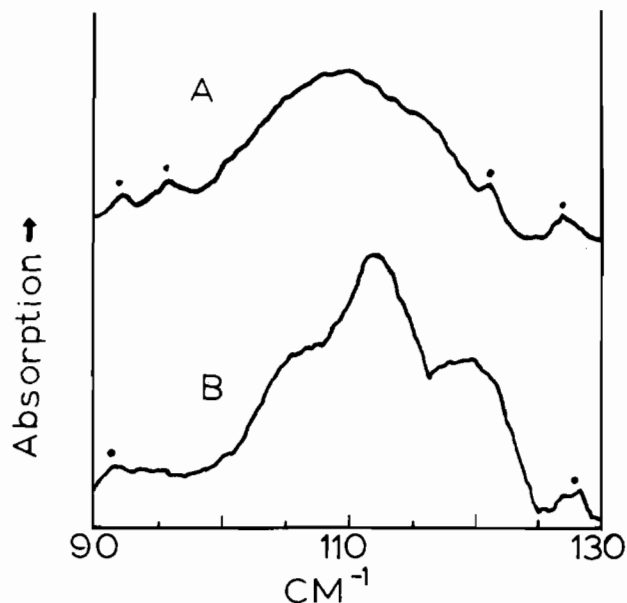


Figure 6. $\nu_9(t_{1u})$ Mode of $\text{Cr}(\text{CO})_6$ (a) at room temperature, (b) at liquid nitrogen temperature. Weak background peaks are dotted.

most probable that the triple degeneracy of ν_9 has thus been resolved although the possibility that inactive fundamentals have been activated by the C_i site symmetry¹⁵ of the crystalline solid cannot be ruled out.

The CMC bending fundamentals were observed to occur at approximately the same frequencies in solution as in nujol mulls, but their exact positions could not be

determined owing to insufficient sensitivity of the instrument.

Acknowledgment. One of us (B.C.) thanks the Consiglio Nazionale delle Ricerche for financial support.

(15) W. Rudorff and U. Hoffmann, *Z. Phys. Chem.*, **B 28**, 351 (1935).