Reassignment of the Infrared-inactive C–O Stretching Frequencies of Decacarbonyldimanganese

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Summary ^{13}CO-enriched $Mn_2(CO)_{10}$ has been prepared, its i.r. spectrum studied, and the i.r.-inactive frequencies determined, in good agreement with recent (unassigned) Raman data.

THE earlier published assignments[1,2] of the C–O stretching vibrations of $Mn_2(CO)_{10}$, which were based mainly on combination spectral data, were not in accord with the positions of those weak bands of the spectrum which were, at least partly, considered[3,4] as ^{13}C–O isotope bands. A more recent assignment[5] gave closer agreement with the observed isotopic frequencies (±3 cm.$^{-1}$), but further study by ^{13}CO enrichment and refined calculations—like those performed with $Ni(CO)_4$,[6] $Fe(CO)_5$, and $Hg[Co(CO)_4]_2$[7]—seemed necessary to obtain more accurate and more definite values for the i.r.-inactive C–O stretching frequencies.

An approximately threefold enrichment of the natural ^{13}CO content could be achieved by irradiating with sunlight a hexane solution of $Mn_2(CO)_{10}$ in contact with ^{13}CO-rich (22·5 per cent) carbon monoxide for several hours.† It was confirmed that the bands reported[4] at 2003·5, 1995·7, 1957·7, and 1950·9 cm.$^{-1}$ belong to one of the two $Mn_2(^{12}CO)_9(^{13}CO)$ isomers. Moreover, another mono-^{13}CO band was observed at 2111·5 cm.$^{-1}$, and additional very weak bands at 2108·4, 1989 (sh), 1968, 1962, and 1947 (sh) cm.$^{-1}$ which could be shown to belong to di-^{13}CO substituted molecules.

Combining the ^{13}CO frequencies with the previously correctly assigned[4] i.r.-active $Mn_2(^{12}CO)_{10}$ C–O stretching

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† The ^{13}CO enrichment experiments were performed in the Hungarian Oil and Gas Research Institute, Veszprém, Hungary (1967).

fundamentals (species b_2: 2045·8 and 1983·8 cm.$^{-1}$, and e_1: 2014·7 cm.$^{-1}$) the i.r.-forbidden C–O stretching frequencies were obtained (see the last column of the Table). The new values for the frequencies in species a_1, e_2, and e_3 are in very good agreement (±1·5 cm.$^{-1}$) with the recently published (although not assigned) Raman data of Clark and Crosse.[8] The mono- and di-^{13}CO frequencies calculated on the basis of the new i.r.-inactive values agree with the measured ones within ±0·5 cm.$^{-1}$. Moreover, the combination spectrum[1,2] can be interpreted completely on the basis of the new assignment.

Assignments given for the i.r.-inactive C–O *stretching frequencies of* $Mn_2(CO)_{10}$

	I[2]	II[1]	III[5]	This work
ν_1 (a_1)	2116	2111	2115	2115·0
ν_2 (a_1)	1976	1981	2002	1997·5
ν_6 (e_2)	2018	2009	2019	2023·0
ν_7 (e_3)	1947	1953	1978	1981·5

The calculations were performed on the basis of a factored C–O stretching model developed[9] for metal carbonyls having two sets of CO ligands. The extent of coupling between radical and equatorial type symmetry co-ordinates was found (in terms of sin β[9]) as 0·80 resulting in a form of normal mode Q_1 (a_1) in which both axial and radical CO ligands have the same vibrational amplitudes. The force and interaction constants in the factored C–O stretching model calculated from the new frequencies are: $k_{eq} = 16{\cdot}50$; $k_{ax} = 16{\cdot}31$; $k_{trans} = 0{\cdot}37$; $k_{cis} = 0{\cdot}17$; $k_{eq,ax} = 0{\cdot}30$; $k^*_{cisoid} = 0{\cdot}22$; $k^*_{transoid} = 0{\cdot}03$; $k^*_{ax,ax'} = 0{\cdot}20$; and $k^*_{eq,ax'} = 0{\cdot}09$ mdyn./Å, the k^* values being the indirect interaction constants acting between CO groups attached to different metal atoms. None of these has been found to be zero or negative, as assumed or found in earlier simplified calculations.[1]

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