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

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Received August 2, 1968

The mechanism for the infrared intensity of the b_1 *C–O stretching mode of* $M(CO)_5X$ *complexes which was suggested recently by Kettle and Paul is discussed and amplified. It is shown that the band may derive part of its intensity from a cubic term in the dipole moment series expansion and part by «stealing» intensity from another hot band involving the* $a_1^{(1)}$ *C–O stretching mode. It would appear however that these mechanisms would be of less significance than distortion caused by the presence of unsymmetrical ligands.*

Introduction

Kettle and Paul[1] have recently suggested a possible explanation of the reported appearance of b_1 C–O stretching modes in the infrared spectra of $M(CO)_5X$ molecules with C_{4v} symmetry. The transition from the fully symmetric ground state to a B_1 state is dipole forbidden, but the transition has been reported on several occasions[2,3,4] and it is of interest to determine possible origins of the intensity. Kettle and Paul suggest that it may be a «hot band», involving excitation from a thermally populated E state to the combination state (b_1+e); such a transition is allowed in z-polarisation by the C_{4v} selection rules, and would have the same frequency as the fundamental ($b_1 \leftarrow 0$) transition. However these authors have not considered the source of the intensity in detail and do not go beyond suggesting that intensity may be «stolen» from other z-polarised transitions. The purpose of this paper is to investigate this mechanism in more detail and to show that if it applied generally there would be some rather disturbing consequences to the interpretation of infrared spectra.

Background Theory

Transitions between energy states may be classified as electric or magnetic dipole, electric quadrupole, or of higher multipolar character. The last can be neglected without discussion. Magnetic dipole and electric quadrupole transitions are expected to be 10^5 and 10^9 times weaker respectively than electric dipole ones, but it is to be noted that their selection rules allow *g–g* and *u–u* transitions whereas these are forbidden for electric dipole radiation. It may also be noted that A_1–B_1 transitions in C_{4v} symmetry are electric quadrupole allowed. However it must be considered that these two possible sources of intensity in electric dipole-forbidden transitions are not likely to operate in the infrared spectra of metal carbonyls; for known centrosymmetric molecules neither *g–g* nor *u–u* transitions have been reported under conditions where any intensity could be unambiguously ascribed to a magnetic dipole or electric quadrupole mechanism. It is therefore reasonable to restrict discussion to the electric dipole mechanism.

The intensity of an electric dipole transition is proportional to the scalar product of the transition dipole with itself, *i.e.* intensity, $A = \text{const.}\,[M_x^2+M_y^2+M_z^2]$; we may consider the components of the transition dipole, M_x, M_y, and M_z separately.

$$M_z = \int \psi'^{*} \mu_z \psi'' d\tau,$$

where ψ' and ψ'' are the upper and lower wavefunctions and μ_z the z component of the dipole moment operator.

$$\mu_z = \sum_i e_i z_i$$

where e_i and z_i are the charge and z coordinate of the i'th particle relative to the centre of gravity. The summation is over all particles in the molecule. The nuclear coordinates are linearly related to the normal coordinates but expression of the electron coordinates in terms of normal coordinates, which is necessary for the evaluation of the transition dipole, requires a knowledge of the electron wavefunctions. A more realistic approach[5] is to consider the molecule to consist of atomic particles of constant mass but variable charge, thereby incorporating the electrons into the nuclear coordinate framework. μ_z can then be expanded as a power series in the normal coordinates,

$$\mu_z = \mu_z^{\circ} + \sum_j \left[\frac{\partial \mu_z}{\partial Q_j}\right]_0 Q_j + \tfrac{1}{2}\sum_i \sum_j \left[\frac{\partial^2 \mu_z}{\partial Q_i \partial Q_j}\right]_0 Q_i Q_j \ldots$$

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(1) S. F. A. Kettle and I. Paul, *Inorg. Chim. Acta, 2,* 15 (1968).
(2) J. B. Wilford and F. G. A. Stone, *Inorg. Chem., 4,* 389 (1965).
(3) F. A. Cotton and C. S. Kraihanzel, *Inorg. Chem., 2,* 533 (1963).
(4) H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Amer. Chem. Soc., 89,* 2844 (1967).
(5) E. B. Wilson, J. C. Decius, and P. C. Cross, «Molecular Vibrations», McGraw-Hill, New York, p. 39-41 (1955).

Each term in the summation must have the same symmetry transformation properties as μ_z.

This series can be written in a slightly different form by making the substitution, $\mu_z = \sum_k e_k z_k$, this sum being taken over all atoms; we obtain

$$\mu_z = \mu_z^\circ + \sum_j\sum_k \left[e_k \frac{\partial z_k}{\partial Q_j}\right]_0 Q_j + \sum_j\sum_k \left[z_k \frac{\partial e_k}{\partial Q_j}\right]_0 Q_j +$$

$$\tfrac{1}{2}\sum_i\sum_j\sum_k \left[2\frac{\partial e_k}{\partial Q_i}\frac{\partial z_k}{\partial Q_j}\right]_0 Q_iQ_j +$$

$$\tfrac{1}{2}\sum_i\sum_j\sum_k \left[z_k \frac{\partial^2 e_k}{\partial Q_i \partial Q_j}\right]_0 Q_iQ_j \ldots$$

If the atomic charges remained constant during vibration the series would terminate at the second term. In the case of metal carbonyls, however, it is virtually axiomatic that charges change during vibration and so the second linear term and the first quadratic term, at least, should be retained. The second linear term has been investigated by Bigorgne and Benlian[6] who consider it to be of major importance in determining the intensities of C–O stretching absorptions. (It should perhaps be emphasised that the z_k are not displacement coordinates and are not zero at equilibrium.)

The transition dipole M_z is obtained as a power series by substituting the μ_z series into the integral. The zero-order term, $\int\psi'^*\mu_z^\circ\psi''d\tau$, is zero as ψ' and ψ'' are orthogonal whatever their detailed form is; hence μ_z° may be eliminated from further discussion. For other terms it will be assumed that any transition is symmetry-allowed, *i.e.* that the product $\psi'\psi''$ transforms in the same way as μ_z. At this point we make the restriction that the wavefunctions be of the harmonic oscillator type; anharmonicity is discussed below. The first-order terms in M_z may be non-zero only if ψ' and ψ'' differ in one quantum number v_i by one unit; this is the usual harmonic oscillator selection rule, $\Delta v_i = \pm 1$, Δv_j *etc.* $= 0$.

The second-order terms, $(\partial^2\mu_z/\partial Q_i\partial Q_j)_0\int\psi' Q_iQ_j\psi''d\tau$ are zero unless ψ' and ψ'' differ by one in both quantum numbers v_i and v_j all others being equal. If $i = j$ then the two functions must differ in the single quantum number v_i by 2 (or zero). Thus the second-order term may not be responsible for the excitation of fundamentals, but contributes to the transition dipole of first overtones and binary combinations. The fact that these transitions are much weaker than are fundamentals is good evidence that the second order terms in M_z are relatively small, even with the proviso about atomic charge variation. It is also reasonable to suppose that cubic and higher terms in M_z will be even smaller.

The specific transition suggested by Kettle and Paul[1] is now discussed, three factors being taken into consideration: (a) the likely population of the low-lying E state, (b) possible contributions to the transition dipole, assuming the wavefunctions to be harmonic, (c) the possible effects of (mechanical) anharmonicity upon the transition dipole, assuming only first-order terms in M_z to operate.

The Population of the Low-Lying E State

It is likely that in the pentacarbonyl halides of manganese and rhenium[7] the *e* CMX bending mode occurs at about 50 cm^{-1} for iodides, 90 cm^{-7} for bromides, and 120 cm^{-1} for chlorides. The two *e* CMC bending modes occur in the range 100-130 cm^{-1}. At 300°K. the populations relative to that of the ground state are 1.57 for 50 cm^{-1}, 1.30 for 90 cm^{-1}, and 1.13 for 120 cm^{-1}. In these systems at room temperature more of the molecules are in low-lying excited states than are in the ground state and therefore transitions from these states make a greater contribution to the observed spectra than do transitions from the ground state.

Possible Contributions to the Transition Dipole, with Harmonic Wavefunctions

We denote the thermally populated E state as 1E and may assume it to be a fundamental without loss of generality. Its wavefunctions are ψ_1 and ψ_2 and the corresponding normal coordinates Q_1 and Q_2 respectively. Thus

$$\psi_1 = N_1RQ_1$$

$$\psi_2 = N_1RQ_2$$

where N_1 is a normalising factor and $R = \exp(\tfrac{1}{2}\Sigma\gamma_iQ_i^2)$, the γ_i's being constants and the sum being over all normal coordinates. R is totally symmetric, and is common to all wavefunctions.

The excited state is denoted by 2E and has wavefunctions ψ_3 and ψ_4; as it is a combination state the wavefunctions may be written

$$\psi_3 = N_2RQ_1Q_b, \text{ and}$$

$$\psi_4 = N_2RQ_2Q_b,$$

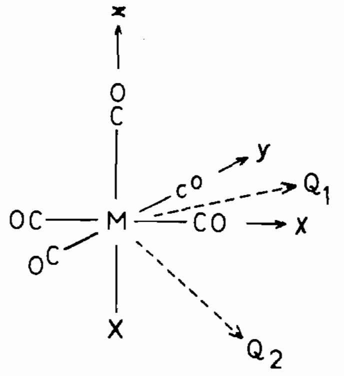

Figure 1. Coordinate system for M(CO)$_5$X molecules.

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(6) M. Bigorgne and D. Benlian, *Bull. Soc. Chim. France*, 4100 (1967).

(7) R. J. H. Clark and B. C. Crosse, private communication.

where Q_b is the normal coordinate of the b_1 C–O stretching mode.

We define an axis system as shown in Figure 1 and further define Q_1 and Q_2 so that they cause distortions in the directions $(x+y)$ and $(x-y)$ respectively. (Any two perpendicular directions in the xy-plane would suffice, but these two simplify the subsequent algebra). We also note that the normal coordinate, Q_b, has the same transformation properties as the function (X^2-Y^2).

With the wavefunctions thus defined, there are four transitions to consider, $\psi_1 \rightarrow \psi_3$, $\psi_1 \rightarrow \psi_4$, $\psi_2 \rightarrow \psi_3$, $\psi_2 \rightarrow \psi_4$. Their transition dipoles are respectively,

$$M_1 = N_1N_2 \int R^2\mu_z Q_1^2 Q_b \, d\tau,$$

$$M_2 = N_1N_2 \int R^2\mu_z Q_1 Q_2 Q_b \, d\tau,$$

$$M_3 = N_1N_2 \int R^2\mu_z Q_1 Q_2 Q_b \, d\tau$$

$$M_4 = N_1N_2 \int R^2\mu_z Q_2^2 Q_b \, d\tau$$

Remembering that μ_z and R^2 are fully symmetric in C_{4v} symmetry it is readily shown that the integrand (M_1+M_4) transforms as B_1, (M_1-M_4) as A_2 and M_2 and M_3 as A_1. (The B_2 component of the $1E \times 2E$ direct product vanishes in the harmonic oscillator approximation but would appear as (M_2-M_3) if the wavefunctions were anharmonic.) Thus only the second and third transitions are allowed. These two, $\psi_1 \rightarrow \psi_4$ and $\psi_2 \rightarrow \psi_3$, involve simultaneous excitation of the b_1 mode and a change in the degenerate mode excitation from one half of the degeneracy to the other. The transitions therefore have the characteristics of *ternary combinations, i.e.* three quantum numbers change by unity in the transition.

If we now examine the series expansion of the dipole moment operator, the lowest-order term which could give a non-zero matrix element must be cubic, and is in fact the term $\left[\dfrac{\partial^3\mu_z}{\partial Q_1 \partial Q_2 \partial Q_b}\right]_0 Q_1Q_2Q_b$. It would be reasonable to suppose the coefficient to be very small.

The Effect of Anharmonic Potential Energies

Mechanical anharmonicity may be treated by perturbation theory, using the energies and wavefunctions of the harmonic oscillator as zero-order solutions. The anharmonic perturbing potentials must be fully symmetric, and can cause mixing only between states of the same symmetry species. Thus in discussing the $1E \rightarrow 2E$ transition it is necessary to consider only the mixing of E states. It may be noted immediately that no $E \rightarrow E$ transition may «steal» intensity from z-polarised transitions between any of the non-degenerate states, *e.g.* from $A_1 \rightarrow A_1$ or $B_1 \rightarrow B_1$ transitions.

Consider first the mixing of the two states 1E and 2E with each other. This may be brought about by a potential which is odd-ordered in Q_1, Q_2, and Q_b and even-ordered in each of the other normal coordinates. The simplest example would be a cubic potential, $V' = gQ_1Q_2Q_b$. The new wavefunctions, marked by primes, may then be written as

$$\psi_1' = c\psi_1 + s\psi_4$$

$$\psi_2' = c\psi_2 + s\psi_3$$

$$\psi_3' = c\psi_3 - s\psi_2$$

$$\psi_4' = c\psi_4 - s\psi_1$$

where $c = \cos\alpha$, $s = \sin\alpha$.

The modified transition dipole for $\psi_1' \rightarrow \psi_4'$ is given by

$$\begin{aligned} M_z' &= \int (c\psi_1 + s\psi_4)\mu_z(c\psi_4 - s\psi_1)\, d\tau \\ &= (c^2 - s^2) M_z \end{aligned}$$

The dipole is thus reduced by this means.

Consider now the mixing of another E state, 3E, into 1E and 2E. The state 3E may be considered to have wavefunctions ψ_5 and ψ_6 chosen so that ψ_5 and ψ_1 have the same polarisation properties and can therefore be mixed by a symmetric operator. ψ_6 is defined similarly to mix with ψ_2. It is simpler to take the mixing into 1E and 2E separately and no new effects appear if they are taken together. Mixing of 3E into 1E, if 3E were a fundamental with a normal coordinate Q_5, could be achieved by means of quartic potentials of the type $V' = hQ_1^3Q_5$ and $V' = hQ_1Q_5^3$. The new wavefunction for this half of the degeneracy would be $\psi_1' = c\psi_1 + s\psi_5$, and the modified dipole for the $\psi_1' \rightarrow \psi_4$ transition would be

$$M_z' = cM_z + s \int \psi_5 \mu_z \psi_4 \, d\tau$$

The second integral is generally of the same type as M_z and would not be large; as s is likely to be small the significance of this term is then very small indeed.

However, if 3E were not a fundamental but a ternary combination state $(1E + b_1 + a_1)$ where a_1 is a fully symmetric fundamental, then ψ_5 would have the form $N_3RQ_2Q_bQ_a$; it could be mixed into ψ_1 by means of a quartic potential, $V' = hQ_1Q_2Q_bQ_a$, giving the new wavefunctions, $\psi_1' = c\psi_1 + s(N_3RQ_2Q_bQ_a)$. The transition dipole, $M_z' = cM_z + s\int N_2N_3R^2\mu_z Q_2^2 Q_b^2 Q_a \, d\tau$; the integral separates and Q_2 and Q_b normalise out so that the integral is equal to the transition dipole for the $(a_1 \leftarrow 0)$ transition, which is non-zero for the first-order term, $(\partial\mu_z/\partial Q_a)_0 Q_a$, in the expansion of μ_z. The main objection to this as a source of intensity in the $1E \rightarrow 2E$ transition is that the energy gap between 1E and 3E must be very large and the mixing coefficient therefore small.

A comparable scheme for mixing 3E into 2E is shown in Figure 2. Here 3E is taken to be the combination state $(1E + a_1^{(1)})$, where $a_1^{(1)}$ is the symmetric C–O stretching mode of lower frequency, which occurs as a strong band in the spectra. The state $(1E + a_1^{(1)})$ can be mixed with 2E by means of a potential, $V' = hQ_1Q_2Q_bQ_a$, which modifies ψ_4 so that

$$\psi_4' = c\psi_4 + s(N_3RQ_1Q_a)$$

and

$$M_z' = cM_z + s \int N_1N_3R^2Q_1^2\mu_z Q_a \, d\tau,$$

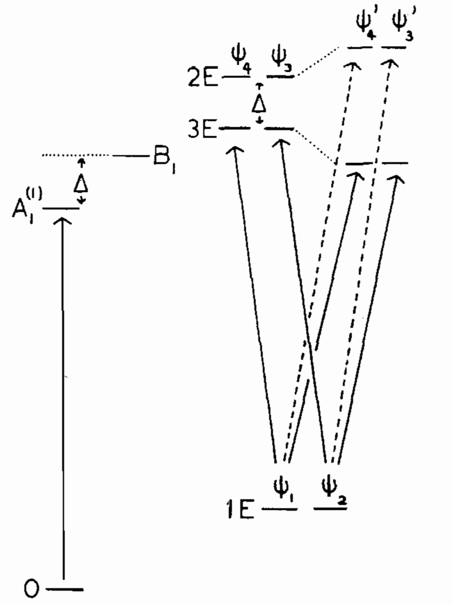

Figure 2. Vibrational energy states of $M(CO)_5X$ molecules. *z*-Polarised transitions shown by vertical arrows; the effect of the 3E—2E resonance is exaggerated.

The integral is equal to the dipole for the $(a_1^{(1)}\leftarrow 0)$ transition which is known to be large. The situation described is that of a Fermi resonance between the two states $(1E+b_1)$ and $(1E+a_1^{(1)})$. The mixing coefficient, $\tan\alpha$, is given by perturbation theory as $-\beta/\Delta$, where $\beta = \int \psi_4 V' \psi_5 d\tau$, and Δ is the 2E–3E energy gap, equal to the $a_1^{(1)}-b_1$ separation which ranges from about 40 cm^{-1} in compounds $R_3PMo(CO)_5$ to 100 cm^{-1} in $ClRe(CO)_5$.[4,8] The intensity ratio for the 1E→2E band to the 1E→3E band should equal $\tan^2\alpha$ if M_z can be neglected, and the two states should move $\Delta\tan^2\alpha$ away from each other due to the resonance. Frequency shifts of about 1 cm^{-1} would not normally be detected but these would correspond to an intensity ratio of 1 to 2½%, *i.e.* the intensity of the 1E→2E transition may be detectable although the associated frequency shift is not.

To summarise the three factors which may be involved in the development of infrared intensity in the 1E→2E transition, the population of low-lying E states is high at room temperature but the difference in population between iodides and chlorides is not sufficient to give noticeably different intensities for the two types of compound; for harmonic wavefunctions the first term in the dipole moment expansion to give a non-zero transition dipole is cubic and likely to be very small in its effect; the presence of a suitable quartic potential energy term allows Fermi resonance between the states $(1E+b_1)$ and $(1E+a_1^{(1)})$ thereby permitting the transition from 1E to the former to steal intensity from the transition from 1E to the latter.

This mechanism for forbidden transitions apparently gaining intensity should be generally applicable in molecules with degeneracy, although not to centrosymmetric molecules for the apparent excitation of g-states. In tetrahedral molecules, for example, a low-lying T_1 or T_2 state could cause the appearance of a band at the same frequency as a fully symmetric fundamental. The fact that substances such as carbon tetrachloride or nickel carbonyl do not show such infrared absorptions leads one to believe that the mechanism outlined above need only be called upon when all else fails.

Kettle and Paul suggested the hot-band mechanism partly because the b_1 mode appears without any detectable splitting of the e C–O stretching mode. This might indicate that the possible distortion from C_{4v} symmetry of the $M(CO)_5$ unit caused by unsymmetrical ligands is of little consequence. However, if we apply, as a perturbation, a harmonic distorting potential $V' = fQ_bQ_c$ where Q_b and Q_c are the normal coordinates of the b_1 and e C–O stretching modes respectively, it is found that the wavefunctions of the b_1 mode and *one* of the e modes will mix; the modified b_1 mode may then steal intensity from the e mode. If the mixing coefficient is t, the intensity ratio (b_1/e) is $\frac{1}{2}t^2$; as the b_1 mode and one half of the degenerate mode have been coupled, the degeneracy should split by an amount Δt^2 where Δ is the unperturbed b_1–e gap. However, as in the earlier theory, it is quite feasible that t^2 may be about 0.05, when the b_1 intensity would be readily detectable but the splitting of the e mode would not. (Δ here is in the region 30-60 cm^{-1}.) It is interesting to note that with the distortion model in this form, there should be a correlation between the b_1 intensity, the e intensity and any splitting of the e frequency.

It has been mentioned above that the hot-band mechanism cannot apply to parity-forbidden transitions in centrosymmetric molecules; in particular the a_{1g} and b_{1g} modes of molecules *trans*-$(R_3P)_2M(CO)_4$ have been recorded in infrared spectra.[9] In these cases the distortion model is the only one available and the intensities give some insight into the contribution made by distortion to the transition dipoles. It may be added that the intensities of these bands appear to be much greater than those of the b_1 mode of pentacarbonyl halides where the only likely distortion is of the unsymmetrical solvation type. It is therefore suggested that the hot-band mechanism is in general less important than ligand distortions in giving intensity to formally forbidden transitions in infrared spectra; if a ligand is monatomic or has the full symmetry of its position in the molecule then it is not likely to cause distortion of the carbonyl framework and, as in the pentacarbonyl halides, the hot-band mechanism may produce a detectable effect.

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(8) R. Poilblanc and M. Bigorgne, *Bull. Chim. Soc. France*, 1301 (1962).

(9) T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Amer. Chem. Soc.*, 83, 3200 (1961).