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THE INFARED SPECTRA OF DIAQUA TETRA-μ - FORMATO DICHROMIUM (II): A NORMAL COORDINATE TREATMENT ON 1:1 FORMATE COMPLEX

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ABSTRACT

The infrared spectrum of diaqua tetra- μ - formato dichromium (II) complex has been obtained in the frequency range 4000 to 400cm^{-1}. A normal coordinate treatment performed on the 1:1 model of the complex gives calculated frequencies in good agreement with the observed ones. In order to assign bands and to see the coupling between various vibrational modes, the potential energy distribution in each normal vibration was calculated with respect to each symmetry coordinate for all the in-plane vibrations. The results show that in spite of the effect of coordination some of the formate ligand based vibrational modes remain localized, though others such as ν_{as}(COO) and δ_s(HCO) couple strongly with ring deformation. The analysis also indicate that bands at 464, 537 and 540 cm^{-1} are assignable to ν_s (CrOO) coupled with ring deformation, Cr-Cr mode coupled with δ (Cr-Cr-O) bending and ν_{as} (CrOO) coupled with δ_{as} (C-O-Cr) bending, respectively.

Keywords: Infrared spectrum, normal coordinate treatment, in-plane fundamental vibrations, tetra- μ- formato dichromium (II) complex, 1:1 (Cr_2^{4+}: $HCOO^-$) complex model

INTRODUCTION

Because of the interest in the nature of the M-M quadruple bond, the vibrational spectra of complexes containing such bond have been studied. As for tetra- μ- carboxylato dichromium (II) $Cr_2(O_2CR)_4L_2$(where R=H, CH_3, etc), which also belong to this class, the only available data on their vibrational spectra are of the infrared spectra observed by Nakamoto (1961) and Ford (1983) and their colleagues. Both groups measured the infrared spectra of the adducts of tetra-μ- acetato dichromium (II) but reported bands which they empirically assigned to v(COO), v(NCS) and v(CS) only. No information is as yet available on the band assignments of the fundamental vibrations of these complexes, either from empirical or a normal coordinate analysis

We have observed the infrared spectrum of solid tetra-μ- formato dichromium (II) dihydrate, $Cr_2(O_2CH)_4$ $(H_2O)_2$. By comparison of its spectrum with the result of a normal coordinate treatment on the 1:1 complex, assignments of the various in-plane fundamental vibrational frequencies of the complex has been made.

EXPERIMENTAL

Tetra-μ - formato dichromium (II) dihydrate, $Cr_2(O_2CH)_4(H_2O)_2$, was prepared according to a reported method (Cotton and Rice, 1978).

A Matson Genesis FT-IR spectrophotometer was used to obtain the spectrum in the range 4000 to 400cm^{-1}. The nujol mull method was employed for the preparation of the sample. The absorption curve and observed frequencies are presented in Fig. 1 and Table 1, respectively.

CALCULATIONS

From the crystal structure of $Cr_2(O_2CH)_4$ $(H_2O)_2$ reported by cotton and Rice (1978), each HCOO group is attached to a Cr_2^{4+} diatomic frame forming a bridge ring or a 1:1 (Cr_2^{4+}/$HCOO^-$) complex shown in Fig. 2(b) and there are four such bridges per molecule. In order to study the effect of coordination on the fundamental frequencies of the normal modes of vibration of the $HCOO^-$ ligand in the $Cr_2(O_2CH)_4(H_2O)_2$ molecule, a normal coordinate treatment has been made on such a bridge ring or 1:1 complex model. This will also enable us study other important normal modes of vibration of the complex such as those involving

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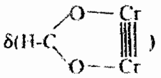
Table 1. Comparison of observed and calculated frequencies in Cr(II) formato complex (cm^{-1})

Species	$HCOO^{-a}$		$Cr_2(O_2CH)_4(H_2O)_2$			Av Shift
	Assignment	Frequency	Observed freq	Calculated freq	Assignment	
A_1						
ν_1	ν(C-H)	2841	2854.25vs	2870.81	ν(C-H) + δ(HCO)	+13.25
ν_2	ν(COO)	1366	1346.07m,sh	1350.24	ν(COO) + δ(OCO)	-19.93
ν_3	-	-	463.64vw	450.38	ν(CrOO) + ring def.	-
ν_4	-	-	537.59m	540.38	ν(Cr-Cr) + δ(Cr-Cr-O)	-
ν_5	ν(HCO)	772	766.96m	760.58		-5.04
B_2						
ν_6	ν(COO)	1567	1582.75vs	1579.18	ν(COO) + ring def	+15.75
ν_7	-	-	540.09m	544.27	ν(CrOO) + δ(C-O-Cr)	-
ν_8	δ(HCO)	1381	1378.85vs	1385.72	δ(HCO) + ν(COO)	+1.85
ν_9	-	-	-	82.49	ring def.	-

[a] qualitative band assignments and observed frequencies taken from Nakamoto (1978) for solid HCOONa

Table 2. Symmetry coordinates for the 1:1 complex

Symmetry Coordinate	Vibrational Mode[a]
A_1 species	
$S_1 = \Delta D$	ν(C-H)
$S_2 = \frac{1}{\sqrt{2}}(\Delta d + \Delta d')$	ν(COO)
$S_3 = \frac{1}{\sqrt{2}}(\Delta r + \Delta r')$	ν(CrOO)
$S_4 = \Delta R$	ν(Cr-Cr)
$S_5 = \frac{1}{\sqrt{2}}(\Delta \beta + \Delta \beta')$	δ(HCO)
$S_6 = \Delta \varepsilon$	δ(OCO)
$S_7 = \frac{1}{\sqrt{2}}(\Delta \alpha + \Delta \alpha')$	δ(COCr)
$S_8 = \frac{1}{\sqrt{2}}(\Delta \delta + \Delta \delta')$	δ(Cr-Cr-O)
B_2 species	
$S_9 = \frac{1}{\sqrt{2}}(\Delta d - \Delta d')$	ν(COO)
$S_{10} = \frac{1}{\sqrt{2}}(\Delta r - \Delta r')$	ν(CrOO)
$S_{11} = \frac{1}{\sqrt{2}}(\Delta \beta - \Delta \beta')$	δ(HCO)
$S_{12} = \frac{1}{\sqrt{2}}(\Delta \alpha - \Delta \alpha')$	δ(COCr)
$S_{13} = \frac{1}{\sqrt{2}}(\Delta \delta - \Delta \delta')$	δ(Cr-Cr-O)

[a] ν, stretching mode; δ, bending mode

Cr-O, Cr-Cr, ring, etc. Because the shifts in $HCOO^-$ fundamental frequencies observed in the spectrum of the complex are small (Table 1), coupling between bridge rings are considered negligible. Thus the 1:1 complex model may be used as a good approximation for this purpose.

The symmetry of an observed representative bridge ring or 1:1 complex such as the one shown in Fig. 2(b) is C_S, with its twelve normal vibrations separable into 9A' in-plane and 3A" out-of-plane vibrations. For the sake of computational convenience, however, we have replaced the values of bond distances and angles of the observed representative 1:1 complex with their averages (Table 3) thus obtaining Fig.2(a). The latter 1:1 complex has a C_{2V} symmetry and the twelve normal vibrations are partitioned into $5A_1$+ $4B_2$ in-plane and A_2 + $2B_1$ out-of-plane vibrations. In the present study, only the nine in-plane vibrations are calculated-all of which are infrared active in both C_s and C_{2v} symmetries. The x-ray data reported by Cotton and Rice (1978), from which we extracted the one given in the second column of Table 3, reveal that $Cr_2(O_2CH)_4$ $(H_2O)_2$ molecule is a distorted or an unsymmetrical molecule. Thus all its vibrational modes are infrared as well as Raman active.

The symmetry coordinates are given in Table 2, and the elements of the G- and F-matrices are given in the appendix. The matrix secular equations of the form $/GF-E\Lambda/=0$ were solved for A_1(8th order) and B_2 (5th order) species. The matrix equations involve three and one redundant coordinates in A_1 and B_2, respectively, which give "zero frequency" in the final results.

In order to express the potential energy, the Urey-Bradly-Shimanouchi force field was employed (Woodward, 1972). After several trials, a satisfactory set of force constants, listed in Table 4, was obtained. In Table 1, the frequencies calculated from this set of the force constants are compared with the values observed for $Cr_2(O_2CH)_4$ $(H_2O)_2$ complex. Agreement between the calculated and observed values is quite satisfactory.

The Jacobian matrix (Nakamoto and Martell, 1960), given in Table 6, was calculated in order to investigate the sensitivity of each normal frequency to the value of each force constant. This matrix was

Table 3. Bond distances and angles in the Cr(II) formato complex

Parameter	$Cr_2(O_2CH)_4(H_2O)_2$	Values used in this calculations
D		1.080^a
d	1.252, 1.263; 1.249, 1.264	1.257
r	2.026, 2.009; 2.017, 2.006	2.015
R	2.373	2.373
α	119.9°, 118.6°, 120.0°, 119.8°	119.58°
β	- - - -	118.50^{ob}
δ	88.3°, 87.6°; 87.6°, 88.1°	87.90°
ε	125.3°, 124.4°	124.85°

[a] taken from Jones and McLaren (1954) in CH_3COO^- data
[b] taken as RCO angle in $Cr_2(O_2CCH_3)_4(H_2O)_2$ x-ray data from Cotton et al (1971)

Table 4. Force constatnts of Cr(II) formato complex (10^5 dyne/cm) and relative atomic masses

Stretching	Bending	Repulsive
$K_1 = K(C\text{-}H) = 4.72$	$H_1 = H(\Delta\beta) = 0.32$	$F_1 = F(H\cdots\cdots O) = 0.02$
$K_2 = K(COO) = 5.12$	$H_2 = H(\Delta\varepsilon) = 0.65$	$F_2 = F(C\cdots\cdots Cr) = 0.05$
$K_3 = K(CrOO) = 2.03$	$H_3 = H(\Delta\alpha) = 0.91$	$F_3 = F(O\cdots\cdots O) = 0.09$
$K_4 = K(Cr\text{-}Cr) = 4.58$	$H_4 = H(\Delta\delta) = 1.97$	$F_4 = F(O\cdots\cdots Cr) = 0.12$

Relative atomic masses

$m_H = 1.00797$ $m_C = 12.0115$ $m_O = 15.9994$ $m_{Cr} = 51.996$

used to adjust the force constants to the observed frequencies. Finally, the potential energy distribution (Nakamoto, 1970) in each normal vibration, which is given by

$$V = \tfrac{1}{2} Q_\lambda \, \Sigma \, F_{KL} L_{K\lambda} L_{L\lambda},$$

was calculated with respect to each symmetry coordinate. The theoretical band assignment thus obtained is shown in Table 7 with numbers indicating relative contributions from each symmetry coordinate.

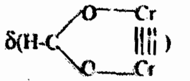
DISCUSSION OF RESULTS

It would have been interesting to compare the force constants used in the formato Cr(II) complex (Table 4) with those of the free formate ion. Unfortunately, such data are simply unavailable for this ligand, though there have been extensive study on the infrared spectra of free sodium formate (Nakamoto, 1978). All the previously reported band assignments for the free fromate ions were empirical. Even for the HCOOH molecule for which theoretical calculation of vibrational frequencies was done (Petterson et al, 1997) no force constants were reported. However, the force constant values we obtained compare very well with those found from normal coordinate analysis of chelating – acetylacetonato (Nakamoto et al, 1961) and – oxalato Cr(III) (Fujita et al, 1962) complexes. Looking at Table 4, it may be observed that the Cr-O force constant, 2.03 X 10^5 dyn/cm, is the lowest amongst stretching force constants. This seems to suggest that the bridging bonds are the weakest in the molecule, though the K(CrOO) value may not be that a reliable measure of the Cr-O bond strength because it is coupled to other vibrational modes as can be seen from Tables 1 and 7.

Table 5 The Jacobian Matrices in Cr(II) formato complex

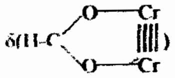
	K_1	K_2	K_3	K_4	H_1	H_2	H_3	H_4	F_1	F_2	F_3	F_4
λ_1	0.06	0.01	0.00	0.00	0.28	0.21	-0.12	0.05	0.16	-0.08	0.17	0.00
λ_2	0.03	0.11	0.09	0.01	-0.14	0.41	-0.32	0.15	0.02	0.22	0.30	-0.09
λ_3	0.00	0.04	0.24	0.12	-0.09	1.36	0.36	-0.43	0.08	0.17	0.28	0.45
λ_4	0.02	0.00	0.09	0.15	0.07	-0.03	0.11	0.68	0.01	-0.37	0.14	0.32
λ_5	0.00	0.06	0.00	0.10	-1.12	0.39	0.16	-0.26	0.22	0.18	-0.44	-0.10
λ_6		0.12	0.00		0.18	0.82	-0.21	0.34	0.17	0.13	-0.30	0.14
λ_7		0.01	0.21		0.02	0.15	0.42	-0.10	0.00	0.23	-0.01	0.04
λ_8		0.06	0.00		0.56	0.00	-0.01	0.00	0.05	0.02	0.00	-0.01
λ_9		0.08	0.03		0.09	0.18	0.27	-0.19	0.04	0.16	-0.13	0.20

Table 6. Classification of the 12 fundamentals of the 1:1 Cr(II) formato complex

C_s	C_{2v}	Assignment in C_{2v}
9A'(IR,R)	$5A_1$(IR,R)	ν(C-H) + δ(HCO), ν(COO) + δ(OCO), ν(CrOO) + ring def , ν(Cr-Cr) + δ(Cr-Cr-O), 
	$4B_2$(IR,R)	ν(COO) + ring def , ν(CrOO) + δ(C-O-Cr), δ(HCO) + ν(COO), ring def
3A''(IR,R)	A_2(R)	Out [illegible]
	$2B_1$(IR,R)	Out-of-plane

R, Raman active; IR, infrared active

Table 7 The potential energy distribution, $F_{ii}L_{i}^{2}$ for each normal mode of vibration

	Symmetry coordinate								Assignment
A_1 species	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	
ν_1	1.00	0.17	0.06	0.00	0.51	0.12	0.06	0.09	ν(C-H) + δ(HCO)
ν_2	0.26	1.00	0.00	0.00	0.02	0.63	0.31	0.18	ν(COO) + δ(OCO)
ν_3	0.00	0.16	1.00	0.00	0.04	0.09	0.56	0.66	ν(CrOO) + ring def.
ν_4	0.00	0.12	0.00	1.00	0.01	0.00	0.18	0.43	ν(Cr-Cr) + δ(Cr-Cr-O)
ν_5	0.28	0.14	0.02	0.00	1.00	0.45	0.37	0.58	
B_2 species	S_9	S_{10}	S_{11}	S_{12}	S_{13}				
ν_6	1.00	0.00	0.12	0.60	0.53				ν(COO) + ring def
ν_7	0.00	1.00	0.07	0.48	0.14				ν(CrOO) + δ(C-O-Cr)
ν_8	0.39	0.01	1.00	0.00	0.23				δ(HCO) + ν(C-O)
ν_9	0.28	0.02	0.00	0.56	1.00				ring def

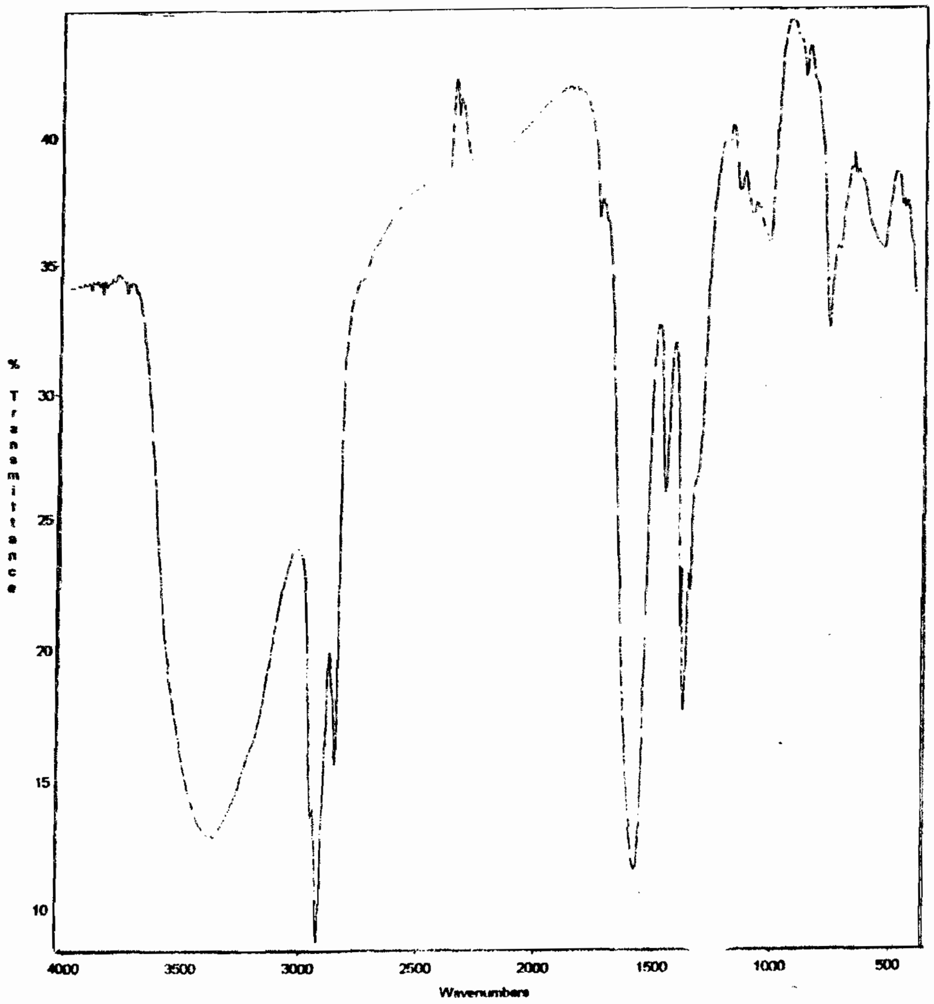
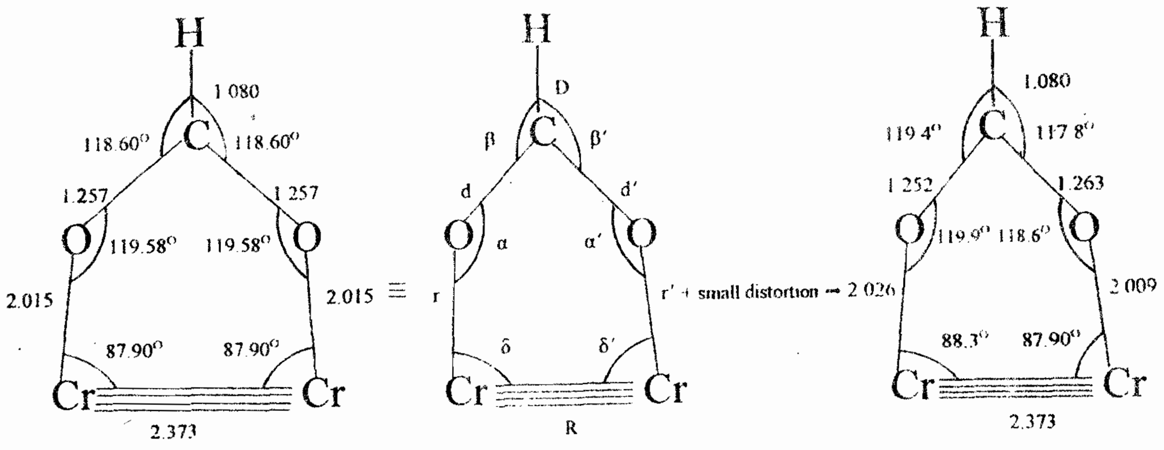


Fig. 1.: The infrared spectrum of $Cr_2(O_2CH)_4(H_2O)_2$ complex.



(a) used in this calculations, C_{2v}

(b) observed, C_s

Fig. 2.: The interatomic distances and angles of the 1:1 complex.

As is shown in Table 7, strong coupling occurs for most of the normal vibrations. This is anticipated on theoretical grounds since the symmetry of the complex is low and the force constants of some of the groups are similar in magnitude. Thus empirical band assignments based on the idea of simple "group frequencies", as was done for the free $HCOO^-$ (Table 1), may be misleading in the bridged compounds. The classification of the twelve fundamentals of the 1:1 complex is shown in Table 6 for both C_S and C_{2V} symmetries. Of the nine in-plane fundamentals we could observe eight bands in the range 3000 to 400cm^{-1}

Table 1 indicate that the agreement between the calculated and observed frequencies is quite satisfactory. However, the v(C-H), v_s(COO) nd δ_{as}(HCO) modes remain primarily ligand vibrations, although the calculations show that they are coupled to δ(HCO)-, δ(OCO)- angle bending and v(COO) local modes, respectively. The other two ligand modes, v_{as} (COO) and δ_s(HCO), are each coupled to in-plane ring deformation and respectively suffer blue and red shifts. Other important modes, if not more, are the vibrational modes involving Cr-O and Cr-Cr groups. As is shown in Table 7, these groups interact with other modes; vibration of the Cr-Cr group is coupled to δ_s(Cr-Cr-O) whereas those of v_s (CrOO) and v_{as}(CrOO) coupled strongly with ring deformation and δ_s(C-O-Cr) angle bending, respectively. Lastly, this normal coordinate treatment reveals that though the asymmetric ring deformation mode is a pure vibration, the symmetric ring deformation couples with δ_s(HCO) to give rise to a whole bridge ring in-plane deformation vibrational mode, v_5. In order to evaluate any coupling effect between the bridge rings, i.e ligand-ligand interactions, quantitatively, the normal coordinate would be extended to 1:2, 1:3 and 1:4 ($Cr_2^{4+}/HCOO^-$) complex models on the basis of the same set of force constants, and the results will be reported in our next paper.

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APPENDIX

G - Matrix elements of the 1:1 complex

A_1 species

$$G_{11}=\frac{1}{m_H}+\frac{1}{m_C},\quad G_{12}=\frac{\sqrt{2}\cos\beta}{m_C},\quad G_{13}=0,\ G_{14}=0,\ G_{15}=\frac{-\sin\beta}{\sqrt{2}\cdot}\,\frac{(D+d)m_H+dm_C}{dm_C m_H},$$

$$G_{16}=\frac{2\cos\beta(\cos\varepsilon-1)}{m_C\sin\varepsilon},\quad G_{17}=\frac{1}{\sqrt{2}}\,\frac{(r+d)\cos\alpha\cos\beta+(r-d)\sin\delta}{dm_C\sin\alpha},\quad G_{18}=0,\ G_{22}=\frac{1+\cos\varepsilon}{m_C}+\frac{1}{m_O},$$

$$G_{23}=0,\ G_{24}=0,\ G_{25}=\frac{\cos\beta(\cos\varepsilon-1)(D^2+Dd)+(\cos^2\beta-\cos\varepsilon)(d^2+Dd)}{2Ddm_C\sin\beta}-$$

$$-\left(\frac{1}{m_C}+\frac{d}{D}\left(\frac{1}{m_C}+\frac{1}{2m_O}\right)\right)\sin\beta,\quad G_{26}=\frac{\sqrt{2}\sin\varepsilon}{m_C},\quad G_{27}=\left(\frac{r}{d\tan\alpha}+\frac{1}{2}\,\frac{\cos\alpha\cos\varepsilon+\cos(\alpha+\varepsilon)}{\sin\varepsilon}+\frac{1}{2}\frac{r}{d}\sin\varepsilon\right)\frac{1}{m_C}+$$

$$+\frac{1}{2}\left(\frac{2r-d\cos\alpha}{d\tan\alpha}-\frac{d}{r}\sin\alpha\right)\frac{1}{m_O},\quad G_{28}=\frac{1}{2}\left(1-\frac{R}{r}\right)\frac{\cos\alpha\cos\delta+\cos(\alpha+\delta)}{m_O\sin\delta},\quad G_{33}=\frac{1}{m_O}+\frac{1}{m_{Cr}},$$

$$G_{34}=\frac{\sqrt{2}\cos\delta}{m_{Cr}},\quad G_{35}=\frac{D^2(\sin\delta-\cos\beta\cos\alpha)+d^2(\cos\beta\sin\delta-\cos\alpha)}{2Ddm_O\sin\beta},\quad G_{36}=0,$$

$$G_{37}=\frac{1}{\tan\alpha}\left(\frac{2}{m_{Cr}}+\frac{\cos\alpha}{m_O}\right)+\frac{2d-r(\cos\alpha-1)}{dm_O\tan\alpha},\quad G_{38}=\frac{1}{2}\left(\frac{\cos(2\delta)+\cos\delta}{m_{Cr}\sin\delta}-\left[2+\frac{3r}{R}\right]\frac{\sin\delta}{m_{Cr}}\right),\quad G_{44}=\frac{2}{m_{Cr}},$$

$$G_{45}=0,\quad G_{46}=0,\quad G_{47}=\frac{1}{\sqrt{2}}\left(\sin\delta+\frac{d}{r}\,\frac{\cos\alpha\cos\delta+\cos(\alpha+\delta)}{\sin\alpha}\right)\frac{1}{m_{Cr}},\ G_{48}=\frac{-1}{\sqrt{2}}\left(1+\frac{R}{r}\right)\frac{\sin\delta}{m_{Cr}}.$$

$$G_{55} = \left(1 + \frac{\cos^2\beta - \cos\varepsilon}{\sin\beta\tan\beta}\right)\frac{1}{m_H} + \left(\frac{d^2\sin^2\beta + D(D - 2d\cos\beta + D\cos^2\beta)}{2d^2 m_c \sin^2\beta} + \frac{-1}{Ddm_c \sin^2\beta}\times\right.$$

$$\left.\times\left\{D\cos\beta\cos\varepsilon(D\cos\beta - d) + d^2(\cos\varepsilon - \cos^2\beta) + D^2(\sin^2\beta - \cos^2\beta)\right\} + \frac{D^2 + d^2 - 2Dd\cos\beta}{D^2}\right) +$$

$$+\frac{1}{2m_O}\left(\frac{D^2}{d^2} + \frac{d^2}{D^2}\right),$$

$$G_{56} = \frac{1}{\sqrt{2}}\left\{\frac{1}{dm_c \sin\beta\sin\varepsilon}[D(\cos\varepsilon - 1)(\cos\beta\cos\varepsilon - \cos\beta) + d\sin^2\varepsilon + 2d\cos^2\beta(\cos\varepsilon - 1)] +\right.$$

$$\left.+\frac{1}{Dm_c \sin\beta\sin\varepsilon}[(D(\cos\varepsilon - 1)(\cos\beta\cos\varepsilon - \cos\beta) + d\sin^2\varepsilon + 2d\cos^2\beta(\cos\varepsilon - 1)]\right\}$$

$$+\frac{1-\cos\varepsilon}{m_O \sin\varepsilon\tan\beta}\left[1 - \frac{d}{D}\cos\beta\right], \; G_{57} = \frac{r}{2d^2 m_c \sin\alpha\sin\beta}[\cos\alpha\cos\beta(d\cos\beta + D) + \sin\delta(d\cos\beta - D) - 2d\cos\alpha] +$$

$$+\frac{1}{2dm_c \sin\alpha\sin\beta}[\cos\alpha\cos\beta(d\cos\beta - D) + \sin\delta(D - d\cos\beta) + \sin\alpha(d\cos\varepsilon - D\cos\beta\sin\varepsilon) + 2\cos\alpha\cos\varepsilon(D\cos\beta - d)] +$$

$$+\frac{r}{2Ddm_c \sin\alpha\sin\beta}[D(\cos\beta\sin\alpha\sin\varepsilon - \cos\alpha\cos\beta - \sin\delta) + d(\cos\beta\sin\delta + \cos^2\beta\cos\alpha - \sin\alpha\sin\varepsilon)] +$$

$$+\frac{(D - d\cos\beta)(\sin\delta - \cos\alpha\cos\beta)}{2Dm_c \sin\alpha\sin\beta} + \frac{D(r - d\cos\alpha)(\cos\alpha\cos\beta - \sin\delta)}{2d^2 m_O \sin\alpha\sin\beta} + \frac{d}{2Drm_O \sin\alpha\sin\beta}[\cos^2\beta(r\cos\alpha - d) +$$

$$+\cos\beta c\sin\delta(d\cos\alpha - r) + d\sin^2\alpha], \quad G_{58} = \frac{1}{2}\left(\frac{Dr\cos\delta(\sin\delta - 2\cos\alpha\cos\beta) + \cos\beta\sin\alpha\sin\delta}{dr\sin\beta\sin\delta} +\right.$$

$$\left.+\frac{d}{D\sin\beta}[\cos\delta(\cos\beta\sin\delta - 2\cos\alpha) + \sin\alpha\sin\delta]\right)\frac{1}{m_O}, \quad G_{66} = \frac{2(1-\cos\varepsilon)}{m_c} + \frac{2}{m_O},$$

$$G_{66} = \frac{2(1-\cos\varepsilon)}{m_c} + \frac{2}{m_O}, \quad G_{67} = \frac{1}{\sqrt{2}}\left\{\frac{r}{d}\frac{(\cos\varepsilon - 1)(2\cos\alpha + \sin\alpha\sin\varepsilon)}{m_c \sin\alpha\sin\varepsilon} + \frac{(\cos\varepsilon - 1)(\cos\varepsilon\cos\alpha + \cos(\alpha + \varepsilon))}{m_c \sin\alpha\sin\varepsilon}\right\} +$$

$$+\frac{1}{\sqrt{2}}\left\{\frac{(r - d\cos\alpha)(\cos\varepsilon\cos\alpha + \cos(\alpha + \varepsilon))}{m_O d\sin\alpha\sin\varepsilon} +\right.$$

$$\left.+\frac{1}{rm_O \sin\varepsilon\cos\varepsilon}[d\cos\alpha(\cos\alpha + \cos(\alpha + \varepsilon)) + r(\cos\alpha - \cos(\alpha + \varepsilon))]\right\},$$

$$G_{68} = \frac{1}{\sqrt{2}}\left\{\frac{R}{r\sin\varepsilon\sin\delta}[\cos\varepsilon\sin\alpha\sin\delta - \cos(\alpha + \delta) - \cos\delta(2\cos\alpha\cos\varepsilon + \cos(\alpha + \varepsilon))] +\right.$$

$$\left.+\frac{1}{\sin\varepsilon\sin\delta}[\cos\varepsilon(2\cos\beta\cos\delta - \sin\alpha\sin\delta) - \cos\delta\sin\alpha\sin\varepsilon - \cos(\alpha + \delta)]\right\}\frac{1}{m},$$

$$G_{77} = \frac{1}{2}\left(\left(\frac{r}{d}\right)^2 \frac{1+3\cos^2\alpha}{\sin^2\alpha} + \frac{2r}{d\sin^2\alpha}[\cos\alpha\cos(\alpha+\varepsilon) + \cos\alpha\sin\alpha\sin\varepsilon + \cos(2\delta) - \sin^2\delta] + 1\right)\frac{1}{m_O} +$$

$$+\frac{1}{2}\left(\frac{1}{d^2\sin^2\alpha}[r^2(1+3\cos^2\alpha) + \cos^2\alpha(3d^2 - 2rd\cos\alpha) + d(d - 6r\cos\alpha)] +\right.$$

$$\left.+\frac{1}{r^2\sin^2\alpha}[d^2\sin^2\alpha + \cos^2\alpha(2rd\cos\alpha - r^2) + r(r - 2d\cos\alpha)]\right)\frac{1}{m_O} + \frac{1}{2}\left(\frac{(1+\cos\alpha)^2}{\sin^2\alpha} + \left(\frac{d}{r}\right)^2\right)\frac{1}{m_{Cr}},$$

$$G_{78} = \frac{1}{2}\Big(\frac{R}{dr}\frac{(d - r\cos\alpha)(\cos\alpha\cos\delta + \cos(\alpha+\delta))}{\sin\alpha\sin\delta} + \frac{1}{r\sin\alpha\cos\delta}[r\cos\alpha\cos(\alpha+\delta) + \cos\delta(r -$$

$$- d\cos\alpha + r\cos^2\alpha) - d\cos(\alpha+\delta)]\Big)\frac{1}{m_O} + \frac{1}{2}\left(\frac{R(\cos\alpha\cos\delta + \cos(\alpha+\delta)) + r(\cos\delta\sin\alpha\sin\delta - 2\cos\alpha)}{r\sin\alpha\sin\delta} +\right.$$

$$+\frac{r}{R\sin\alpha\sin\delta}[\cos\alpha(\cos(2\delta) - \sin^2\delta) + \cos\delta\sin\alpha\sin\delta - \cos(\alpha+\varepsilon)] + \frac{d}{r\sin\alpha\sin\delta}[\sin\varepsilon(\sin\alpha - \cos\alpha) +$$

$$\left.+\cos\delta\cos(\alpha+\delta) + 2\cos\alpha\cos(2\delta)] + \frac{d}{Rr\sin\alpha\sin\delta}[(r\cos\delta - R)(\cos\alpha\cos\delta + \cos(\alpha+\delta))]\right)\frac{1}{m_{Cr}},$$

$$G_{88} = \frac{1}{2}\left(\left(\frac{R}{r}\right)^2 + 1\right)\frac{1}{m_O} + \frac{1}{2}\left(1 + \frac{1}{r^2\sin^2\delta}[\sin^2\delta(R^2 + r^2) + 2Rr\cos\delta(\cos^2\delta - 3)] +\right.$$

$$+\frac{2r}{Rr\sin^2\delta}[2(R\cos\delta - r)\cos(2\delta)] + \frac{2}{R\sin^2\delta}[2\cos(2\delta)(R\cos\delta - r)] +$$

$$\left.+\left[\frac{r}{R}\right]^2 + \frac{1}{R^2\sin^2\delta}[R^2\sin^2\delta + (1 - 2\cos^2\delta)(r^2 - Rr\cos\delta)]\right)\frac{1}{m_{Cr}}.$$

B_2 species

$$G_{11} = \frac{1-\cos\varepsilon}{m_C} + \frac{1}{m_O},\ G_{12} = 0,\ G_{13} = \frac{1}{2}\left(\left[1 + \frac{d}{D}\left(\frac{1}{m_C} + \frac{1}{2m_O}\right)\right]\sin\beta + \frac{D\cos\beta(\cos\varepsilon - 1) + d(\cos^2\beta - \cos\varepsilon)}{m_C(D+d)\sin\beta}\right),$$

$$G_{14} = \left(\frac{r}{d\tan\alpha} - \frac{\cos\alpha\cos\varepsilon + \cos(\alpha+\varepsilon)}{2\sin\alpha} - \frac{r\sin\varepsilon}{2d}\right)\frac{1}{m_C} + \left(\frac{2r\cos\alpha - d(\cos^2\alpha + 1)}{2d\sin\alpha} - \frac{d}{r}\frac{\sin\alpha}{2}\right)\frac{1}{m_O},$$

$$G_{15} = \frac{r(\cos\alpha\cos\delta + \cos(2\delta)) - R(\cos\alpha\cos\delta + \cos(\alpha+\delta))}{2rm_O\sin\delta},\quad G_{22} = \frac{1}{m_O} + \frac{1}{m_{Cr}},$$

$$G_{23} = \frac{D^2(\sin\delta - \cos\beta\cos\alpha) + d^2(\cos\beta\cos\delta - \cos\alpha)}{2D^2m_O\sin\beta},\ G_{24} = \frac{1}{\tan\alpha}\left(\frac{1}{m_{Cr}} + \frac{\cos\alpha}{2m_O}\right) + \frac{2d\cos\alpha - r(1+\cos^2\alpha)}{2dm_O\sin\alpha},$$

$$G_{25} = \left(\frac{r}{R} - 1\right)\frac{\sin\delta}{m_{Cr}} - \frac{\cos(2\delta) + \cos\delta - \sin^2\delta}{2m_{Cr}\sin\delta},\ G_{33} = \left(1 - \frac{2\cos^2\beta - \cos\varepsilon}{\sin\beta\tan\beta}\right)\frac{1}{m_{Cr}} + \frac{1}{2}\left(\frac{d^2\sin^2\beta + D(D - 2d\cos\beta - D\cos^2\beta)}{d^2\sin^2\beta}\right.$$

$$\left.-\frac{2}{Dd\sin^2\beta}[\cos^2\beta(D^2\cos\varepsilon - d^2) + \cos\varepsilon(d^2 - 2Dd\cos\beta) + D^2(\sin^2\beta - \cos^2\beta)] + \frac{D^2 + d^2 - 2Dd\cos\beta}{D^2}\right)\frac{1}{m_C} +$$

B_2 species

$F_{11} = f_d - f_{dd}$, $F_{12} = f_{dr}$, $F_{13} = f_{d\beta}$, $F_{14} = f_{d\alpha}$, $F_{15} = 0$, $F_{22} = f_r$, $F_{23} = 0$, $F_{24} = f_{r\alpha}$,
$F_{25} = f_{r\delta}$, $F_{33} = f_\beta$, $F_{34} = 0$, $F_{35} = 0$, $F_{44} = f_\alpha$, $F_{45} = 0$, $F_{55} = f_\delta$

Force Constants in Urey-Bradly-Shimanouchi Force Field

$$f_D = K_1 + 2(t_1^2 F_1' + s_1^2 F_1),\quad f_d = K_2 + t_2^2 F_1' + s_2^2 F_1 + t_3^2 F_2' + s_3^2 F_2 + t_5^2 F_3' + s_5^2 F_3,\quad f_r = K_3 + t_4^2 F_2' + s_4^2 F_2 +$$

$$+ t_7^2 F_4' + s_7^2 F_4,\quad f_R = K_4 + 2(t_6^2 F_4' + s_6^2 F_4),\quad f_\beta = H_1 - s_1 s_2 \frac{d}{D} F_1' + t_1^2 F_1,\quad f_\varepsilon = H_2 - s_5^2 F_3' + t_5^2 F_3,$$

$$f_\alpha = H_3 - s_3 s_4 \frac{r}{d} F_2' + t_3^2 F_2,\quad f_\delta = H_4 - s_6 s_7 \frac{r}{R} F_4' + t_6^2 F_4,\quad f_{Dd} = -t_1 t_2 F_1' + s_1 s_2 F_1,\quad f_{D\beta} = t_1 s_2 \frac{d}{D} F_1' +$$

$$+ s_1 t_1 F_1,\quad f_{dd} = -t_5^2 F_3' + s_5^2 F_3,\quad f_{dr} = -t_3 t_4 F_2' + s_3 s_4 F_2,\quad f_{d\beta} = t_2 s_1 F_1' + s_2 t_1 F_1,\quad f_{d\varepsilon} = t_5 s_5 F_3' + s_5 t_5 F_3,$$

$$f_{d\alpha} = t_3 s_4 F_2' + s_3 t_3 F_2,\quad f_{rR} = -t_6 t_7 F_4' + s_6 s_7 F_4,\quad f_{r\alpha} = t_4 s_3 F_2' + s_4 t_3 F_2,\quad f_{r\delta} = t_7 s_6 F_4' + s_7 t_6 F_4,$$

$$f_{R\delta} = t_6 s_7 F_4' + s_6 t_6 F_4$$

$$t_1 = d\sin\beta/\rho_{H\text{—}O},\quad t_2 = D\sin\beta/\rho_{H\text{—}O},\quad t_3 = r\sin\alpha/\rho_{C\text{—}Cr},\quad t_4 = d\sin\alpha/\rho_{C\text{—}Cr},\quad t_5 = d\sin\varepsilon/\rho_{O\text{—}O},$$

$$t_6 = r\sin\delta/\rho_{O\text{—}Cr},\quad t_7 = R\sin\delta/\rho_{O\text{—}Cr},$$

$$s_1 = (D - d\cos\beta)/\rho_{H\text{—}O},\quad s_2 = (d - D\cos\beta)/\rho_{H\text{—}O},\quad s_3 = (d - r\cos\alpha)/\rho_{C\text{—}Cr},\quad s_4 = (r - d\cos\alpha)\ \rho_{C\text{—}Cr},$$

$$s_5 = (d - d\cos\varepsilon)/\rho_{O\text{—}O},\quad s_6 = (R - r\cos\delta)\ \rho_{O\text{—}Cr},\quad s_7 = (r - R\cos\delta)\ \rho_{O\text{—}Cr}$$

$$\rho_{H\text{—}O}^2 = D^2 + d^2 - 2Dd\cos\beta,\quad \rho_{C\text{—}Cr}^2 = d^2 + r^2 - 2dr\cos\alpha,\quad \rho_{O\text{—}O}^2 = d^2 + d^2 - 2dd\cos\varepsilon,$$

$\rho_{O\text{—}Cr}^2 = R^2 + r^2 - 2Rr\cos\delta$, $\rho_{i\text{—}j}$ *is the distance between non-bonded atoms i and j.*