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The b_1 C≡O Strectching Mode in the Infrared Spectra of C_{4v} $M(CO)_5X$ Complexes

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Received November 18, 1967

The observation of a peak in the infrared spectra of $M(CO)_5X$ complexes (C_{4v} symmetry) attributable to the b_1 C≡O stretching mode is discussed. A mechanism is suggested whereby this formally forbidden mode becomes active. The mechanism involves excitation of the b_1 mode in molecules which are not in the vibrational ground state.

Introduction

Because of recent interest in both relative[1,2] and absolute[3,4] band intensities of infrared active carbonyl stretching frequencies of metal carbonyls and their derivatives, we comment on several features of the CO stretching vibrations of molecules of the type $XM(CO)_5$, where X may be atomic or a group IVb ligand. Where required, the remarks may be adapted to other carbonyl systems.

Within the context of separated high-frequency CO stretching modes, it has been suggested[3,5,6] that the intensity of the highest-energy a_1 CO stretching mode of $XM(CO)_5$ (of C_{4v} symmetry) involving motion of the radial CO groups (Figure 1a) derives from at least three distinct mechanisms: (i) with other a_1 modes, (ii) non-coplanarity of the radial carbonyl groups, and (iii) electronic migration due to axial asymmetry. However such mechanisms are not available for the formally infrared forbidden b_1 CO stretching mode (Figure 1b). Its detection has therefore been attributed to a lowering of the local symmetry,[6,7,8] a conclusion that agrees with the observation that its appearance is frequently associated with the removal of the degeneracy of the two remaining radial CO stretching modes (Figures 1c, 1d).

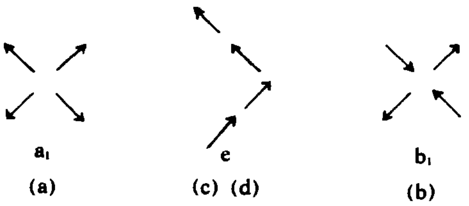

Figure 1. Radial CO stretching modes for $XM(CO)_5(C_{4v})$.

However, in many instances an infrared active b_1 mode is recorded, apparently without concomitant relief of the CO radial e mode degeneracy.[6,7,8] It therefore appears that an alternative mechanism for intensity gain must be available.

A transition is infrared allowed if the direct product of the states before and after the transition transforms like a co-ordinate axis. If the initial state is vibrationally totally symmetric this rule reduces to the requirement that only those vibrations which transform like co-ordinate axes be observed. It is on these grounds that the b_1 mode is forbidden. If the initial state is not vibrationally totally symmetric it is necessary to evaluate the direct product explicitly. Consider an $XM(CO)_5$ molecule with its low-energy C–M–X bending e mode thermally excited. The vibrational state symmetry is E. If the b_1 mode is additionally excited to give a combination level with both b_1 and e modes singly excited the vibrational state transforms as $B_1 \times E = E$. Now the direct product $E \times E$ is equal to $A_1 + A_2 + B_1 + B_2$ so that the excitation of the b_1 mode is formally allowed in z polarization. That is, of the four transition moment densities that transforming as A_1 will couple with, and steal intensity from, one with a non-zero transition moment in a zeroth order harmonic approximation. It should be noted that the selection rules and polarizations of transitions which are formally allowed for a vibrationally totally symmetric ground state are unaltered when the ground state has E symmetry. (Excitation of the a_1 mode gives an excited state of E symmetry and $E \times E \subset A_1$. Similarly, excitation of another e mode gives excited states of A_1, A_2, B_1, and B_2 symmetries. The direct product of any of these with E is E.) This mechanism for making excitation of the b_1 formally infrared allowed is shown in Figure 2.

Clearly, the greater the population of the initial state, in this instance the E(C–M–X) bending mode, *mutatis mutandis*, the greater the observed intensity of the b_1 band. Consequently, with, in general, heavier X in $XM(CO)_5$, the more readily detectable the b_1 mode will be. The latter accords with recent spectral studies. For example, for $XMn(CO)_5$, the b_1 mode is just detectable in the infrared when X = Br (at 2079 cm^{-1}), occurs as a weak band for X = I (at 2072.1 cm^{-1})

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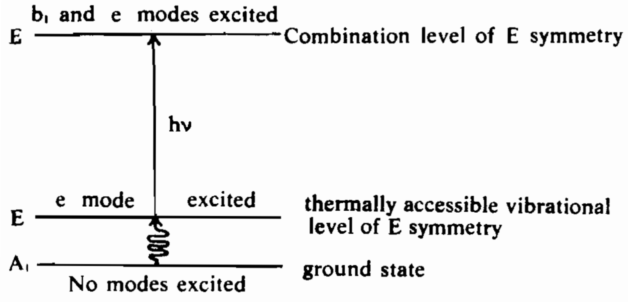

Figure 2.

but has not been reported when X=Cl.[9] For a series of complexes $R_3M'M(CO)_5$ where M=Mn or Re, M'≡Si, Ge, Sn or Pb, and R=Me, Ph, Cl or Br, the b_1 mode is observed and in many instances has appreciable intensity despite the retention of the e mode degeneracy.[6]

This approach may be generalized. This generalization is given in the next section.

General Theory

The condition for a transition to be infrared active is

$$\Gamma_i \times \Gamma_d \times \Gamma_e \subset \Gamma_s \qquad (1)$$

where the Γ_x's are the irreducible representations of the initial state (x=i), the excited state (x=e), the totally symmetric representation (x=s) and the dipole moment operator (x=d).

Now,

$$\Gamma_e = \Gamma_i \times \Gamma_v \qquad (2)$$

where Γ_v is the irreducible representation of the additionally excited vibrational level and thus, from (1) and (2)

$$\Gamma_i^2 \times \Gamma_d \times \Gamma_v \subset \Gamma_s \qquad (3)$$

since $\Gamma^2_x \subset \Gamma_s$ there are two conditions of interest.

Condition (a). When Γ_i refers to a non-degenerate initial state then

$$\Gamma_d \times \Gamma_v \subset \Gamma_s \qquad (4)$$

which requires that the same infrared selection rules hold for both the initial and ground state transitions. In practice, this means that no additional bands should be observed.

An example of this circumstance is the molecule $Mn_2(CO)_{10}$ with its non-degenerate b_1 twisting vibration thermally populated. As predicted, no additional infrared active bands are observed.[10,11]

Condition (b). When Γ_i refers to a degenerate initial state then, as before,

either

$$\Gamma_d \times \Gamma_v \subset \Gamma_s \qquad (4a)$$

or

$$\Gamma_d \times \Gamma_v \not\subset \Gamma_s \qquad (5)$$

In the latter case, from (3), it may be concluded that additional infrared bands arise provided the overall condition

$$\Gamma_j \times \Gamma_d \times \Gamma_v \subset \Gamma_s$$

holds, such that $\Gamma_d \times \Gamma_v \not\subset \Gamma_s$ and $\Gamma_j \not\subset \Gamma_s$ but with $F_i^2 \subset F_j$. In particular, the case considered in detail in this paper, $XMn(CO)_5$, with its C–M–X e bending mode thermally populated, fulfils these conditions.

Conclusion

We have suggested a mechanism whereby the formally forbidden CO stretching fundamental of B_1 symmetry in a C_{4v} $M(CO)_5X$ complex may gain intensity. This mechanism is applicable to the isolated molecule and does not depend upon a reduction of symmetry of the equilibrium molecular geometry. The intensity results, at least in part, from coupling with formally allowed A_1 transitions.

It should be pointed out that this effect will only be realized in situations where both group frequencies are sufficiently well resolved and a thermally excited initial state of suitable symmetry is available. The spectra of the metal carbonyls are, therefore, ideal, though similar effects might be observed with, for example, nitrosyl and cyanide complexes.

Acknowledgment. One of us (I.P.) is indebted to the S.R.C. for the award of a Post-Doctoral Fellowship.

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