isoenergetic with the Ru^{2+} Fermi level. This condition requires that their energy levels be about 2.5 V below the Fermi level of the hydrocarbon chain. It is difficult to imagine, however, the sort of molecular organization that would lead to orbital stabilization to this extent. Ultimately, electron transfer may prove to be more appropriately described in terms of superexchange-type coupling mechanisms, e.g., as discussed by Jortner.[5a] In this regard, both the phosphatidylcholine monomers and alkyl substituent chain of the ruthenium coordination complex used in these studies possess olefinic unsaturation, the relatively low-lying unoccupied orbitals of which might engage in electronic mixing with donor and acceptor orbitals. Current research is directed at characterizing the rate-influencing factors inherent in the ligand and membrane molecular structures.

Acknowledgment. Financial support was provided by the U. S. Public Health Service (Grant GM-20943) and U.S. Department of Energy (Contract DE-AC06-83ER13111). Light-scattering measurements were made in the laboratory of Professor Michael Grätzel (Lausanne, Switzerland), to whom we are indebted for his generosity and hospitality.

Registry No. $(NH_3)_5RuL^{3+}$ (L = 4-(11′-dodecenyl)pyridine), 92669-57-3; Cr, 7440-47-3; V, 7440-62-2; ascorbic acid, 50-81-7; dipalmitoyl-L-α-phosphatidylcholine, 63-89-8.

Infrared Spectra of $MeMn(CO)_5$ and $MeRe(CO)_5$ Species: Methyl Group Geometry and the Effects of Internal Rotation

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Abstract: Infrared spectra in the CH and CD stretching regions are reported for various $MeMn(CO)_5$ and $MeRe(CO)_5$ species. Interpretation is made in terms of a freely internally rotating methyl group whose individual bond-stretching force constants vary during the rotation. The "average" "isolated" CH stretching frequencies of 2955.0 and 2934.6 cm^{-1} observed in the CHD_2 spectra are used to predict r_0^{CH} values of 1.095_9 Å (Mn) and 1.098_0 Å (Re), respectively, HCH angles, A_0, and $D°_{298}(C–H)$ values. The CH bonds are of medium strength, that in the Re compound being slightly weaker than the Mn one and displaying an inverse relationship to $D(M–CH_3)$.

The methyl pentacarbonyls of manganese and rhenium have been the subject of a number of structural studies, involving gas-phase electron diffraction[2,3], X-ray diffraction and incoherent inelastic neutron scattering,[4] and vibrational spectroscopy.[4-8] These have left uncertain two structural features associated with the methyl group, its geometry, and its internal rotational motion. The disordered structure of the Mn crystal meant that no geometric information could be obtained from the X-ray study, while the hydrogen positions were not located by the electron-diffraction experiments.[2,3] This situation may be remedied through a study of the CH stretching region of the CHD_2 species, from whose "isolated" CH stretching frequencies, bond lengths and HCH angles may be predicted by the use of correlation graphs.[9a,b]

Prior evidence relating to the internal rotation problem in the Mn compound is of three kinds. A Raman line at 174 cm^{-1} and part of a broad IINS feature at 169 cm^{-1}, both in the crystal at 10 K, have been assigned to a torsional mode of the CH_3 group.[4] As discussed below, this would be impossible with a V_{12} potential term and would require a high barrier of >350 cm^{-1} with a V_4 one. The second and third observations are from infrared spectra and apparently conflict with each other. The antisymmetric stretching mode of the methyl group is split into two components in the gas phase, while in solution and in the solid it presents a single broad band whose width varies little with temperature.[6] The latter observation leads to an estimate of the barrier height of 944 ± 175 cm^{-1}.[24]

Here again the infrared study of partially deuterated species may throw some light, at the cost, however, of introducing a further complication. Previous work in this field[8a] has revealed a variety of circumstances in which CH bonds within a methyl group vary in strength according to their angular position within the molecule. Where internal rotation is restricted, these have straightforward effects in the spectra. Infrared bands appear at frequencies corresponding to bonds in each of the various potential minima. However, for the case of low barriers, as in $MeNO_2$, MePh,[10,11] $MeBF_2$, $MeCl_2$, Me_3B, and $(MeBO)_3$,[12] the spectra and their interpretation are more complex. Theoretical treatments of a CH_3 group and of a CHD_2 one rotating against an infinitely heavy, planar skeleton, as in the above molecules, have been given by Sheppard and Woodman[13] and Cavagnat and Lascombe[11] (hereafter SW and CL, respectively).

Taken together, this prior work yields strong evidence for a variation of CH bond strength during the essentially free internal rotation in the above cases. While no corresponding theory exists for the vibration–rotation transitions of a methyl group rotating against a C_{4v} skeleton, as in the pentacarbonyls, features similar to the earlier ones may reasonably be expected to occur if the barrier is likewise very low. Since this work is little known, it will be necessary to give a more detailed review of it before we can conduct a meaningful discussion of the pentacarbonyl spectra.

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[1] (a) Present address: National Institute for Higher Education, Dublin 9, Ireland. (b) Present address: Robert Gorden's Institute of Technology, St. Andrew St., Aberdeen, Scotland.

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Vibrational Spectra of Me_2M, $MeXY_2$, and MeXYZ (Planar Skeleton) Systems

(a) High-Barrier Case (Local C_s Symmetry). In systems such as CH_3CHO, $CH_3CH{=}CH_2$,[14] and *o*-xylene[15] there is a relatively high barrier to internal rotation of the methyl group which adopts a conformation in which one bond, designated CH_s or $CH_{\parallel}$ lies in the skeletal plane of the molecule, and the other two lie above and below it, respectively (CH_a), but not of course in a plane at right angles to the skeletal one for which we reserve the symbol $CH_{\perp}$. Two $\nu^{is}(CH)$ bands[16] are seen, the higher frequency one due to CH_s and the lower to the two CH_a bonds. These may be identified by means of their band contours, or through the use of the frequency sum rule[17] for CH stretches: $\sum_i^3 \nu^{is}(CH) = \sum_i^3 \nu(CH_3)$. Use of this rule of course necessitates initially correcting the CH_3 group frequencies for the universal Fermi resonances, on $\nu_s(CH_3)$ especially. A slightly more sophisticated approach is to interrelate the $\nu^{is}(CH)$ and $\nu(CH_3)$ frequencies through the "3 × 3" refinement[18] which essentially deduces stretch–stretch interaction force constants from the displacements of the $\nu_{as}(CH_3)$ frequencies from the $\nu^{is}(CH)$ ones.[19] If an incorrect assignment has been made, anomalous values of these interaction constants appear.

(b) Low-Barrier Systems. (i) Me_2M Systems (M = Zn, Cd, Hg). In this series of molecules, the barrier to internal rotation is very low indeed and the perpendicular bands of the CH_3 or CD_3 species exhibit K spacings characteristic of a single, freely internally rotating methyl group. No variation of CH stretching force constant with orientation seems likely, and the CHD_2 spectrum is in agreement with this.[20] As seen in Figure 1, for $Zn(CHD_2)_2$, the CH stretching band is hybrid in nature, with both parallel and perpendicular components, the latter showing broad Q branches with a spacing appropriate for a single CHD_2 rotor.

(ii) CHD_2XY_2 Systems. The vibration–internal rotation levels and the resulting infrared and Raman spectra have been treated by CL.[11] The effect of a change in CH force constant during the internal rotation is introduced through a large V_2 term and a smaller V_4 term which are added to the small V_6 term derived from the conventional barrier to rotation. A curious result of this in the two cases studied, i.e., CHD_2NO_2 and CHD_2Ph, is that the minimum in the torsional potential in the ground vibrational state is determined by the zero-point energy of the single CH bond, which is a minimum when this bond is at right angles to the skeletal plane ($CH_{\perp}$). The torsional potential barrier in the first excited vibrational state is derived almost wholly from the V_2 and V_4 terms and is much greater than that in the ground state, but not so great as to prevent many transitions occurring to states well above the barrier, both in the Raman isotropic scattering spectrum and in the infrared. The former yields a frequency which is an *average* over all torsional angles, and the same average band appears with a type A contour in the infrared from the component of the dipole derivative parallel to the top axis. A small number of transitions from the ground torsional states give rise to Raman and infrared bands at the frequency $\nu(CH_{\perp})$, the infrared one having a type C contour. Components of $(\partial\mu/\partial r)_{CH}$ perpendicular to the top axis produce two irregular series of frequencies respectively above and below $\nu(CH)^{av}$. Thus far theory and experiment agree satisfactorily. Earlier infrared spectra of CHD_2BY_2 compounds,[12] however, were fundamentally different in appearance from those of CHD_2NO_2 or CHD_2Ph in that two broad bands of similar intensity were seen in each case, the lower one of which in several instances had a contour recognizably type C in character. The Raman spectrum in each case consisted of a single, broad, often asymmetric line intermediate in frequency between those of the two infrared bands. The relationship between these frequencies suggested that the Raman one was $\nu(CH)^{av}$, as in the CHD_2NO_2 and CHD_2Ph cases, whereas the upper and lower infrared bands represented $\nu(CH_{\parallel})$ and $\nu(CH_{\perp})$, respectively, arising from the *x* and *y* components of $(\partial\mu/\partial r)_{CH}$.[21] The absence of $\nu(CH)^{av}$ in the infrared was attributed to a negligible *z* component of $(\partial\mu/\partial r)_{CH}$, which idea is supported by the absence or low intensity of $\nu_s(CH_3)$ in the CH_3BY_2 infrared spectra. The principal weakness of the above interpretation is the lack of any theoretical basis for assigning the higher band as $\nu(CH_{\parallel})$ since existing theory predicts only an irregular series of K lines above $\nu(CH)^{av}$, whose center of gravity is indeterminate.[22] There seems little doubt, however, that in all these molecules the CH bond strength is a maximum in the skeletal plane ($\nu(CH_{\parallel})$), and a minimum at right angles to it ($\nu(CH_{\perp})$).

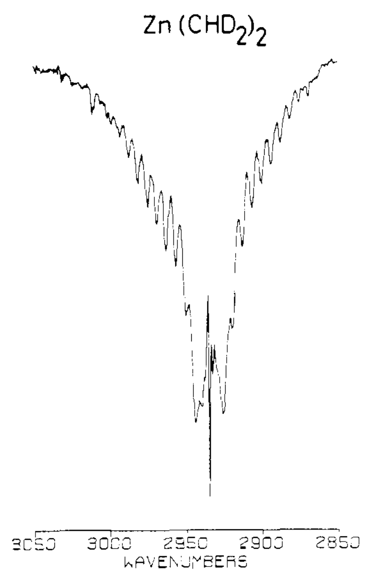

Figure 1. Infrared spectrum of $Zn(CHD_2)_2$ in the gas phase (resolution 0.12 cm^{-1}) showing parallel and perpendicular components of the hybrid $\nu(CH)$ band, the latter with K spacing characteristic of a freely internally rotating CHD_2 group with unvarying force constant.[20]

(iii) CH_3XY_2 Species. If one assumes a cos 2ϕ (V_2) variation in the strength of each individual CH bond, the 3 × 3 refinement shows that the CH_3 group has three different vibration frequencies which remain essentially constant for different chosen internal rotation angles, the higher two of course being essentially antisymmetric motions. For the conformation I in Figure 2A the symmetry coordinates $2r_1 - r_2 - r_3$ and $r_2 - r_3$ describe the higher and lower antisymmetric stretches, respectively (the former approximately, the latter exactly): however, after a 90° rotation in which II is reached, the frequencies have been reversed. This situation is the one treated by SW[13] for the case of a CH_3 group, also rotating against an infinitely heavy framework, the in-plane higher frequency $\nu_{as}(\parallel)$ and the out-of-plane lower one $\nu_{as}(\perp)$ being assumed to be precisely constant.[23] The perturbation to the vibration–internal rotation levels, which is produced by this change in vibration frequency of a particular symmetry coordinate during internal rotation, causes a hole to develop in the perpendicular type band which would have arisen if the two vibrations had been degenerate. No K transitions in fact occur within the limits $\nu^{av} \pm {}^1/_2\Delta\nu$ which describe the maximum ($\nu_{as}(CH_3)(\parallel)$) and minimum ($\nu_{as}(CH_3)(\perp)$) frequencies, respectively. For fast rotation, at high

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[14] McKean, D. C. *Spectrochim. Acta, Part A* **1975**, *31A*, 861.

[15] Gough, K. M.; Henry, B. R.; *J. Phys. Chem.*, **1984**, *88*, 1298.

[16] $\nu^{is}(CH)$ designates an "isolated" CH stretching frequency, as found here in CHD_2-substituted species.

[17] Lavalley, J. C.; Sheppard, N. *Spectrochim. Acta, Part A* **1972**, *28A*, 2091.

[18] McKean, D. C. *Spectrochim. Acta, Part A* **1973**, *29A*, 1559.

[19] This is another example of an "energy factored" force field more familiar as applied to CO stretches in organometallic compounds.

[20] McKean, D. C.; McQuillan, G. P.; Thompson, D. W. *Spectrochim. Acta, Part A* **1980**, *36A*, 1009.

[21] BMe_3 appears to be a special case not readily interpretable on any model.

[22] Since in the model assumed the XY_2 portion is assumed to be infinitely heavy.

[23] Calculation of the $\nu_{as}(CH_3)$ frequencies with both V_2 and V_4 terms as found in CHD_2NO_2 and CHD_2Ph[11] leads to two frequencies which are far from being constant during rotation, the variation in each being about 20 cm^{-1}. This would necessitate a modification of the SW treatment.

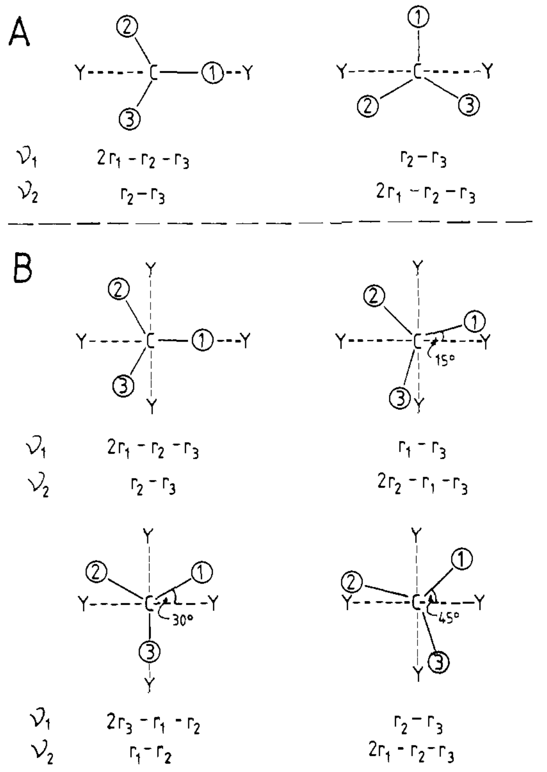

Figure 2. The description of the high (ν_1) and low (ν_2) $\nu_{as}(CH_3)$ vibrations for various internal rotation angles, ϕ, over a half cycle: (A) CH_3XY_2 and (B) CH_3XY_4 systems.

K values, the K spacings settle down to those expected for a normal perpendicular band with $\nu_0 = \nu^{av} \pm A(1 - 2\zeta)$. The treatment does not take into account the overall rotation of the molecule so that quantitative prediction of actual band contours is not possible. However, in all planar $MeXY_2$ systems, type C contours may be expected from transitions in the neighborhood of $\nu_{as}(CH_3)(\perp)$, while those near $\nu_{as}(CH_3)(\|)$ give rise to type B contours in $MeNO_2$, MePH, and $MeBF_2$ but a type A one in $MeBCl_2$. The extent to which such contours may be discerned is discussed by Dempster, Powell, and Sheppard,[24] in connection with the spectra of C_6H_5–CD_3 and C_6D_5–CH_3, and appears to depend on the magnitude of the vibrational splitting $[\nu_{as}(\|) - \nu_{as}(\perp)]$ relative to the K line separation, which of course reflects the inertial constant of the rotating group. Thus, much better defined A-, B-, or C-type contours are expected, and usually found, for CD_3 species than for CH_3 ones. The well-defined centers of such contours surely then define $\nu_{as}(\|)$ and $\nu_{as}(\perp)$. An important conclusion from this work therefore is that observation of characteristic A-, B-, or C-type contours for $\nu_{as}(XY_3)$ motions does *not* mean that internal rotation is necessarily restricted.

This splitting of $\nu_{as}(CH_3)$ or $\nu_{as}(CD_3)$ due to force constant variation is in contrast to the SW analysis of the effect of a conventional V_6 barrier on a $\nu_{as}(CH_3)$ mode whose degeneracy remains unlifted. Here holes develop on each side of the band center as the barrier is raised, but the intensity at the center increases at the same time. This suggests that where it is hard to tell from the CHD_2 spectrum whether the effects seen are due to a conventional V_6 barrier or to a V_2/V_4 variation in vibration frequency, a choice might be made from the appearance of the $\nu_{as}(CH_3)$ spectrum.

The ultimate aim should of course be to integrate the information from both $\nu_{as}(CH_3)$ and $\nu(CHD_2)$ spectra. Efforts to do this on a purely vibrational basis, through the "3 × 3" refinement, have been made[12] but cannot be said to be successful, in so far as the data can only be fitted, and that not too well, by angular variations in the stretch–stretch interaction force constants which are so large as to be implausible.

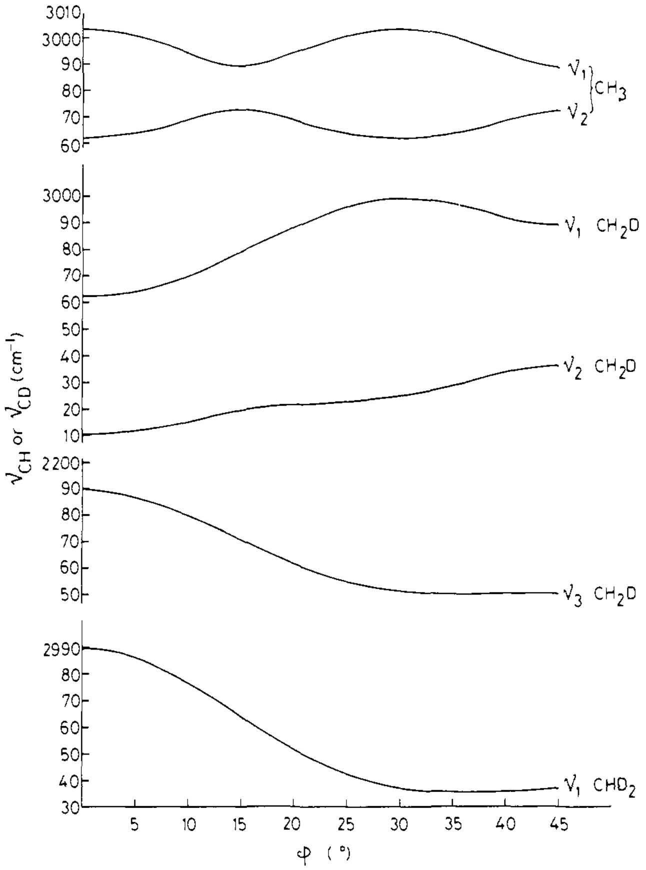

Figure 3. Plots of selected ν(CH) and ν(CD) values for CH_3, CH_2D, and CHD_2 groups as a function of rotation angle, ϕ, over a half cycle of change for the parameters of case 2, Table I.

(iv) **Extension to $MeXY_5$ Systems (M = Mn, Re; Y = CO).** We note first that a further infrared study of the carbonyl stretching regions of these compounds, in the gas phase, shows no sign of any departure of the skeleton from C_{4v} symmetry.[25] Thus the degeneracy of the e species fundamental remains unlifted, to within about 1 cm^{-1} as seen in Figure 9 for $CH_3Re(CO)_5$. There is no reason therefore to suppose that a torsional barrier of order less than 12 (V_{12}) can be present in a symmetrical (CH_3) methyl group.

For a CHD_2 group, a variation in the individual CH force constant will lead to a V_4 term with the possibility also of a smaller V_8 term, by analogy with the V_3 and V_6 components of the CHD_2NO_2 potential. Again, by analogy with $MeNO_2$, the V_4/V_8 terms should greatly exceed the V_{12} one of conventional origin.

The plane of the V_4 barrier is hard to predict. If the variation in individual CH bond strength is determined mainly by the relative positions of the nuclei, then by analogy with $MeXY_2$ systems the maximum strength, and therefore the barrier, would occur when the CH bond eclipses an equatorial CO bond. If by contrast repulsive interactions between CH bonding electrons and filled π-type orbitals are the dominant effect in weakening the CH bond, as has been suggested for propene,[14] then two effects have to be considered, involving the d_{xy} and d_{xz}, d_{yz} pair, respectively. All three of these d orbitals are filled, apart from donation to the π orbitals of the carbonyls. The d_{xz}, d_{yz} pair is much closer to the CH bonds than the d_{xy} orbital, which lies in the equatorial plane, and will be coplanar with the CH and CO bonds in the eclipsed conformation. Repulsive interactions will therefore involve mainly the d_{xz} and d_{yz} orbitals, so that the CH bonds are likely to be weakest in the eclipsed conformation and strongest when staggered.

It will be apparent that we approach the problem with a VSEPR type model in mind, rather than by invoking hyperconjugation. The latter may represent a satisfactory MO *description* of the phenomena, but it cannot be seen to be directly related to terms

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[24] Dempster, A. B.; Powell, D. B.; Sheppard, N. *Spectrochim. Acta, Part A* **1975**, *31A*, 245.

Table I. Sample Calculations of Vibration Frequencies for V_4 and V_8 Variations in CH Bond Stretching Force Constant (f_4 = 0.0874)[a]

		(1) $f_8 = 0$			(2) $f_8 = 0.3f_4$		
group		extremes[b]	span	av	extremes[b]	span	av
CH_3	ν_1	2997.2, 2993.7	3.5	2995.5	3003.4, 2989.6	13.8	2997.0
	ν_2	2966.3, 2971.1	4.8	2968.7	2962.2, 2972.7	10.5	2967.0
	ν_3	2893.3, 2892.2	1.1	2892.0	2891.2, 2894.6	3.4	2892.7
CD_3[c]	ν_1	2245.7, 2244.4	1.3	2245.1	2249.7, 2241.3	8.4	2245.7
	ν_2	2223.9, 2225.4	1.5	2224.6	2220.8, 2227.7	6.9	2223.9
	ν_3	2102.2, 2102.0	0.2	2102.1	2101.3, 2102.8	1.5	2102.0
CHD_2[c,d]	ν_1	2981.8, 2928.0	53.8	2955.0	2989.8, 2935.7	54.1	2955.4
	ν_2	2223.9, 2244.4	20.5	2235.6	2220.8, 2244.7	23.9	2235.5
	ν_3	2134.9, 2154.2	19.0	2143.1	2132.0, 2151.4	19.4	2142.7
CH_2D[c,d]	ν_1	2966.3, 2994.4	28.1	2984.3	2962.2, 2999.6	37.4	2984.3
	ν_2	2913.4, 2940.7	27.3	2923.2	2910.4, 2936.8	26.4	2922.7
	ν_3	2207.7, 2167.9	39.8	2187.8	2213.6, 2173.9	39.7	2188.2
	G_{100}[e]	6998.5, 7033.3	34.8		7005.3, 7049.5	44.2	
	G_{000}[e]	4032.2, 4039.4	7.2		4043.1, 4050.2	7.1	

[a] $f_i = f_0 + f_4 \cos 4(\phi + \delta_i) + f_8 \cos 8(\phi + \delta_i)$ where $f_0 = 4.7765$, $f_4 = 0.0874$ for both cases above, and δ_i = 0°, 120°, and 240° for i = 1, 2, and 3. Throughout, $f' = 0.026$. The value of f_4 yields maximum and minimum values of $\nu_1(CHD_2)$ agreeing approximately with the observed wings. This may represent an overestimate (see text). [b] Over 15° in ϕ for CH_3, CD_3, 45° for CHD_2 and CH_2D. [c] Computed $\nu(CD) \times 1.011$ to offset anharmonicity. [d] The minima and maxima in ν_1, ν_2, and ν_3 do not always occur at the same value of ϕ. [e] Excited and ground-state energies (cm^{-1}) in the three CH/CD stretching vibrations.

in the Hamiltonian and therefore does not supply a *reason* for the effect.

The effect of a V_4 variation in the individual CH stretching force constant on the vibrations of a CH_3 group is illustrated in Figure 3 and Table I, which includes also the effect of an added V_8 contribution. Three frequencies result, which in the absence of the V_8 term are essentially constant, as in CH_3XY_2 systems. However, a particular symmetry coordinate now yields the same frequency every 90°, as seen in Figure 2B. Thus it is no longer possible to associate the higher antisymmetric stretching frequency with one particular direction (say, x) and the lower such frequency with the y direction, as in CH_3XY_2 and the SW model.[26] It would be surprising, however, if the resulting spectrum were not similar to that predicted by the SW model, namely, a perpendicular band with no transitions inside the limits $\nu_{as}(\max) - \nu_{as}(\min)$.

For a CH_3XY_5 molecule where $\nu_{as}(CH_3)$ remains degenerate, and the methyl group suffers a V_{12} potential, calculations of energy levels have been made for V_{12} barriers in the range 1–10 cm^{-1},[27] and the results for a CD_3 group are illustrated in Figure 4, for states derived from K = 0–6. The values differ very little from those for V_3 or V_6 barriers, and like them, they increase linearly with increase in V_{12}, the spacings remaining unchanged. However, the first K level to be split by the perturbation is the K = 6 one, in contrast to the K = 3 one in the V_6 case. The resulting spectrum should resemble that of Figure 4 of ref 13 except that the holes on each side of the center develop further out than in the CH_3XY_2 case, having even more intensity in between.

We note finally that for these methyl pentacarbonyl compounds, the substituent dimensions are such that the molecules are approximately spherical tops for whose infrared bands PQR-type contours should be found with PR spacing of about 10 cm^{-1}, having no marked dependence on the orientation of the dipole derivative within the skeleton of the molecule. For the parallel bands, the PR separations calculated from the electron-diffraction dimensions, using the formula of Gerhard and Dennison,[28] are 9.5 (Mn) and 8.9 cm^{-1} (Re), respectively.

Experimental Section

Infrared spectra in the gas phase were obtained on a Nicolet 7199 FTIR spectrometer, with a resolution of 0.12–0.5 cm^{-1}, using gas cells of 10–20 cm length or a multiple reflection cell with path lengths up to 11 m, gas pressures being in the range from 1 torr up to the vapor pressure at room temperature. Infrared crystal spectra were obtained from films deposited on a CsI window at 78 K with use of a Perkin-Elmer 225 spectrometer. Samples were prepared by reacting the appropriately labeled methyl iodide with $NaM(CO)_5$ in tetrahydrofuran.

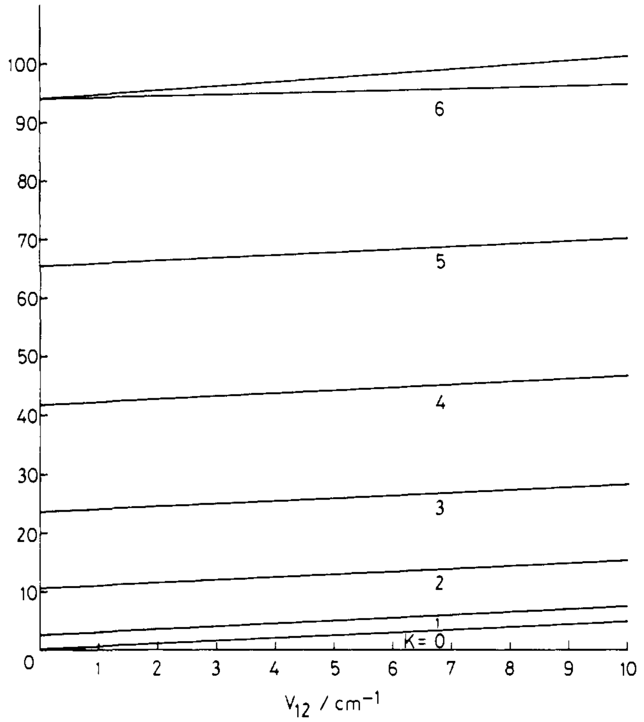

Figure 4. Internal rotation energy levels for a CD_3 group with A = 2.614 cm^{-1}, experiencing a V_{12} sinusoidal barrier.

Results

The frequencies observed for the various $MeM(CO)_5$ species are listed in Tables II (Mn) and III (Re), respectively.

Figure 5 compares the gas-phase infrared spectra of $CH_3Mn(CO)_5$ and $CH_3Re(CO)_5$, respectively, in the CH stretching region. The spectrum of $CH_3Mn(CO)_5$ is as reported earlier.[6] The origin of the bands at 3010.0 and 2950.2 cm^{-1}, earlier identified as components of $\nu_{as}(CH_3)$,[6] is confirmed by their shifts of 10 and 11.5 cm^{-1}, respectively, on ^{13}C substitution. By contrast, the ^{13}C shifts on $\nu_s(CH_3)$ and $2\delta_a(CH_3)$ at 2917.6 and 2830.7 are much smaller, 4.5 and 5.5 cm^{-1}, respectively.

The spectrum of the rhenium compound has all the features of the manganese one but in addition has a weak broad asymmetric band centered at ~2967 cm^{-1}, also with a ^{13}C shift appropriate to $\nu_{as}(CH_3)$. Both $\nu_s(CH_3)$ bands have an incipient PQR-type contour. The smaller separation of the $\nu_s(CH_3)$ and $2\delta_a(CH_3)$ Re bands is in keeping with the stronger intensity of the latter

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(25) Long, C.; Morrisson, A. R.; McKean, D. C.; McQuillan, G. P.; Torto, I., to be published.

(26) A complete cycle in the value of each CH_3 frequency is of course achieved in 30° of rotation, compared with 60° for CH_3XY_2 systems.

(27) Cavagnat, D., private communication. Calculations for CH_3XY_5 using programs described in ref 11.

(28) Gerhard, S. L.; Dennison, D. M. *Phys. Rev.* **1933**, *43*, 197.

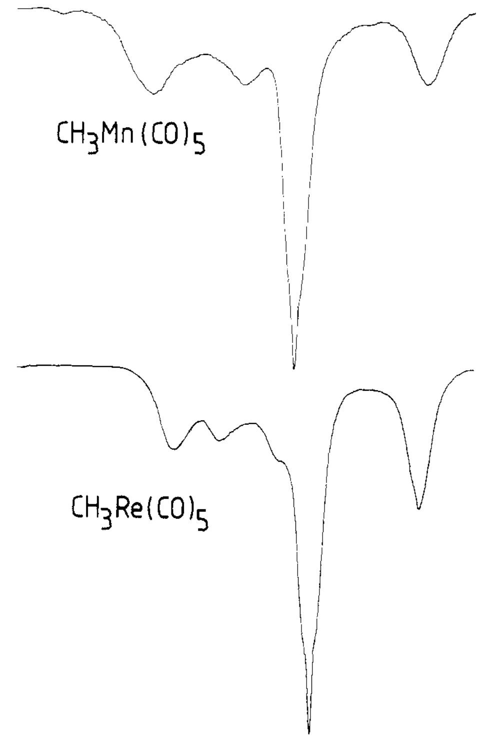

Figure 5. Infrared spectra of gaseous $CH_3Re(CO)_5$ (resolution 0.5 cm^{-1}) and $CH_3Mn(CO)_5$ (resolution 0.25 cm^{-1}), ν(CH) region.

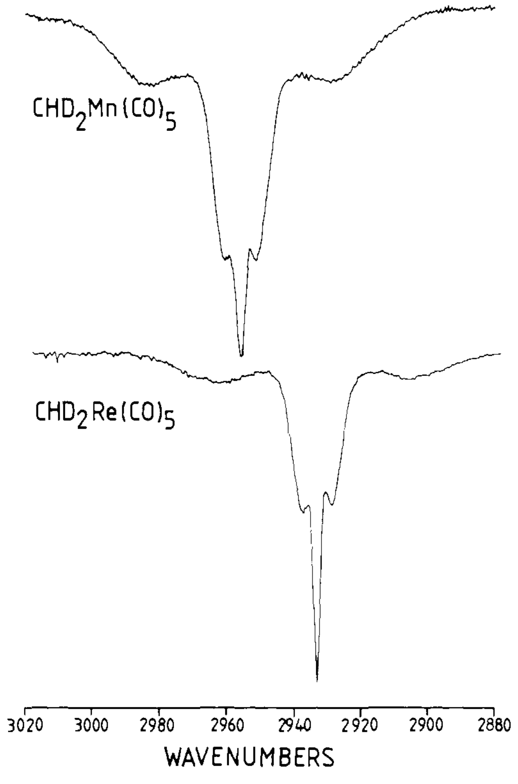

Figure 6. Infrared spectra of gaseous $CHD_2Re(CO)_5$ and $CHD_2Mn(CO)_5$, (resolution as for Figure 5), ν(CH) region.

relative to the former, and increased Fermi resonance.

Figure 6 shows the infrared gas-phase spectra of the two CHD_2 compounds. Each has a relatively strong PQR-type band with exactly the spacings predicted above for a symmetric top parallel band, and in addition there are broad weak wings on each side, spaced almost symmetrically.

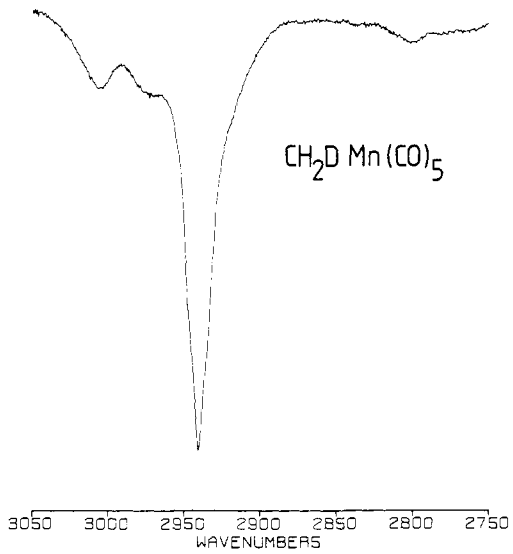

Figure 7. Infrared spectrum of gaseous $CH_2DMn(CO)_5$, (resolution 0.5 cm^{-1}), ν(CH) region.

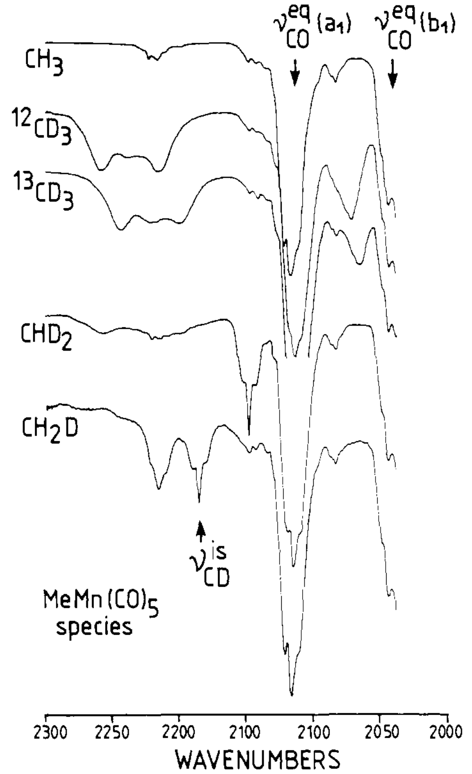

Figure 8. Infrared spectra of gaseous $MeMn(CO)_5$ species, ν(CD) region (resolutions: ^{12}C samples, 0.12–0.5 cm^{-1}; ^{13}C samples, 1 cm^{-1}). Both active a_1, ν(CO), and "inactive" b_1, ν(CO), fundamental bands are also seen. (See also ref 25.)

Figure 7 shows the spectrum of $CH_2DMn(CO)_5$ in the gas phase. This contains two weak broad bands at high frequency, and a third stronger one with shape reminiscent of $\nu_s(CH_3)$, at 2940.6 cm^{-1}.

The infrared spectra in the CD stretching region are complicated by the presence of both fundamentals and combinations arising from the CO stretching vibrations. The spectra of the Mn compounds are compared in Figure 8. $\nu_{as}(CD_3)$ is associated with the peaks at 2256.8, 2237, and 2213.5 cm^{-1}, which all appear to move about 14 cm^{-1} on ^{13}C substitution. There may be slight interference from the carbonyl combination band which in the CH_3 compound has two maxima at 2222 and 2215 cm^{-1}. The latter probably reappear in the CHD_2 compound as the maxima at 2219.6 and 2213 cm^{-1}.

Table II. Infrared Bands in the CH and CD Stretching Regions of MeMn(CO)$_5$ Species[a]

CH_3			CHD_2	
gas[b]	cryst[c]	soln[d]	gas[e]	cryst[c]
3010.0 w (10)			2983 w, bd	
	2992 w, bd (10.5)	2983	2960.0 r }	2966 w, bd
	2964 sh (~10)		2955.0 q } m	2953 vw, sh
			2950.5 p }	
2950.2 w (11.5)			2928 w, bd	
2917.6 ms (4.5)	2918 m, as (4.0)	2910		
2830.7 w (5.5)	2816 w (5.6)		2256.2 w	2266 vw
2222 } w (0)			2219.6 w	2231 w
2215 } w (0)			2213 w	
2147.6 vw, q			~2200 w, bd	
2142.2 vw, q			2147.5 pqr, s	2151 m
2133.8 sh				
2083.4 q				
CD_3			**CH_2D**	
gas[b]	cryst[c]	soln[d]	gas[f]	cryst
2256.8 w (14.2)			3006 w, bd	2988 w, bd
2237 vw (19?)	2240 w (14)	2233	2977 w, bd, as	
2213.5 w (13.9)	2216 vw, sh		2940.6 q, m	2946 m
2147.4 vw, q, (0.4)			2800 vw	2918 sh 2786 vvw
2141.1 sh (~0)			2214.8 w	2201 w
2133.3 sh (~0)			2184.5 pqr, w	2178 vw
2182 sh (~0)			2147.5 q, vw	
2071 m (5.5)			1409 vw	

[a] Excluding ν(CO) fundamentals. In brackets, ^{13}C shifts. [b] Resolution 0.25 cm^{-1}. [c] Resolution ~ 1 cm^{-1}. [d] Reference 6. [e] Resolution 0.12 cm^{-1}. [f] Resolution 0.5 cm^{-1}.

A band in the CD_3 compound at 2071 cm^{-1} with a marked ^{13}C shift of 5.5 cm^{-1} must be associated with $\nu_s(CD_3)$. It is, however (see below), much too low for an unperturbed $\nu_s(CD_3)$ frequency. The CHD_2 compound has two broad features in the 2200–2260 cm^{-1} region, the lower of which is badly overlapped by the probable combination band, plus a well-defined PQR band at 2147.5 cm^{-1}. The latter frequency coincides exactly with that of a very weak combination band in the CH_3 and CD_3 spectra, raising the possibility that it may be the same combination but with greatly enhanced intensity due to breakdown of selection rules following the asymmetric substitution. The CH_2D spectrum shows what may be the same effect—a band at 2214.8 cm^{-1} which could be merely an enhanced version of the 2215-cm^{-1} band seen in the CH_3 spectrum. The PQR-type band at 2184.5 cm^{-1} is clearly the CD stretching counterpart of the parallel ν(CH) band in the CHD_2 spectrum. Any wings that it might possess are obscured by neighboring bands.

Figure 9 shows the spectra of $CH_3Re(CO)_5$ and $CD_3Re(CO)_5$ (^{12}C and ^{13}C) in the region 2300–1900 cm^{-1}. This shows all the ν(CO) fundamentals and certain combinations, including one at 2216.8 cm^{-1} in the CH_3 compound. The latter coincides with the central maximum of three peaks clearly due mainly to $\nu_{as}(CD_3)$, at 2241, 2219, and 2193.5 cm^{-1} in the $^{12}CD_3$ compound. In the $^{13}CD_3$ the highest peak at 2223 cm^{-1} is clearly enhanced in intensity by reason of this combination, while the $^{13}CD_3$ shoulder at 2204 cm^{-1} is evidence that $\nu_{as}(CD_3)$ on its own exhibits a central maximum.

Changes in the band contour near 2120 cm^{-1} are presumably due to the intervention of $\nu_s(CD_3)$.

There may also be extra absorption in the CD_3 spectrum near 2080 cm^{-1}.

Crystal Phase. Figure 10 shows the spectra of the CH_3Mn and CHD_2Mn compounds, and Figure 11 shows the rhenium compounds. In both CH_3 compounds the $\nu_{as}(CH_3)$ region features a broad band with two likely components. In the Mn compound, the higher frequency band is much more intense than the lower, whereas in the Re compound, the lower band is on initial deposition (spectrum a) slightly stronger than the higher frequency one. Annealing (spectrum b) reverses the intensities. The CHD_2 bands in both cases are broad, the Mn one showing a weak sharp maximum at 2953 cm^{-1}, in addition to the broad one at 2966 cm^{-1}. The shift of intensity toward higher frequency seen in ν_{as}-

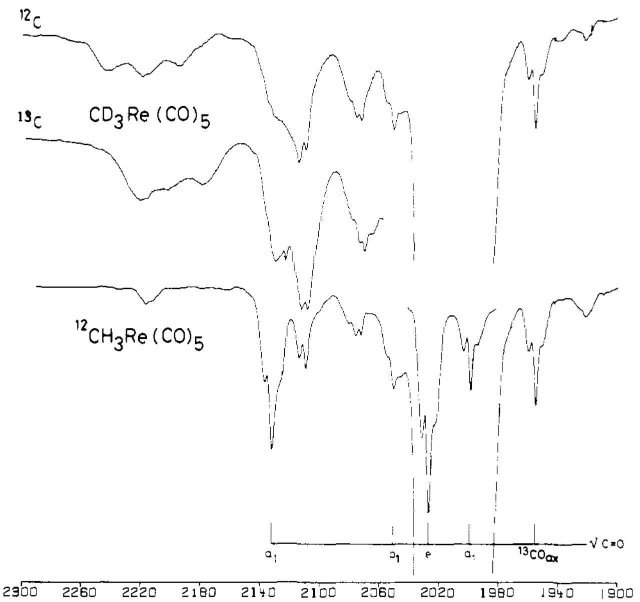

Figure 9. Infrared spectra of gaseous MeRe(CO)$_5$ species in the ν(CD) region. (Resolution 0.5 cm^{-1}). All four ν(CO) fundamental bands are also shown for the $^{12}CH_3$ species.

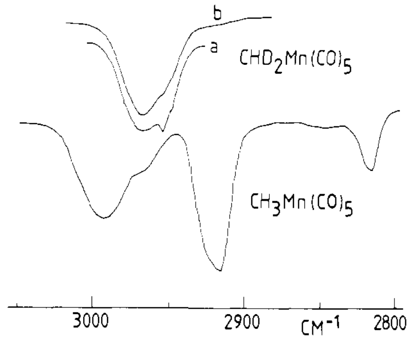

Figure 10. Infrared spectra at 78 K of solid films of CH_3 and CHD_2 species of MeMn(CO)$_5$: (a) initial film, (b) after annealing.

Table III. Infrared Bands in the CH and CD Stretching Regions of $MeRe(CO)_5$ Species

CH_3			CHD_2		
gas[a]	solid (1)[b]	solid (2)[b]	gas[a]	solid (1)[b]	solid (1)[b]
2996.5 w (10.5)			2963 bd, as		
	~2974 w, bd	~2974 w, bd			
2967 w, as (11.5)			2939.3		
	~2951 w, bd	~2954 w, bd	2934.6 } s	2930[c]	2939[c]
2929 sh[d]			2930.4		
			2906 bd, as		
2907.1 s (4.7)	2903.8 m	2907.5 m			
	2848 vw	n.o.			
2835.8 m (3.2)	2827.3 w	~2827 w			
2216.8 vw				2212 w, bd	
				2143 w	
2132.8 s (0)	2130 s	n.o.		2125 s	
	(1428.6 w)				

CD_3	
gas[a]	solid (1)[b]
2241 w (18)	
2219 w (15)	2219 w, bd
2193.5 w (12.2)	
2131 sh (~7)	2132 w
2114.3 s (0.4)	2119 m

[a] Resolution 0.5 cm^{-1}; Nicolet FTIR. In brackets, ^{13}C shifts. [b] Resolution ~0.8 cm^{-1}; Perkin-Elmer 225, ~78 K on CsI window; (1) unnealed, (2) annealed. [c] Half-widths in solid: (1) 35 cm^{-1} (2) 38 cm^{-1}. [d] Submerged by band at 2902.4 cm^{-1} in ^{13}C species.

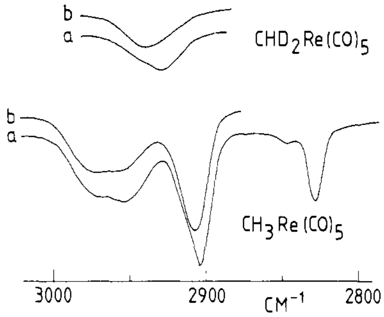

Figure 11. Infrared spectra at 78 K of solid films of CH_3 and CHD_2 species of $MeRe(CO)_5$: (a) initial film, (b) after annealing.

$(CH_3)(Re)$ upon annealing is reproduced also in the CHD_2Re spectrum where the maximum moves up about 9 cm^{-1}.

Discussion

Our first attempt to analyze the spectra will be based on the frequency sum rule. We must first estimate corrections to $\nu_s(CH_3)$ for Fermi resonances involving $2\delta_{as}(CH_3)$ and $2\delta_s(CH_3)$. These we make by borrowing W values of 34 cm^{-1} from CH_3Cl[29] and of 40 cm^{-1} from CH_3F[30] for the two resonances, respectively. The displacements to $\nu_s(CH_3)$ from $2\delta_{as}(CH_3)$ alone are then calculated to be 16.4 (Mn) and 24.8 cm^{-1} (Re), respectively. The higher value for the Re compound is in keeping with the altered intensity ratio and frequency separation observed for it.

Bands due to $2\delta_s(CH_3)$ were not identified, but they may be expected near 2370 cm^{-1} in both cases. The further shift on $\nu_s(CH_3)$ due to $2\delta_s(CH_3)$ is then estimated to be about 3 cm^{-1}. We therefore predict $\nu_s°(CH_3)$ at 2898 (Mn) and 2879 cm^{-1} (Re), respectively.

In calculating the frequency sum for the CH_3 group, we take the highest and lowest frequencies of the band due to $\nu_{as}(CH_3)$, in each case, plus $\nu_s°(CH_3)$ and divide by three to obtain the "average" CH stretching frequencies of 2953 (Mn) and 2936 cm^{-1} (Re). These averages are remarkably close to the centers of the observed parallel-type bands at 2955.0 (Mn) and 2934.6 cm^{-1} (Re), in the CHD_2 compounds, which constitutes strong prima facie evidence for the assignment of the latter as average frequencies. The same interpretation then follows for the band at 2184.5 cm^{-1} in the $CH_2DMn(CO)_5$ spectrum, whose frequency relative to the CHD_2Mn band yields an acceptable anharmonicity factor of 1.007.[31]

Two possibilies then arise for these "average frequency" bands. The first is that they represent a CH bond whose force constant is constant and independent of internal rotation angles. Any torsional barrier must then arise from the conventional origin with the first term expected to be a V_{12} one. If this term were negligible then the $\nu_{as}(CH_3)$ band should have the appearance of a normal perpendicular band with K spacing characteristic of the freely rotating CH_3 group with an A value of about 5 cm^{-1}. Moreover the CHD_2 band would be hybrid in character, and its perpendicular component would be similar to the $\nu_{as}(CH_3)$ one, but with K spacing reflecting the smaller A value of about 3.2 cm^{-1} for the CHD_2 group, exactly as seen in the infrared spectrum of $(CHD)_2Zn$ in Figure 1.[20] Clearly neither of these bands has the expected appearance. However, the wings on the CHD_2 band have so wide a spacing that it is difficult to resist the conclusion that they derive from an internally rotating CHD_2 group. That these wings are present as *maxima* then implies that a barrier exists to internal rotation.

With use of the same argument as was employed in the case of carbon monoxide in a quinol clathrate,[32] the height of the barrier is approximately the rotational energy at the wing maximum, which is 59 cm^{-1} for a K value of 4.3. Preliminary calculations suggest that this barrier is more likely to be of V_4 than of V_{12} origin, since the lowest energy levels and wave functions for a V_{12} potential are much more rotational in character than those of a V_4 one, whose lowest levels are distinctly torsional in nature. The V_4 potential according to the earlier discussion would derive from a *varying* CH force constant, whose *average* value gives rise to the parallel CHD_2 band.

The appearance of the $\nu_{as}(CH_3)$ band appears to discriminate sharply between the two possible origins of the torsional barrier. A V_{12} potential introduces holes centered on transitions to K = 6 levels, on each side of a strong central maximum. The absence of the latter in the $CH_3Mn(CO)_5$ spectrum, with instead a widely spaced doublet, can only be interpreted in terms of a splitting of the $\nu_{as}(CH_3)$ degeneracy, with consequences as in the SW model, and such a splitting, we believe, invariably stems from a CH force constant variation.

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(29) Bensari-Zizi, N.; Alamichel, C. *J. Mol. Spectrosc.* **1983**, *99*, 98.
(30) Champion, J. P.; Robiette, A. G.; Mills, I. M.; Graner, G. *J. Mol. Spectrosc.* **1982**, *96*, 422.
(31) This factor equals $(G_{CH}/G_{CD})^{1/2}/(\nu(CH)/\nu(CD))$.
(32) Ball, D. F.; McKean, D. C. *Spectrochim. Acta* **1962**, *18*, 933.

Table IV. 3 × 3 Refinements of Average Frequencies of MeM(CO)$_5$ Species

	M = Mn		M = Re	
	Frequencies Assumed			
$\nu(CHD_2)$	2955.0		2934.6	
	(1)	(2)	(1)	(2)
$\nu_{as}(CH_3)$	2980	2975.4	2962.8	2958.1
	Frequencies and Constants Calculated[a]			
f	4.777	4.778	4.708	4.712
f'	0.026	0.042	0.007	0.025
$\nu_s(CH_3)$	2897.0	2907.0	2868.7	2880.5
$\nu_{as}(CD_3)$[b]	2234.1	2230.8	2220.1	2216.6
$\nu_s(CD_3)$[b]	2103.7	2110.9	2085.7	2094.2
$\nu_2(CHD_2)$[b]	2234.1	2230.8	2220.1	2216.6
$\nu_3(CHD_2)$[b]	2144.6	2149.0	2125.9	2132.8
$\nu_1(CH_2D)$	2980.0	2975.5	2962.8	2958.1
$\nu_2(CH_2D)$	2927.6	2932.0	2903.6	2908.9
$\nu_3(CH_2D)$[b]	2187.9	2188.8	2171.9	2173.4

[a] HCH angles as in Table VI. [b] Computed frequencies × 1.011 to alleviate CH/CD anharmonicity differences.

Table V. Methyl Group ν_{as} and $\nu(CHD_2)$ Splittings (cm^{-1})[a]

	$\Delta\nu_{as}(CH_3)$	$\Delta\nu_{as}(CD_3)$	$\Delta\nu(CHD_2)$
High-Barrier Cases (C_s Local Symmetry)			
CH_3COCH_3[b]	51	42	58
CH_3CHO[b]	48	38	57
$CH_3CH{=}CH_2$[b]	22	21	28
$(CH_3)_2C{=}CH_2$[b]	35	32	41
CH_3CFO[c]	40		45.3
CH_3CClO[c]	26.4		25.5
CH_3CCNO[c]	49.3		52.5
Low-Barrier Cases			
CH_3NO_2[d] gas	36 ?	32	42
CH_3NO_2[d] cryst	34	34	48
CH_3BF_2[e]	55 ?	38	60
CH_3BCl_2[e]	64.5	56	73
$(CH_3)_3B$[e]	66	54	71
$(CH_3BO)_3$[e]	68	42	60
$CH_3Mn(CO)_5$[f]	60	43.3	55
$CH_3Re(CO)_5$[f]	67.5	47.5	57

[a] Gas phase except where otherwise indicated. [b] Reference 14. [c] Reference 33. [d] Reference 10 and 11. [e] Reference 12. [f] This work.

There are, however, weak central maxima on the $\nu_{as}(CD_3)$(Mn) and $\nu_{as}(CH_3)$(Re) bands, and possibly also in the $\nu_{as}(CD_3)$(Re) one. These could indicate the existence of a small V_{12} barrier. By analogy with toluene and nitromethane, this is unlikely to exceed ~5 cm^{-1}. The ground ($K = 0$) state lies below the barrier in all cases, and for a CD$_3$ group the $K = 1$ state lies at or below the barrier for a height >5 cm^{-1} (Figure 4). The possibility of intensity derived from $\Delta K = 0$ transitions then arises. There is, however, an alternative source of intensity near the center of a $\nu_{as}(CH_3)$ band. There is no reason why the dipole derivative of a CH bond should be invariant during internal rotation, and one can imagine an overall dipole derivative for the whole group developing a component parallel to the top axis, which would lead to $\Delta K = 0$ transitions. Either mechanism might be expected to be more prominent in the Re compound where the carbon-metal bond is significantly stronger than that in the Mn compound, leading to greater interaction between the methyl group as a whole and the metal d orbitals.

The conclusion that a variation in ν(CH) with rotation angle is responsible for the strange appearance of both CHD$_2$ and CH$_3$ spectra also enables us to understand the spectra in condensed phases. The great breadth of *both* $\nu(CHD_2)$ and $\nu_s(CH_3)$ bands in the solid and the relatively low sensitivity of the latter both in solid and in solution to temperature variation is readily explained if the breadth is due largely to force constant variation and not to free internal rotation. It then becomes unnecessary to assume the unrealistically high barrier of ~944 cm^{-1} deduced by Dempster et al.[24]

It will be apparent that it would be very hard to reconcile our picture of a low (<10 cm^{-1}) V_{12} barrier in the ground state of a CH$_3$ group with the supposed torsional frequency of 174 cm^{-1} in the crystal phase.[4] We observe first that the harmonic oscillator approximation

$$V_n = \nu_t^2/n^2B$$

is valueless for situations where B and n are large, although for a smaller value of n such as 3 it gives a barrier of ~635 cm^{-1}, not far below the one estimated by Cavagnat of ~710 cm^{-1}.[27] For $n = 6$, the first excited torsional state, which derives from the levels K = 3, 4, 5, and 6, is still split by about 61 cm^{-1} when V_6 = 400 cm^{-1}, and no well-defined torsional frequency could be expected.[27] For n = 12, an enormous barrier would be needed before well-defined torsional levels would appear, deriving as they do each from *seven* K levels. It is difficult to resist the conclusion that torsional–rotational transitions in the crystal must be spread over a wide region of the spectrum and thus remain undetected.

It remains to attempt a semiquantitative interpretation of the CH$_3$ and CHD$_2$ frequencies, which may also help us to understand the CH$_2$D spectrum.

3 × 3 Refinement Calculations. We first attempt to fit average CHD$_2$ and CH$_3$ frequencies, derived from transitions well above the barrier, with two parameters, one diagonal stretching and one off-diagonal stretch–stretch interaction constant. For the latter, if we take the average of the two extreme $\nu_{as}(CH_3)$ frequencies to represent $\nu_{as}{}^{av}(CH_3)$, we obtain the results under (1) of Table IV. For the Mn compound, the value of f' of 0.026 is close to those normally found (0.03–0.04) in non-rotating CH$_3$ groups.[33] The values of $\nu_s(CH_3)$ and $\nu_{as}{}^{av}(CD_3)$ are very close to those estimated or observed (2898 and 2235 cm^{-1}, respectively). In the case of the Re compound, however, the value of f' of 0.007 is anomalously low, and the prediction of $\nu_s{}^0(CH_3)$ and $\nu_{as}(CD_3)$ distinctly poorer (these should be 2879 and 2217 cm^{-1}, respectively). A possible factor contributing to the latter might be that the midpoint of the $\nu_{as}(CH_3)$ doublets should be equated to $\nu_{vib}{}^0 + A(1 - 2\zeta)$, rather than $\nu_{vib}{}^0$. When a ζ value of 0.065 from CH$_3$Cl is borrowed, $\nu_{as}{}^0(CH_3)$ is found to be 2975.4 (Mn) and 2958.1 (Re) cm^{-1}, respectively. These then give the calculated quantities listed under (2) in Table IV. The prediction of $\nu_s{}^0(CH_3)$ and $\nu_{as}{}^{av}(CD_3)$ for the Re compound then becomes very good, with f' satisfactory, whereas the agreement for the Mn compound is poorer than before. While part of the discrepancies involved may arise from errors in the Fermi resonance corrections on $\nu_s(CH_3)$, there does appear to be a real difference in the value of f' for the Mn and Re compounds.

The calculations also give some guidance as to the assignment of other bands in the spectra. Thus the prediction of $\nu_s{}^0(CD_3)$(Mn) in the range 2104–2111 cm^{-1} means that the band observed at 2071 cm^{-1} with pronounced ^{13}C shift must be at best a Fermi resonating component, the other component underlying the A$_1$ ν(CO) band near 2120 cm^{-1}. The strong band with PQR-type contour at 2147.5 cm^{-1} in the CHD$_2$Mn compound is, however, at an appropriate frequency for ν_3 of the CHD$_2$ group, although its coincidence with a ν(CO) combination band in the CH$_3$Mn spectrum may indicate another origin, as discussed earlier. ν_2 for the CHD$_2$Mn group, predicted in the range 2231–2234 cm^{-1}, lies slightly above the mean of the observed CHD$_2$ doublet (~2228 cm^{-1}) although the lower component of the doublet is very poorly defined due to overlap with another ν(CO) combination. ν_1 for the CH$_2$D group is calculated in the range 2975–2980 cm^{-1} which encompasses that of a broad observed maximum at 2977 cm^{-1}, while ν_2 for the same group, calculated in the range 2928–2932 cm^{-1}, can just be reconciled with the observed band at 2940.6 cm^{-1} if a Fermi resonance correction of the order of 10 cm^{-1} be applied to the latter.[34]

A final comment on this aspect of the calculations is that the central maximum observed at 2967 cm^{-1} in the $\nu_{as}(CH_3Re)$ band

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(33) McKean, D. C.; Torto, I. *J. Mol. Struct.* **1982**, *81*, 51.

(34) $\delta_s(CH_2)$ in CH$_2$DMn(CO)$_5$ is seen at 1409 cm^{-1}. Allowing 10 cm^{-1} for a normal anharmonicity deficit, $2\delta_s(CH_2)$ might be expected at 2808 cm^{-1}, whereas it is observed at 2800 cm^{-1}.

Table VI. Predictions of Methyl Group Geometries and Other Parameters for $MeM(CO)_5$

M =	$r_0(CH)$,[a] Å	∠HCH,[b] deg	A_0,[c] cm^{-1}				$D°_{298}(CH)$,[d] kcal mol^{-1}
			CH_3	CH_2D	CHD_2	CD_3	
Mn	1.095_9	108.0_3	5.320	3.997	3.203	2.672	100.0
Re	1.098_0	107.0_7	5.363	4.031	3.229	2.693	98.3

[a] From $r_0(CH) = 1.3982 - 0.0001023\nu^{is}(CH)$.[9] [b] From $\angle HCH = 0.04709\nu^{is}(CH) - 31.12$.[9] [c] Assuming $\delta r_0(CH-CD) = 0.002$ Å. [d] From $D°_{298}(CH) = 0.08616\nu^{is}(CH) - 154.6$.[9]

is significantly higher than the higher of the two average values chosen in Table IV and cannot easily be reconciled with $\nu_{as}{}^{av}(CH_3)$, particularly if the $A(1 - 2\zeta)$ connection is applied to the latter without a smaller value of f'.

While these results must be considered not unsatisfactory, immediate difficulties arise if one attempts to reconcile the $\nu_{as}(CH_3)$ and $\nu(CHD_2)$ splittings on a purely vibrational basis. Table V shows the variety of $\nu_{as}(CH_3)$, $\nu_{as}(CD_3)$, and $\nu(CHD_2)$ splittings found previously for molecules *with* free internal rotation and *without* it, the latter being chosen from cases where the methyl group retains a local plane of symmetry. It is apparently normal for the CHD_2 splitting to be greater than the CH_3 one, exceptions being the cases of $(MeBO)_3$ and CH_3COCl.

The data for $\Delta\nu(CHD_2)$ for the current Mn and Re compounds are based on the observed wing maxima, which must surely represent the maximum variation in $\nu(CH)$ possible. It is seen that the pentacarbonyl splittings parallel those for $(MeBO)_3$, with $\Delta\nu_{as}(CH_3)$ appreciably larger than $\Delta\nu(CHD_2)$, and a big difference between $\Delta\nu_{as}(CH_3)$ and $\Delta\nu_{as}(CD_3)$. It follows that on a vibrational basis they could only be explained by a large and implausible variation with angle of the interaction constant, as for $(MeBO)_3$.[12] What happens to the vibration frequencies for a constant interaction force constant is illustrated in Table I and Figure 3 where the three frequencies for each of the CH_3, CD_3, CH_2D, and CHD_2 groups are shown as a function of angle ϕ, over half a cycle in ϕ, on the assumption that each individual stretching force constant varies according to

$$f_i = f_0 + f_4 \cos 4(\phi + \delta) + f_8 \cos 8(\phi + \delta)$$

where $\delta = 0$, 120, and 240° for the three H atoms, respectively. The values of f_0 and f_4 were chosen so as to yield $\nu_1(CHD_2)$ frequencies agreeing closely with the wing maxima and central band frequencies of that group. Calculations were made for two cases: (1) for $f_8 = 0$ and (2) for a value of $f_8 = 0.3f_4$, analogous to the $f_4 = 0.3f_2$ relationship found in nitromethane.[11] In case 1, the 54-cm^{-1} variation in $\nu_1(CHD_2)$ is accompanied by a $\nu_{as}(CH_3)$ $(\nu_1 - \nu_2)$ splitting varying from 30.9 to 22.6 cm^{-1}, with an average value of 26.8 cm^{-1}. The $\nu_{as}(CD_3)$ splitting similarly varies from 21.8 to 19.0 cm^{-1} with an average value of 20.4 cm^{-1}. These calculated splittings are therefore less than half of the observed ones. In case 2 the variations with ϕ in both ν_1 and ν_2 are somewhat greater than the above.

The situation in fact may be rather worse than this. The CHD_2 wings on our interpretation are due to barriers in the *upper* $\nu(CH)$ vibrational state, where the energy is $^3/_2(\nu_{vib} \pm {}^1/_2\Delta\nu)$. A barrier of about 60 cm^{-1} here therefore implies a $\Delta\nu(CH)$ of about 40 cm^{-1}, not 54 cm^{-1} as in the above simple calculation.

Another feature of the calculations is a pronounced, non-sinusoidal variation in both ν_1 and ν_2 of the CH_2D group (and similarly for ν_2 and ν_3 of CHD_2). This gives rise to what is basically a V_4 barrier of about 7 cm^{-1} in the ground vibrational state (see G_{000} in Table I) but about 35 or 44 cm^{-1} in the 100 state depending on whether an f_8 contribution is included or not. This then leads to a possible interpretation of the $\nu(CH)$ region of the CH_2D group in the Mn compound. The band at 2977 cm^{-1} could arise from a parallel component of the dipole derivative associated with ν_1, or to transitions between states essentially torsional in character, also associated with ν_1, while the maximum at 3006 cm^{-1} could be a wing of the perpendicular type band associated with ν_1, whose inner parts are missing, as in the $\nu(CH)$ band of the CHD_2 group. The other wing would be concealed by the 2940.6-cm^{-1} band whose incipient PQR contour identifies it as the parallel band arising from the essentially symmetric stretching mode ν_2, itself an "average" frequency, like the $\nu(CH)$ CHD_2 parallel band. The difficulty with this interpretation is that the wing spacing would then be about 58 cm^{-1} [=2(3006 − 2977)] which is larger than that observed for the CHD_2 group (55 cm^{-1}), whereas the model predicts a significantly smaller barrier. There has of course been no attempt here to consider the possibility of perturbations between K levels of the ν_1 and ν_2 vibrations of the CH_2D group which might be analogous to those which lead to the observed wings in $\nu_{as}(CH_3)$ in the CH_3 group.

Perhaps the strongest evidence for a combination of variation of $\nu^{is}(CH)$ with orientation, together with free internal rotation of the methyl group, in these molecules, is just the difficulty experienced here in applying the "3 × 3" refinement which accounts so well for the CH_3 and CD_3 spectra of non-rotating methyl groups.

It remains to list the main features that a comprehensive treatment of the energy levels and transitions of these systems should embody, even within the confines of an energy-factored force field. Variations with internal rotation angle must be considered in (1) the individual CH stretching force constants, (2) the stretch–stretch interaction force constants, (3) the direction and magnitude of the dipole derivatives, and (4) the CH bond lengths and HCH angles. These variations should include the possibility of both V_4 and V_8 terms. For the pentacarbonyl molecules, and for the earlier CH_3XY_2 ones, the calculations will need to include the overall rotation of the molecule as well as the internal rotation, in order to predict the observed spectra satisfactorily.

Geometry of the Methyl Group and Chemical Significance. The average frequencies of the CHD_2 groups, in conjunction with established correlations between $\nu^{is}(CH)$ and $r_0(CH)$, αHCH, and $D_0{}^{298}(C-H)$,[9a] yield the values listed in Table VI.

The first point to make is that these CH bonds are of normal strength and length.[35] That in $CH_3Mn(CO)_5$ (2955 cm^{-1}) is comparable with that in $(CH_3)_2Hg$ (2953.8 cm^{-1})[20] or $(CH_3)_4Ge$ (2954 cm^{-1})[36] and slightly stronger than that in ethane (2950 cm^{-1})[9a]. The CH bond in $CH_3Re(CO)_5$ (2934.6 cm^{-1}) is similar to those in $(CH_3)_2Zn$ (2935.0 cm^{-1})[20] and neopentane (2934 cm^{-1})[9a] and marginally weaker than that in $(CH_3)_4Si$ (2939 cm^{-1})[36].

Secondly, the range of frequency from Mn to Re (20 cm^{-1}) is similar but in the opposite direction to that from Me_2Zn to Me_2Hg or Me_4Si to Me_4Sn (2960 cm^{-1}).[35] In all three groups, however, $\nu^{is}(CH)$ exhibits an inverse relationship to $\bar{D}_0(M-CH_3)$.[20] Thus $D_0(Re-CH_3) - D_0(Mn-CH_3) = 25.3$ or 22.3 kcal mol^{-1}.[37] The possibilities for predicting $D_0(M-CH_3)$ values from $\nu^{is}(CH)$ are thereby increased. More usefully, perhaps, data for groups 2B, 4A, and 7B indicate that differences of 1 cm^{-1} in $\nu^{is}(CH)$ in structurally related molecules imply differences of the order of 0.7–1.3 kcal mol^{-1} in $D_0(M-CH_3)$.

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(35) The conclusion of Andrews et al.[4] that these bonds are anomalously weak apparently rests on the extrapolation to MeM compounds of a correlation between $\nu(CH)$ values in CH_3X (X = F, Cl, Br, I) and $\nu(HX)$ ones. In view of the numerous specific effects *not* associated with electronegativity which $\nu^{is}(CH)$ values exhibit (including one in CH_3F), we feel that this approach is unfruitful. Speculation about the specific effects of metal d orbitals on antisymmetric and symmetric CH_3 stretching frequencies is also likely to be unhelpful. The primary concern must be to identify effects on the individual CH stretching force constant. This achieved, examination of stretch–stretch interaction constants, which determine the ν_{as}/ν_s separation, might follow.

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Thirdly, we predict a variation in r_0(CH) with internal rotation angle of the order of 0.004–0.006 Å, in both compounds. While the absence of a fully quantitative treatment of the potential function precludes an exact prediction, the general resemblance of the $\nu_{as}(CH_3)$ and $\nu(CHD_2)$ splittings to those in $(MeBO)_3$, where a variation of the above order is confirmed by ab initio calculations,[38] provides additional support for the proposed bond length fluctuation in the $MeMn(CO)_5$ and $MeRe(CO)_5$ compounds.

Conclusions

1. The infrared spectra of $MeMn(CO)_5$ and $MeRe(CO)_5$ species in the CH and CD stretching regions can be qualitatively interpreted in terms of a CH stretching force constant which varies with internal rotation angle of an essentially freely rotating methyl group.
2. The ground-state barrier to internal rotation is probably of V_{12} origin and very low, <10 cm^{-1}.
3. Mean CH bond lengths of 1.095_9 and 1.098_0 are predicted for the Mn and Re compounds, respectively, with variations of the order of 0.004–0.006 Å during internal rotation.
4. The CH bonds are of average strength, that in the Re compound being slightly the weaker, and bear an inverse relationship to $D_0(M-CH_3)$, as in other MeM compounds.
5. Further development of theory is needed for a quantitative interpretion of the spectra, especially the $\nu_{as}(CH_3)$ and $\nu_{as}(CD_3)$ splittings.

Acknowledgment. We are much indebted to Dr. D. Cavagnat for detailed calculations of CH_3 and CD_3 internal rotation/torsion energy levels. We thank the S.E.R.C. for supporting this work.

Registry No. $Zn(CHD_2)_2$, 92525-33-2; $CH_3Re(CO)_5$, 14524-92-6; $CH_3Mn(CO)_5$, 13601-24-6; $CHD_2Re(CO)_5$, 92525-30-9; $CHD_2Mn(CO)_5$, 92525-31-0; $CH_2DMn(CO)_5$, 20792-56-7; $CD_3Mn(CO)_5$, 15653-52-8; $CD_3Re(CO)_5$, 92525-32-1.

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[38] Although described earlier as 4-31G calculations,[12] these were in fact STO-3G ones, scaled up according to STO-3G/4-31G differences in $MeNO_2$ and $MeBF_2$ (P. D. Mallinson, private communication).

Molecular Structure of *s-cis-* and *s-trans-*Acrolein Determined by Microwave Spectroscopy

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Abstract: The rotational spectra of highly enriched single D-, ^{13}C-, and ^{18}O-substituted species of acrolein have been measured and analyzed over 12–58 GHz. The complete substitution structure has been determined for the less abundant s-cis conformer from the ground-state rotational constants. In addition newly assigned μ_b-type transitions for all isotopic species of the more abundant *s-trans*-acrolein have improved the structure of this conformer. Careful measurements of the Stark effect have resulted in an accurate determination of the electric dipole moment of the s-trans conformer. A comparison of the molecular structures of the two conformers has revealed significant differences in the central C–C bonds.

Among the simplest 1,3-conjugated double-bond systems butadiene ($CH_2{=}CH{-}CH{=}CH_2$), acrolein ($CH_2{=}CH{-}CH{=}O$), and glyoxal ($O{=}CH{-}CH{=}O$) only acrolein possesses a non-vanishing electric dipole moment in the most abundant s-trans conformer.[1] Acrolein represents a crucial system for studying the effect of the change of conformation on the structure in a 1,3-conjugated double-bond system by the microwave method. Several investigations of the rotational spectra of *s-trans*-acrolein have been reported.[2-5] They include the assignment of μ_a-type transitions of isotopically substituted species measured in natural abundance except for the deuterated species.[3] Their analysis allowed the determination of a substitution structure of the planar s-trans conformer. Only recently the rotational spectrum of the less abundant *s-cis*-acrolein has been assigned.[6] Its analysis established that this conformer is likewise a planar molecule.

The present contribution continues our earlier work on *s-cis*-acrolein,[6] providing now the complete substitution structure of this conformer. Highly enriched isotopically substituted species of acrolein had to be prepared since the intensities of the rotational transitions of the s-cis conformer were only 2% of those of the s-trans conformer. In the course of this study it became clear that more accurate data for the isotopic species of *s-trans*-acrolein were needed in order to make a comparison of the structural parameters of s-cis and s-trans conformers possible. Therefore we have remeasured the rotational spectra of D-, ^{13}C-, and ^{18}O-substituted species of *s-trans*-acrolein and have also assigned μ_b-type transitions. With the help of the newly measured transition frequencies three rotational and five quartic centrifugal distortion constants could be determined for all isotopic species, improving the previous analysis.[3] In addition accurate measurements of the Stark splittings of optimally selected transitions have allowed a better determination of the electric dipole moment, especially of the μ_b component.

Experimental Details

Chemicals. Five isotopic species of acrolein were prepared by an aldol condensation from appropriate isotopic species of formaldehyde and acetaldehyde.[7] The reactions were carried out in the gas phase at 280 °C in a reactor filled with an alkaline catalyst following the modifications by Renaud and Stephens.[8] The catalyst was composed of silica gel 40 (70–230 mesh, Fluka AG) treated with a 10% sodium carbonate solution.[7] The crude products from the aldol condensation were purified by gas chromatography (Perkin-Elmer F-21, 4.5-m packed column with 15% QF-1 on Chromosorb W, 40 °C).

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(1) s-trans refers to the trans orientation of the conjugated double bonds about the C–C single bond, s-cis to the cis orientation.

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