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Reduction of the Symmetry of the $V(CO)_4$ Fragment in $(h^5\text{-}C_5H_5)V(CO)_4$ upon Acetylation. Limits of the Applicability of the Method of Local Symmetry in the Interpretation of Metal Carbonyl Spectra

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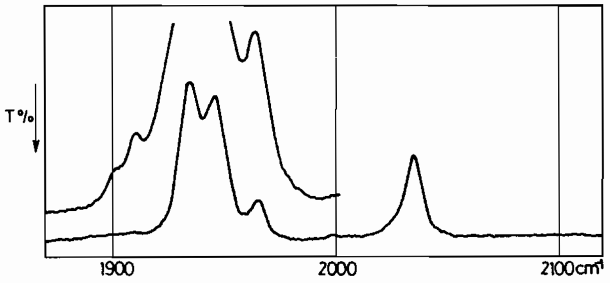
During the last two decades the method of "local" symmetry[1] (MLS) was often used for the interpretation of the spectra of metal carbonyls. However, presently available experimental data do not clearly define the limits of its applicability. We suggest that this method is applicable *until the molecular orbitals* of the carbonyl *became enough deformed* to produce *observable spectroscopic effects,* such as *e*-splitting or appearance of "inactive" bands which are governed not by the "local" but by the overall symmetry of the molecule. This paper describes some observations on the spectra of cyclopentadienylvanadium tetracarbonyl derivatives in the ν(C–O) region which help to define the limits of applicability of the MLS.

Monometallic metal carbonyl derivatives of π-bonded organic ligands (benzene, cyclopentadienyl, allyl, *etc.*) provide a useful tool in investigation of the limits of applicability of MLS. Convincing cases of *e*-splitting could be observed.[2-7] Nevertheless several counter-examples could be found[8-14] and not only in the earlier literature where perhaps the lack of high resolution spectrometers could be a reason. There are even examples where in the detailed analysis of the spectra of rather similar metal carbonyl derivatives the MLS once was found applicable and once not[6,14] by the same research group (these authors abstain from comments to this finding).

$(h^5\text{-}C_5H_5)V(CO)_4$ and its derivatives seem to be particularly useful to study the limits of applicability of MLS in metal carbonyls. The $V(CO)_4$ moiety has a C_{4v} local symmetry which leads to infrared active a_1 and e and an infrared inactive but Raman active b_1 ν(C–O) frequencies. If the C_{4v} symmetry is reduced to C_s or C_1 not only the splitting of the e band but also the appearance of a new band (a derivative of the ir-inactive $C_{4v}b_1$ band) should be observed as it was in the case of appropriately chosen perfluoroalkyl-metal pentacarbonyl derivatives[15] $R_FM(CO)_5$ (M = Mn, Re). However it was found in earlier work[16,17] that a vibrational analysis of both $(h^5\text{-}C_5H_5)V(CO)_4$ and $(h^5\text{-}AcC_5H_4)V(CO)_4$, based mainly on the non-carbonyl part of the ir and Raman spectra, could be performed according to the C_{4v} "local" symmetry of the $V(CO)_4$ entity. This paper reports a reinvestigation of the ν(C–O) spectra of these compounds aiming to resolve this contradiction.

Results and discussion

The results obtained under high resolution conditions are shown in the Figure and the Table. The fundamental ν(C–O) spectrum of $(h^5\text{-}C_5H_5)V(CO)_4$ consists of two lines, which we assigned as shown in the Table taking in regard that the a_1 band can be expected[18,19] at higher wavenumbers while the *e*-band should be the more intense. This result means that the electronic effect of the penta*hapto*-cyclopentadienyl ring (with a five-fold axis) does not cause spectroscopically observable deformation of the MOs connecting the metal and the carbonyl groups. The ν(C–O) spectrum of $(h^5\text{-}AcC_5H_5)V(CO)_4$ which contains four fundamentals, however, corresponds already to the C_1 overall symmetry of the whole molecule most probably because of deformation in the electron system caused by the strong electronic effect of the acetyl group. The assignment given in the Table is suggested on the basis of obvious filiation from the spectrum of $(h^5\text{-}C_5H_5)V(CO)_4$.



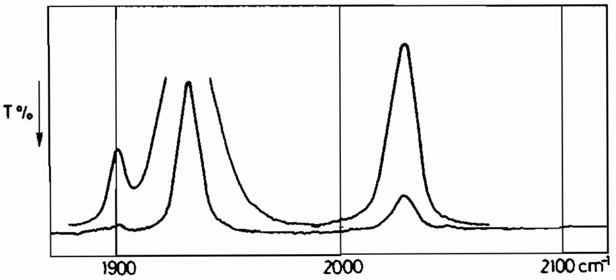


TABLE. ν(C–O) Ir Spectra of $(h^5\text{-}C_5H_5)V(CO)_4$ and $(h^5\text{-}AcC_5H_4)V(CO)_4$ (n-hexane solution, LiF prism, UR-20, Carl Zeiss Jena, DCl calibration[20]).

Assignment according to C_{4v} Compound	a_1	b_1	e	$\nu(^{13}C–O)$
$(h^5\text{-}C_5H_5)V(CO)_4$	2029.9(m)	–	1933.2(vs)	1901.6(vw)
$(h^5\text{-}AcC_5H_4)V(CO)_4$	2035.5(m)	1965.5(mw)[a]	1947.2(s) 1934.7(vs)	1910.3(vw), 1902.5(sh, vw)

[a] This band probably corresponds to the "shoulder" reported[12] to appear at 1972 cm^{-1}.

We conclude that the observed behaviour of the ν(C–O) spectra of the two vanadium carbonyls fits thus well in the picture which could be generalized from earlier data.

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