

Normal Coordinate Analysis and Molecular Constants of $\text{Cl}_3\text{MCo}(\text{CO})_4$, where M is Si, Ge, or Sn

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A complete normal coordinate analysis has been carried out for the molecule series $\text{Cl}_3\text{MCo}(\text{CO})_4$ (M = Si, Ge and Sn). The mean amplitudes of vibration, Coriolis coupling constants, and linear Bastiansen-Morino shrinkages have also been evaluated.

Watters *et al.*¹ have recently made a complete infrared and Raman spectral study of the molecule series $\text{Cl}_3\text{MCo}(\text{CO})_4$, where M = Si, Ge, and Sn, and included a tentative vibrational assignment. Their work also contains some force field calculations. In the present work we have carried out for the first time a complete normal coordinate analysis with the aim to determine the mean amplitudes of vibration,² Bastiansen-Morino shrinkage² of the linear chains M - Co - C - O and Co - C - O, and the most important Coriolis coupling constants.

SYMMETRY COORDINATES

According to Robinson and Ibers³ the molecule has a staggered C_{3v} symmetry. Consequently the normal modes of vibration are distributed according to the representation

$$\Gamma_{\text{vib}} = 9A_1 + 2A_2 + 11E$$

A suitable set of symmetry coordinates is given below.

A_1 Species

$$\begin{aligned} S_1 &= t \\ S_2 &= u \\ S_3 &= v \\ S_4 &= 3^{-\frac{1}{2}}(r_1 + r_2 + r_3) \\ S_5 &= 3^{-\frac{1}{2}}(s_1 + s_2 + s_3) \\ S_6 &= 3^{-\frac{1}{2}}(d_1 + d_2 + d_3) \\ S_7 &= (RS/3)^{\frac{1}{2}}(\chi_1' + \chi_2' + \chi_3') \end{aligned}$$

$$\begin{aligned}
 S_8^* &= (SU/3)^{\frac{1}{2}}(\eta_1 + \eta_2 + \eta_3) \\
 S_8^{**} &= (SV/3)^{\frac{1}{2}}(\eta_1' + \eta_2' + \eta_3') \\
 S_9^* &= 3^{-\frac{1}{2}}D(\alpha_1 + \alpha_2 + \alpha_3) \\
 S_9^{**} &= (DV/3)^{\frac{1}{2}}(\beta_1 + \beta_2 + \beta_3)
 \end{aligned}$$

The final S_8 and S_9 coordinates are constructed using the relationship

$$S_j = m_j' S_j^* - m_j'' S_j^{**}; \quad j = 8, 9, \quad (1)$$

where m_j' and m_j'' are constants which make

$$m_j'' S_j^* + m_j' S_j^{**} = 0, \quad (2)$$

and $(m_j')^2 + (m_j'')^2 = 1$. Eqn. (2) represents the normalized zero coordinates.

A_2 Species

$$\begin{aligned}
 S_{10} &= (RS/3)^{\frac{1}{2}}(\chi_1 + \chi_2 + \chi_3) \\
 S_{11} &= (DS/3)^{\frac{1}{2}}(\tau_1 + \tau_2 + \tau_3)
 \end{aligned}$$

$E_{(a)}$ Species

$$\begin{aligned}
 S_{12a} &= 6^{-\frac{1}{2}}(2r_1 - r_2 - r_3) \\
 S_{13a} &= 6^{-\frac{1}{2}}(2s_1 - s_2 - s_3) \\
 S_{14a} &= 6^{-\frac{1}{2}}(2d_1 - d_2 - d_3) \\
 S_{15a} &= (TU)^{\frac{1}{2}}\phi_x \\
 S_{16a} &= (RS/2)^{\frac{1}{2}}(-\chi_2 + \chi_3) \\
 S_{17a} &= (RS/6)^{\frac{1}{2}}(2\chi_1' - \chi_2' - \chi_3') \\
 S_{18a} &= 6^{-\frac{1}{2}}S(2\theta_1 - \theta_2 - \theta_3) \\
 S_{19a} &= (SU/6)^{\frac{1}{2}}(2\eta_1' - \eta_2' - \eta_3) \\
 S_{20a} &= (SV/6)^{\frac{1}{2}}(2\eta_1' - \eta_2' - \eta_3') \\
 S_{21a} &= 6^{-\frac{1}{2}}D(2\alpha_1 - \alpha_2 - \alpha_3) \\
 S_{22a} &= (DV/6)^{\frac{1}{2}}(2\beta_1 - \beta_2 - \beta_3)
 \end{aligned}$$

$E_{(b)}$ Species

$$\begin{aligned}
 S_{12b} &= 2^{-\frac{1}{2}}(r_2 - r_3) \\
 S_{13b} &= 2^{-\frac{1}{2}}(s_2 - s_3) \\
 S_{14b} &= 2^{-\frac{1}{2}}(d_2 - d_3) \\
 S_{15b} &= (TU)^{\frac{1}{2}}\phi_y \\
 S_{16b} &= (RS/6)^{\frac{1}{2}}(2\chi_1 - \chi_2 - \chi_3) \\
 S_{17b} &= (RS/2)^{\frac{1}{2}}(\chi_2' - \chi_3') \\
 S_{18b} &= 2^{-\frac{1}{2}}S(\theta_2 - \theta_3) \\
 S_{19b} &= (SU/2)^{\frac{1}{2}}(\eta_2 - \eta_3) \\
 S_{20b} &= (SV/2)^{\frac{1}{2}}(\eta_2' - \eta_3') \\
 S_{21b} &= 2^{-\frac{1}{2}}D(\alpha_2 - \alpha_3) \\
 S_{22b} &= (DV/2)^{\frac{1}{2}}(\beta_2 - \beta_3)
 \end{aligned}$$

The various internal coordinates applied above are defined in Fig. 1. The capital letters T , U , R , S , V , and D are the equilibrium C-O(ax), Co-C(ax), C-O(eq), Co-C(eq), Co-M, and M-Cl bond lengths, respectively.

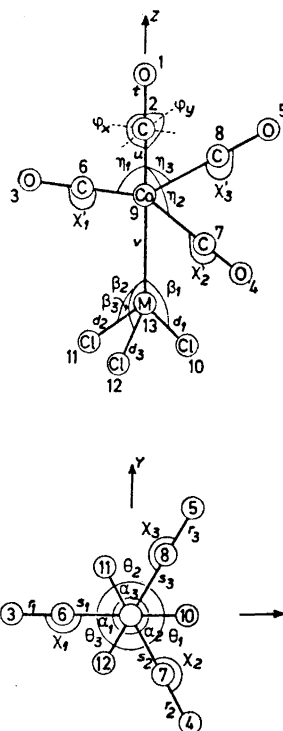


Fig. 1. The $\text{Cl}_3\text{MCo}(\text{CO})_4$ staggered C_{3v} type molecule model. All the applied valence coordinates are indicated, except the three torsional coordinates, τ_1 , τ_2 and τ_3 , which involve the atoms 10-13-9-6, 11-13-9-7 and 12-13-9-8, respectively.

POTENTIAL ENERGY CONSTANTS

The standard Wilson GF matrix method⁴ in terms of symmetry coordinates was used. The molecular parameters were taken from Robinson and Ibers³ and Watters *et al.*¹ The valence force constants given by Watters *et al.*¹ were used to evaluate the F matrix numerically, and this was taken as the starting point for iterative calculations in order to improve the agreement between the experimental and calculated frequencies, which was not very good in the start. The final force constants of our analysis reproduce practically all the observed frequencies with exactness; *cf.* Table 1. The complete symmetry F matrices are too voluminous to be reproduced here. Therefore we only give the most important valence stretching force constants; see Table 2. When the potential energy distribution was determined the assignments for the fundamental frequencies appeared to be almost the same as those of Watters *et al.*¹ Although the fundamentals of the A_2 species are inactive in both infrared and Raman we have estimated a vibrational frequency for the CoCO bending on the basis of force constant values from the other species. The torsional frequency remains as unknown.

Table 1. Observed and calculated vibrational frequencies (cm⁻¹) of Cl₃MCo(CO)₄.

Species	Cl ₃ SiCo(CO) ₄		Cl ₃ GeCo(CO) ₄		Cl ₃ SnCo(CO) ₄	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
A ₁	2118	2118	2123	2121	2121	2123
	2066	2066	2070	2072	2069	2069
	641	641	637 ^a	626	639 ^a	639
	549	549	465	469	463	461
	471	471	411	413	405	409
	411	411	391	391	365	365
	309	309	240	240	204	204
	179	179	160	160	125	125
	100	100	89	89	89 ^a	89
	A ₂	641 ^b	641	635 ^b	640	639 ^b
100 ^c		100	100 ^c	99	100 ^c	100
E	2039	2039	2050	2038	2048	2050
	571	571	548	548	545	547
	506	506	485	477	490	490
	483	483	484 ^a	484	484 ^a	484
	437	437	441	441	449 ^a	449
	372	372	371	371	360	360
	200	200	182 ^a	182	129 ^a	125
	138	138	129	129	107	102
	118	118	107	110	92 ^a	91
	80	80	87 ^a	82	69	69
	65	65	45	45	29 ^a	25

^a Calculated values from Ref. 1. ^b Estimated. ^c Arbitrarily chosen.

Table 2. Valence stretching force constants (mdyn/Å) of Cl₃MCo(CO)₄.

Molecule	Cl ₃ SiCo(CO) ₄	Cl ₃ GeCo(CO) ₄	Cl ₃ SnCo(CO) ₄
<i>f</i> _{C-O(ax)}	17.46	17.52	17.47
<i>f</i> _{Co-C(ax)}	2.87	2.83	2.75
<i>f</i> _{Co-M}	1.43	1.07	1.23
<i>f</i> _{C-O(eq)}	16.77	16.91	16.87
<i>f</i> _{Co-C(eq)}	2.19	2.21	2.17
<i>f</i> _{M-Cl}	2.54	2.43	2.82

MEAN AMPLITUDES AND LINEAR SHRINKAGES

The developed force fields were used to calculate the mean amplitudes of vibration with the results given in Tables 3, 4, and 5 for Cl₃SiCo(CO)₄, Cl₃GeCo(CO)₄, and Cl₃SnCo(CO)₄, respectively. The mean amplitudes for only two distance types out of the totality of twenty-seven may be expected to depend significantly on the unknown torsional frequency. They are the O₃...Cl₁₁ and C₆...Cl₁₁ types. The corresponding mean amplitude values are given in brackets in the tables, and are based on rather arbitrarily chosen

Table 3. Mean amplitudes of vibration (u in Å) for $\text{Cl}_3\text{SiCo}(\text{CO})_4$.

Distance	(Equil. dist.)	u (0 K)	u (298 K)
$\text{C}_2 - \text{O}_1$	(1.136)	0.0342	0.0342
$\text{O}_1 \cdots \text{O}_3$	(4.137)	0.1045	0.1912
$\text{O}_1 \cdots \text{C}_6$	(3.424)	0.0862	0.1370
$\text{O}_1 \cdots \text{C}_{\text{O}_9}$	(2.933)	0.0453	0.0497
$\text{O}_1 \cdots \text{Cl}_{10}$	(6.275)	0.0842	0.1667
$\text{O}_1 \cdots \text{M}_{13}$	(5.187)	0.0596	0.0763
$\text{C}_2 \cdots \text{O}_3$	(3.427)	0.0891	0.1421
$\text{C}_2 \cdots \text{C}_6$	(2.520)	0.0788	0.1127
$\text{C}_2 - \text{C}_{\text{O}_9}$	(1.797)	0.0448	0.0486
$\text{C}_2 \cdots \text{Cl}_{10}$	(5.202)	0.0803	0.1505
$\text{C}_2 \cdots \text{M}_{13}$	(4.051)	0.0595	0.0756
$\text{O}_3 \cdots \text{O}_4$	(5.054)	0.0944	0.1856
$\text{O}_3 - \text{C}_6$	(1.151)	0.0347	0.0347
$\text{O}_3 \cdots \text{C}_7$	(4.098)	0.0808	0.1395
$\text{O}_3 \cdots \text{C}_{\text{O}_9}$	(2.918)	0.0484	0.0546
$\text{O}_3 \cdots \text{Cl}_{10}$	(5.678)	0.0830	0.1508
$\text{O}_3 \cdots \text{Cl}_{11}$	(3.988)	[0.1163] ^a	[0.2562]
$\text{O}_3 \cdots \text{M}_{13}$	(3.687)	0.0849	0.1602
$\text{C}_6 \cdots \text{C}_7$	(3.061)	0.0757	0.1165
$\text{C}_6 - \text{C}_{\text{O}_9}$	(1.767)	0.0486	0.0543
$\text{C}_6 \cdots \text{Cl}_{10}$	(4.750)	0.0766	0.1233
$\text{C}_6 \cdots \text{Cl}_{11}$	(3.558)	[0.0975]	[0.1936]
$\text{C}_6 \cdots \text{M}_{13}$	(2.864)	0.0763	0.1251
$\text{C}_{\text{O}_9} \cdots \text{Cl}_{10}$	(3.583)	0.0633	0.1133
$\text{C}_{\text{O}_9} - \text{M}_{13}$	(2.254)	0.0463	0.0602
$\text{Cl}_{10} \cdots \text{Cl}_{11}$	(3.234)	0.0617	0.0877
$\text{Cl}_{10} - \text{M}_{13}$	(2.033)	0.0448	0.0494

^a Values in brackets depend on the chosen torsional frequency.

Table 4. Mean amplitudes of vibration (u in Å) for $\text{Cl}_3\text{GeCo}(\text{CO})_4$.

Distance	(Equil. dist.)	u (0 K)	u (298 K)
$\text{C}_2 - \text{O}_1$	(1.136)	0.0342	0.0342
$\text{O}_1 \cdots \text{O}_3$	(4.137)	0.1025	0.1848
$\text{O}_1 \cdots \text{O}_6$	(3.424)	0.0840	0.1317
$\text{O}_1 \cdots \text{C}_{\text{O}_9}$	(2.933)	0.0454	0.0500
$\text{O}_1 \cdots \text{Cl}_{10}$	(6.392)	0.0959	0.2363
$\text{O}_1 \cdots \text{M}_{13}$	(5.333)	0.0574	0.0818
$\text{C}_2 \cdots \text{O}_3$	(3.427)	0.0879	0.1391
$\text{C}_2 \cdots \text{C}_6$	(2.520)	0.0772	0.1094
$\text{C}_2 - \text{C}_{\text{O}_9}$	(1.797)	0.0449	0.0489
$\text{C}_2 \cdots \text{Cl}_{10}$	(5.323)	0.0905	0.2127
$\text{C}_2 \cdots \text{M}_{13}$	(4.197)	0.0573	0.0812
$\text{O}_3 \cdots \text{O}_4$	(5.054)	0.0948	0.1876
$\text{O}_3 - \text{C}_6$	(1.151)	0.0346	0.0346
$\text{O}_3 \cdots \text{C}_7$	(4.098)	0.0805	0.1392
$\text{O}_3 \cdots \text{C}_{\text{O}_9}$	(2.918)	0.0482	0.0545
$\text{O}_3 \cdots \text{Cl}_{10}$	(5.819)	0.0850	0.1600

Table 4. Continued.

$O_3 \cdots Cl_{11}$	(4.068)	[0.1230] ^a	[0.2990]
$O_3 \cdots M_{13}$	(3.778)	0.0853	0.1772
$C_6 \cdots C_7$	(3.061)	0.0753	0.1151
$C_6 - Co_9$	(1.767)	0.0484	0.0542
$C_6 \cdots Cl_{10}$	(4.891)	0.0781	0.1324
$C_6 \cdots Cl_{11}$	(3.665)	[0.1022]	[0.2322]
$C_6 \cdots M_{13}$	(2.980)	0.0737	0.1322
$Co_9 \cdots Cl_{10}$	(3.716)	0.0709	0.1561
$Co_9 - M_{13}$	(2.400)	0.0439	0.0662
$Cl_{10} \cdots Cl_{11}$	(3.427)	0.0633	0.0929
$Cl_{10} - M_{13}$	(2.114)	0.0411	0.0474

^a See Table 3.Table 5. Mean amplitudes of vibration (u in Å) for $Cl_3SnCo(CO)_4$.

Distance	(Equil. dist.)	u (0 K)	u (298 K)
$C_2 - O_1$	(1.136)	0.0342	0.0342
$O_1 \cdots O_3$	(4.137)	0.1012	0.1793
$O_1 \cdots O_6$	(3.424)	0.0831	0.1284
$O_1 \cdots Co_9$	(2.933)	0.0456	0.0505
$O_1 \cdots Cl_{10}$	(6.590)	0.1113	0.3597
$O_1 \cdots M_{13}$	(5.333)	0.0559	0.0814
$C_2 \cdots O_3$	(3.427)	0.0876	0.1369
$C_2 \cdots C_6$	(2.520)	0.0768	0.1081
$C_2 - Co_9$	(1.797)	0.0450	0.0493
$C_2 \cdots Cl_{10}$	(5.526)	0.1052	0.3310
$C_2 \cdots M_{13}$	(4.197)	0.0557	0.0806
$O_3 \cdots O_4$	(5.054)	0.0972	0.2061
$O_3 - C_6$	(1.151)	0.0346	0.0347
$O_3 \cdots C_7$	(4.098)	0.0823	0.1531
$O_3 \cdots Co_9$	(2.918)	0.0486	0.0551
$O_3 \cdots Cl_{10}$	(6.022)	0.0860	0.1691
$O_3 \cdots Cl_{11}$	(4.215)	[0.1356] ^a	[0.3934]
$O_3 \cdots M_{13}$	(3.778)	0.0837	0.1752
$C_6 \cdots C_7$	(3.061)	0.0766	0.1262
$C_6 - Co_9$	(1.767)	0.0488	0.0548
$C_6 \cdots Cl_{10}$	(5.099)	0.0818	0.1657
$C_6 \cdots Cl_{11}$	(3.848)	[0.1152]	[0.3335]
$C_6 \cdots M_{13}$	(2.980)	0.0735	0.1344
$Co_9 \cdots Cl_{10}$	(3.926)	0.0828	0.2516
$Co_9 - M_{13}$	(2.400)	0.0410	0.0642
$Cl_{10} \cdots Cl_{11}$	(3.659)	0.0770	0.1479
$Cl_{10} - M_{13}$	(2.300)	0.0384	0.0442

^a See Table 3.

torsional frequencies of 100 cm^{-1} . In order to test numerically the influence of the torsional frequency on mean amplitudes the calculation for $Cl_3SiCo(CO)_4$ was repeated with a torsional frequency of 25 cm^{-1} instead of 100 cm^{-1} . This calculation confirmed that all but two mean amplitudes were unaffected. The two mean amplitudes in question became $u(O_3 \cdots Cl_{11}) = 0.1297 - 0.3655 \text{ Å}$

and $u(\text{C}_8 \cdots \text{Cl}_{11}) = 0.1048 - 0.2614 \text{ \AA}$ at 0–298 K. Calculations of this type combined with electron diffraction studies of mean amplitudes might help to estimate the order of magnitude of the torsional frequency.

Table 6 shows the calculated Bastiansen-Morino linear shrinkage effects. They are all unaffected by variations in the torsional frequency.

Table 6. Bastiansen-Morino linear shrinkages (\AA) for $\text{Cl}_3\text{MCo}(\text{CO})_4$.

Distance	$\text{Cl}_3\text{SiCo}(\text{CO})_4$		$\text{Cl}_3\text{GeCo}(\text{CO})_4$		$\text{Cl}_3\text{SnCo}(\text{CO})_4$	
	0 K	298 K	0 K	298 K	0 K	298 K
$\text{O}_1 \cdots \text{C}_{10}$	0.0060	0.0081	0.0055	0.0070	0.0055	0.0071
$\text{C}_2 \cdots \text{M}_{13}$	0.0031	0.0097	0.0029	0.0101	0.0029	0.0106
$\text{O}_1 \cdots \text{M}_{13}$	0.0093	0.0209	0.0085	0.0209	0.0086	0.0212
$\text{O}_3 \cdots \text{C}_{10}$	0.0055	0.0072	0.0054	0.0073	0.0054	0.0073

Table 7. First order Coriolis coupling constants for $\text{Cl}_3\text{MCo}(\text{CO})_4$.

	$\text{Cl}_3\text{SiCo}(\text{CO})_4$	$\text{Cl}_3\text{GeCo}(\text{CO})_4$	$\text{Cl}_3\text{SnCo}(\text{CO})_4$
ζ_{12}	0.0009	0.0007	0.0007
ζ_{13}	0.7914	0.7774	0.7788
ζ_{14}	0.6237	0.3371	0.2903
ζ_{15}	0.4377	0.1490	0.1401
ζ_{16}	0.0071	0.5289	0.3211
ζ_{17}	0.3407	0.1727	0.1905
ζ_{18}	-0.8415	-0.6547	0.5023
ζ_{19}	0.2037	0.4922	-0.1471
ζ_{20}	0.4080	0.1909	-0.3804
ζ_{21}	-0.1111	-0.0041	0.3343
ζ_{22}	0.4525	0.3100	0.2610

CORIOLIS CONSTANTS

The most important Coriolis coupling constants in a symmetrical top molecule are the first order ones, which correspond to the diagonal elements of the $\zeta^2(E_a \times E_b)$ matrix. The calculated results for these constants are shown in Table 7.

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