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Structure of $Ir_4(CO)_{12}$ from its Vibrational Spectrum**

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The vibrational spectrum of $Ir_4(CO)_{12}$ (Infrared and Laser-Raman) gives evidence for a T_d structure of the molecule. A partial vibrational assignment is proposed. Vibrational parameteres (Force costants in Cotton-Kraihanzel method) have been calculated and discussed.

Introduction

The study of the vibrational spectrum of polynuclear carbonyl compounds of transition metals is of particular interest for the elucidation of their structure and for the study of the type of bonding between atoms. In this note we discuss the vibrational spectrum of Iridium dodeca-carbonyl $Ir_4(CO)_{12}$ and try to deduce some structural information.

Experimental Section

$Ir_4(CO)_{12}$ was prepared by the carbonylation of Na_3IrCl_6 at atmospheric pressure of carbon monoxide.[1]

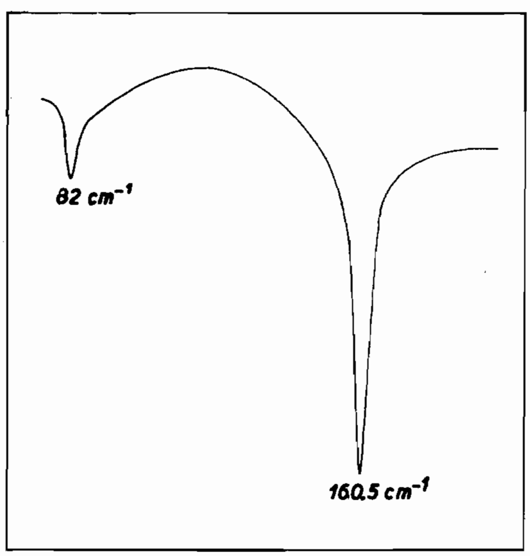

Figure 1. Far infrared spectrum of crystalline $Ir_4(CO)_{12}$.

The infrared spectra were obtained with Perkin Elmer 125, 621 and 301 spectrophotometers (Figures 1, 2) Standard sampling techniques were adopted. The Raman spectrum of the solid was recorded on a Cary laser-Raman spectrometer at the University of Southampton using a laser radiation of 6328 A as exciting line (Figure 3). The spectrum was recorded on a powdered sample enclosed in a glass ampoule which was held against the hemispherical collector lens of the machine.

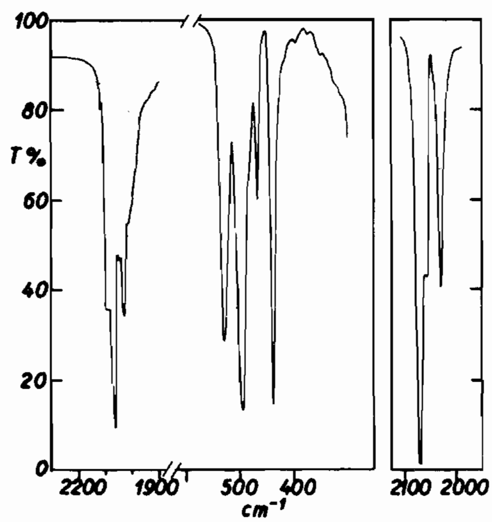

Figure 2. Sections of the infrared spectrum of crystalline $Ir_4(CO)_{12}$ from 2200 to 1900 cm^{-1} and from 600 to 300 cm^{-1}; infrared spectrum from 2100 to 2000 cm^{-1} of $Ir_4(CO)_{12}$ in CH_2Cl_2 solution (10 mm cell).

The structure of $Ir_4(CO)_{12}$. Wei and Dahl have recently announced[2] that from X ray studies it can be shown that the four Iridium atoms occupy the apex of a tetrahedron; to each Ir atom three CO molecules are coordinated and symmetrically placed about a three fold axis. If the 12 CO groups are suitably placed in space and rigidly tied to the Ir frame-work the molecule belongs to the T_d point group. Point groups of lower symmetry are obtained if one lets the $(CO)_3$ groups rotate about their local three fold axis. We wish first to collect some spectroscopic evidence which may confirm independently the structure proposed by Dahl.

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(1) L. Malatesta, G. Caglio, *Inorg. Synthesis*, in press.
(2) Chin. H. Wei, L. F. Dahl, *J. Am. Chem. Soc.*, *88*, 1821, (1966).

The first rigorous approach to the vibrational analysis of this molecule should consider the distribution of the 78 vibrational degrees of freedom into the irreducible representations of the various point groups which are taken as possible models. Table I gives the structure of the representation for a T_d model together with the corresponding infrared and Raman activities. From Table I it can be deduced that, rigorously, if the isolated molecule has a T_d structure we should expect 11 bands in the infrared, 23 bands in the Raman spectrum 5 of which should be polarized. Furthermore we should expect 11 infrared-Raman coincidences. Because of the peculiar structural features of thes types of compounds, and their chemical behaviour (low solubility in solvents etc.) a rigorous interpretation of the spectrum becomes an impossible task and one is forced to accept a series of approximations whose validity is still the subject of discussion among various authors.[3]

tion is supported by the comparison between the spectra of the solid and of the CH_2Cl_2 solution. Vibrational perturbations because of lattice forces are indeed observed. Correlation field splittings (originated from space group selection rules) and static field effect (where site-symmetry is operating) will be then discussed only for C–O stretching motions. The high population of strongly overlapping bands in the lower frequency region together with the lack of any other information on the symmetry properties of the vibrational transitions involved deny any discussion for the C–Ir stretching and the corresponding bending motions. The inner tetrahedron is considered unaffected by lattice forces and considered then independently.

(b) No lattice translational and vibrational motions are sought because of the possible strong overlapping with very low energy internal modes, together with their strong mechanical coupling.

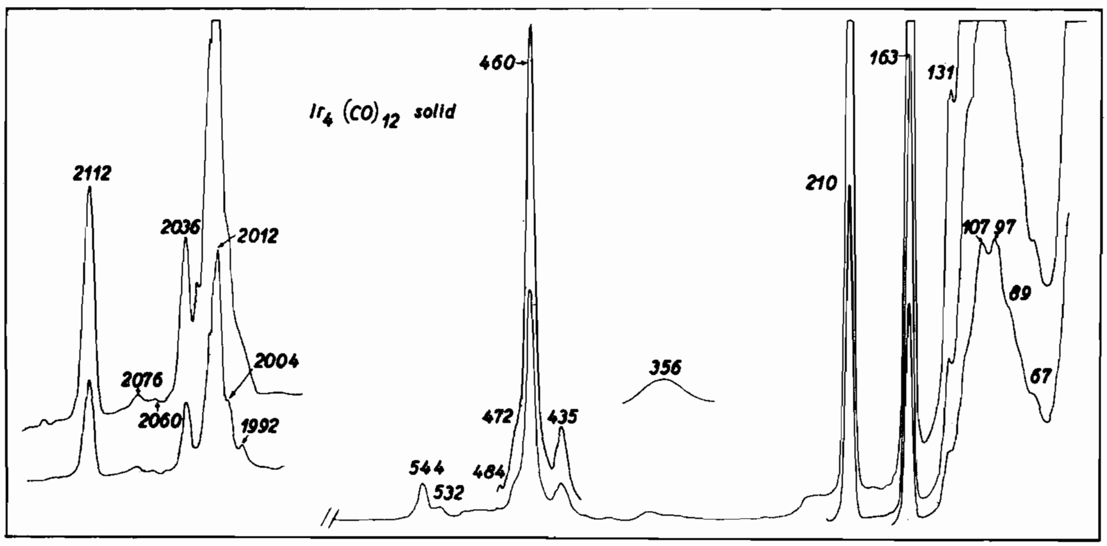

Figure 3. Laser-Raman spectrum of crystalline $Ir_4(CO)_{12}$.

Table I. Distribution of normal modes of $Ir_4(CO)_{12}$ into symmetry species for a T_d structure and spectral activity.

Species	Infrared	Raman
5 A_1	inactive	active, pol.
2 A_2	inactive	inactive
7 E	inactive	active, depol.
8 F_1	inactive	inactive
11 F_2	active	active, depol.

In our analysis we proceed in the following way:

(a) Since the spectra of the solid sample are the largest source of information, the intermolecular coupling in the crystal must be considered together with the electrical field effects. We assume that because of the spatial arrangements of the atoms the vibrations of the external CO groups may be affected to a greater extent than the inner Ir_4 core. This assump-

(3) L. M. Bower and M. H. B. Stiddard, *Inorg. Chim. Acta*, *1*, 231, (1967).

(c) Because of their highly localized character C–O stretching motions can be considered almost group frequencies and then analyzed using the method proposed by Cotton and Kraihanzel[4] for the interpretation of the 2000 cm^{-1} region of the spectrum of many carbonyl compounds. Cotton-Kraihanzel's method is applied in this work as orientative method for the assignment of some bands. Its validity is still matter of discussion (3, 5, 6) and its limitations based on theoretical approximations should be kept in mind when vibratinal assignment and the so derived force costants are interpreted in terms of the chemical and electronic structures of the molecule. In this work we consider as evidence the experimental data and take as suggestions the data from calculations.

(4) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, *84*, 4432, (1962).
(5) L. H. Jones, *Inorg. Chem.*, 7, 1681, (1968).
(6) F. A. Cotton, *Inorg. Chem.*, 7, 1683, (1968).
(7) C. O. Quicksall and T. G. Spiro, *Chem. Comm.*, 839, (1967).

(d) The determination of the whole structure of the molecule could be based on the splitting of some fundamental bands if intramolecular coupling is not negligibly small. Since the lower frequenct spectrum is too crowded, a careful analysis of the finer details of the 2000 cm^{-1} region may perhaps give the required information.

We then first proceed in the attempt of locating the fundamental vibrations of the inner Ir_4 tetrahedron. For a T_d symmetry of an isolated molecule six stretching motions are distributed into one A_1 (R, pol), one E(R, dp) and one F_2(IR, R dp) irreducible representations. They are expected to occur roughly between 200 and 100 cm^{-1}. Since the sample is crystalline the prediction of depolarisation ratios of Raman lines derived for the model of the isolated molecule is not any more valid. Nevertheless we can reasonably assume that of the zero wave vector space group modes the totally symmetrical A_1 mode give rise to Raman lines stronger than the E and F_2 modes. There is no doubt that the strong Raman line at 210 cm^{-1} with no correspondence in the infrared is the A_1 mode, while the strong Raman line at 163 cm^{-1} with a corresponding infrared absorption at 160 cm^{-1} is the F_2 mode. The location of the E mode is not unambiguous. The likely candidates are the Raman lines at 131 and 107 cm^{-1}. The latter line is very strong compared with the former. Since we expect in this spectral range also the totally symmetrical C–Ir–C bending modes we take, with the usual criteria, the line at 107 as A_1 C–Ir–C bending and assign the desired Ir–Ir stretching E mode to the 131 cm^{-1} line*. The experimental evidence collected is enough, alone, to propose, a T_d structure for the Ir_4 part of the molecule. The proposal of Dahl[2] is then satisfactorily verified by an independent physical method.

The local structure of the $Ir(CO)_3$ group is verified according to the following criteria: if the $Ir(CO)_3$ groups are taken as independent from each other the three C=O stretches give rise to one A_1 (R pol; IR) and one E(Rdp,IR) modes. Two strong absorption bands at 2067 and 2017 cm^{-1} are actually observed in the spectrum of the substance in CH_2Cl_2 solution, thus supporting a local C_{3v} structure.

For a complete structure determination one must then decide whether the $Ir(CO)_3$ groups are vibrationally independent or whether they do somehow interact either kinetically or through some interatomic forces. The only way is to decide whether the CO stretching motions are split into the irreducible representations which are expected for the T_d group. This means that in addition to the already used 2067 and 2027 cm^{-1} bands we must find evidence for other symmetry species (*i.e.* one E, one A_1 and one F_1). The A_1 mode for an isolated molecule is silent in the IR and active in the Raman. A strong Raman band is observed at 2112 cm^{-1} for the solid sample. The infrared spectrum of the crystal shows a weak band at same frequency. Its occurrence is well accounted for if site or factor group activations are taken into account. For a T_d structure the bands at 2067 and 2027 cm^{-1} (in solution) become the two expected F_2 motions. The location of the E mode is very uncertain even if the Raman spectrum of the solid shows several bands which could be the likely candidates. Since we feel that any assignment could be proposed only on the basis of almost philosophical evidence we do not propose any "preferred" choice.* The occurrence of the A_1 mode is, however, a good evidence for the existence of intramolecular coupling discussed above.

(*) In a recent communication (ref. 7) Quicksall and Spiro report that they have obtained the Raman spectrum of solid $Ir_4(CO)_{12}$. While the experiments reported in this paper agree with theirs when frequencies are considered, we do not agree on the intensities. As is shown in Figure 3 the intensities of the 210, 163, and 107 cm^{-1} bands are not equal as the former authors report.

It can then be concluded that the vibrational spectrum of $Ir_4(CO)_{12}$ is mostly consistent with a molecule which posseses a T_d structure. The four Ir atoms are at the apex of a tetrahedron and the four $(CO)_3$ groups are placed in space such to give rise to a whole T_d structure. Slight distortions from the ideal model may well occur either for the isolated molecule or even more for the molecule in the crystal. Such a distortions must be, however, below the level of detectability of the classical infrared methods. It could be argued that the occurrence of the band at 2112 cm^{-1} together with the large number of Raman lines in the spectra of the solid could be evidence of a much lower symmetry due to a drastic distortion of the model considered. In this case the idea of the existence of coupling among the four $Ir(CO)_3$ groups would be wrong. Evidence of such a molecular distortion is not found in the present work.

Normal coordinate calculations. A guide in the vibrational assignment especially in the 2000 cm^{-1} region has been provided by the application of the simplified normal coordinate treatment as proposed by Cotton and Kraihanzel.[4] Since the inverse of the kinetic energy matrix is reduced into a diagonal form by the principle of the method, the whole vibrational problem consists in factoring the force constant matrix into symmetry blocks (see Table II). Symmetry coordinates relative to the C=O stretching motions have been constructed for a T_d point group and reported in Table III. The numbering of the atoms is given in

Table II. Secular equation for CO stretching vibrations of $Ir_4(CO)_{12}$ using Cotton-Kraihanzel method.

A_1 $$K+2K_1+2K_2+2K_3+4K_4+K_5=\frac{\lambda}{\mu}$$

E $$K-K_1-K_2+2K_3-2K_4+K_5=\frac{\lambda}{\mu}$$

F_2 $$\begin{vmatrix} K+K_1+K_2-2K_4-K_5-\frac{\lambda}{\mu} & \sqrt{2}(K_2-K_1) \\ \sqrt{2}(K_2-K_1) & K-2K_3+K_5-\frac{\lambda}{\mu} \end{vmatrix} = 0$$

F_1 $$K-K_1-K_2+2K_4-K_5=\frac{\lambda}{\mu}$$

(*) For a discussion of the results of normal coordinate calculations see later in this paper.

Table IIIa. Internal symmetry coordinates for CO stretching modes.

$$S_{A_1} = \frac{1}{2\sqrt{3}}(\Delta r_1+\Delta r_2+\Delta r_3+\Delta r_4+\Delta r_5+\Delta r_6+\Delta r_7+\Delta r_8+\Delta r_9+\Delta r_{10}+\Delta r_{11}+\Delta r_{12})$$

$$\begin{cases} S_E^a = \frac{1}{2\sqrt{6}}(\Delta r_1-2\Delta r_2+\Delta r_3+\Delta r_4+\Delta r_5-\Delta 2r_6+\Delta r_7+\Delta r_8-2\Delta r_9+\Delta r_{10}-2\Delta r_{11}+\Delta r_{12}) \\ S_E^b = \frac{1}{2\sqrt{2}}(\Delta r_3-\Delta r_1+\Delta r_4-\Delta r_5+\Delta r_7-\Delta r_8+\Delta r_{12}-\Delta r_{10}) \end{cases}$$

$$\begin{cases} S_{F_2}^a = \frac{1}{2\sqrt{2}}(\Delta r_1+\Delta r_2-\Delta r_5-\Delta r_6-\Delta r_8-\Delta r_9+\Delta r_{10}+\Delta r_{11}) \\ S_{F_2}^b = \frac{1}{2\sqrt{2}}(\Delta r_2+\Delta r_5-\Delta r_4-\Delta r_6+\Delta r_7+\Delta r_9-\Delta r_{11}-\Delta r_{12}) \\ S_{F_2}^c = \frac{1}{2\sqrt{2}}(\Delta r_1+\Delta r_3+\Delta r_4+\Delta r_7-\Delta r_7-\Delta r_4-\Delta r_{10}-\Delta r_{12}) \end{cases}$$

$$\begin{cases} S_{F_2}^a = \frac{1}{2}(\Delta r_6-\Delta r_3+\Delta r_7-\Delta r_{12}) \\ S_{F_2}^b = \frac{1}{2}(\Delta r_5-\Delta r_1+\Delta r_{10}-\Delta r_8) \\ S_{F_2}^c = \frac{1}{2}(\Delta r_9-\Delta r_2+\Delta r_{11}-\Delta r_6) \end{cases}$$

$$\begin{cases} S_{F_1}^a = \frac{1}{2\sqrt{2}}(\Delta r_3-\Delta r_1+\Delta r_6-\Delta r_5-\Delta r_7+\Delta r_8+\Delta r_{10}-\Delta r_{12}) \\ S_{F_1}^b = \frac{1}{2\sqrt{2}}(\Delta r_2-\Delta r_3+\Delta r_4-\Delta r_6-\Delta r_7+\Delta r_9-\Delta r_{11}+\Delta r_{12}) \\ S_{F_1}^c = \frac{1}{2\sqrt{2}}(\Delta r_1-\Delta r_2-\Delta r_5+\Delta r_6-\Delta r_8+\Delta r_9+\Delta r_{10}-\Delta r_{11}) \end{cases}$$

Δr_i = change in bond length of i—th CO group

Table IIIb. Internal symmetry coordinates for Ir—Ir stretching modes.

$$S_{A_1} = \frac{1}{\sqrt{6}}(\Delta r_{12}+\Delta r_{13}+\Delta r_{14}+\Delta r_{23}+\Delta r_{24}+\Delta r_{34})$$

$$\begin{cases} S_{F_2}^a = \frac{1}{\sqrt{2}}(\Delta r_{12}-\Delta r_{34}) \\ S_{F_2}^b = \frac{1}{\sqrt{2}}(\Delta r_{13}-\Delta r_{24}) \\ S_{F_2}^c = \frac{1}{\sqrt{2}}(\Delta r_{14}-\Delta r_{23}) \end{cases}$$

$$\begin{cases} S_E^a = \frac{1}{2\sqrt{3}}(2\Delta r_{12}+2\Delta r_{34}-\Delta r_{14}-\Delta r_{24}-\Delta r_{13}-\Delta r_{23}) \\ S_E^b = \frac{1}{2}(\Delta r_{14}+\Delta r_{23}-\Delta r_{13}-\Delta r_{24}) \end{cases}$$

Δr_{ij} = change of bond length between the i—th and j—th Ir atoms

Figure 4. In Figure 4 the C=O groups 2 and 6 lie in the plane defined by bond 1-2 and the—z axis. Analogously C=O groups 9 and 11 lie in the plane defined by bond 3-4 and the+z axis.

In such structure Ir atoms have a octahedral coordination. Calculations were first carried out using a reasonable set of constants for obtaining an indication of the location of the A_1 mode, and of the corresponding normal vibrations of the mono isotopic derivative. As discussed earlier in this paper we have settled on the assignment of the A_1 mode whose location is in agrement with other works on analogous carbonyl derivatives.[8] We have left open the assignment of the E mode.

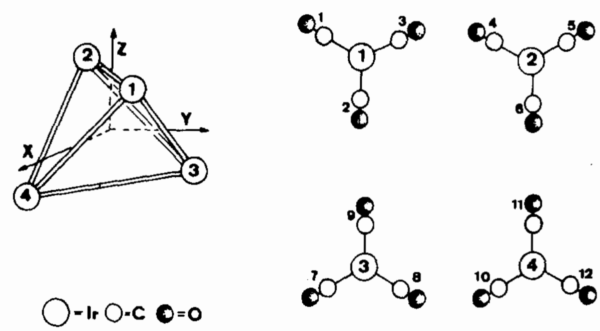

Figure 4. Schematic drawing of the structure of $Ir_4(CO)_{12}$. (The numbering of atoms refers to the calculations reported in the text).

Table IV. Vibrational parameters of CO groups (force constants in Cotton-Kraihanzel method) of $Ir_4(CO)_{12}$

K	= 16.85990	K_3	= 0.137900
K_1	= 0.18700	K_4	= 0.000000
K_2	= 0.22440	K_5	= 0.000000

K = C—O vibrational parameter
K_1 = interaction between C—O of the type 1 and 2; 1 and 3 see fig. 4
K_2 = interatcion between C—O of the type 1 and 4; 1 and 11 see fig. 4
K_3 = interaction between C—O of the type 1 and 5; 1 and 10 see fig. 4
K_4 = interaction between C—O of the type 1 and 6; 1 and 12 see fig. 4
K_5 = interaction between C—O of the type 1 and 8, 2 and 6 see fig. 4

Table V. Central field force constants for the Ir_4 skeleton found in $Ir_4(CO)_{12}$ (mdyne/Å)

$$K^a = 1.50$$

$$K^a: \frac{1}{\mu} = \frac{1}{m_{Ir}} + \frac{1}{m_{Ir}};$$

$$K^b = 2.15$$

$$K^b: \frac{1}{\mu} = \frac{1}{m_{Ir}+3m_{CO}} + \frac{1}{m_{Ir}+3m_{CO}}$$

For the least square refinement we have used one A_1 frequency (2110 cm^{-1}) from the Raman spectrum of the solid, two F_2 (2067.2; 2026.8 cm^{-1}) frequencies from the infrared in solution and one isotopic band (2058 cm^{-1}) from the infrared in solution.

Several least squares refinements have been carried out in order to obtain a set of "vibrational parameters"[9] which reproduce the observed frequencies.

The final choice among various possible sets of "vibrational parameters" has been guided by the attempt of reproducing the intensity ratio between the two F_2 modes according to Bor.[10] Because of the

(8) G. Bor, *Spect. Acta, 19,* 1209, (1963).
(9) K. Edgar, J. Lewis, A. R. Manning, and J. R. Miller, *J. Chem. Soc.* (A), 1217, (1968).
(10) G. Bor, *Inorg. Chim. Acta, 1,* 81, (1967).

oversimplification of Cotton-Kraihanzel method and because of the paucity of the esperimental data at the moment we do not wish to commit ourselves with any conclusion on the interaction between C=O groups which may be considered physically valid.

The validity of the parameters obtained can only be judged within the validity of the Cotton-Kraihanzel method. We report in Table IV the set of parameters obtained (chosing $K_4=K_5=O$).

Of more interest is the value of the force constants which can be derived for the essentially Ir-Ir stretching using the low frequency experimental data. If we apply a central force field to a tetrahedron[11] we obtain two sets of force constants as reported in Table V. These values can be qualitatively compared with those reported by Gager *et al.*[12] and by Hartley *et al.*[13] It has to be remarked, however, that Hyans *et al.*[14] have recently cast some doubt on the assignment of the Re-Re stretching frequency in $Re_2(CO)_{10}$ proposed by Lewis *et al.*[15] and by Cotton *et al.*[16] and adopted in references 11 for the calculation of the force constants.

Acknowledgments. We wish to thank Dr. G. Caglio for the gift of a sample of $Ir_4(CO)_{12}$, Dr. J. P. Hendra for recording the Raman spectrum and Mr. C. Forese for the far infrared experiments.

(11) G. Herzberg, «Infrared and Raman Spectra», vol. II, Van Nostrand, New York, p. 162.
(12) H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Comm.*, 616, (1966).
(13) D. Hartley, P. A. Kilty, and M. J. Ware, *Chem. Comm.*, 493, (1968).
(14) I. J. Hyams, D. Jones, and E. R. Lippincott, *J. Chem. Soc.* (A), 1987, (1967).
(15) J. Lewis, A. R. Manning, J. R. Miller, and F. Nyman, *Nature*, *207*, 142, (1965).
(16) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, *4*, 1328, (1965).