

Vibrational Analysis and Mean Bond Displacements in $M(\text{XY})_6$ Complexes

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Abstract: An empirical quadratic GVFF potential for $M(\text{XY})_6$ molecules, coupled with explicit anharmonicities in the form of a Morse potential and a Urey-Bradley interaction between each nearest-neighbor nonbonded pair of X atoms, is used to model the stretching anharmonicities of the MX and XY bonds. Mean V-C, C-O, Co-C, and C-N bond displacements and mean square amplitudes are calculated for $\text{V}(\text{CO})_6^-$ and $\text{Co}(\text{CN})_6^{3-}$.

NMR chemical shifts of transition metal nuclei are very sensitive to the metal-ligand distance. Measures of the sensitivity of transition metal shielding to the metal-ligand distance are the observed large chemical shifts with temperature and upon isotopic substitution. For example, ^{59}Co shifts of 1.4 to 3 ppm/deg and ^{51}V shifts of 0.3 to 1.5 ppm/deg have been reported.¹ Isotope shifts are also large: -4.7, -6, and -10 ppm on D substitution in $\{\text{CpM}(\text{CO})_3\text{H}\}$ for $M = ^{51}\text{V}$, ^{93}Nb , and ^{183}W , respectively.² Furthermore, the temperature coefficients of the shifts of ^{51}V in various vanadium carbonyl complexes show an interesting correlation with the chemical shifts at 300 K. A theory to interpret these very large shifts requires the knowledge of the mean bond length changes in these molecules in the form of various rovibrational averages, $\langle \Delta r \rangle$ and $\langle (\Delta r)^2 \rangle$. $\text{V}(\text{CO})_6^-$ is a reasonable prototype of these octahedral complexes. In this paper we use the vibrational frequencies of $\text{V}(\text{CO})_6^-$ to determine an empirical quadratic force field which is consistent with the ones which have been established for the analogous $M(\text{CO})_6$ neutral molecules ($M = \text{Cr}, \text{Mo}, \text{W}$). We augment this with cubic force constants calculated using an anharmonic model for stretching and nonbonded interactions, a model which has been successful in reproducing the 10 stretching-mode anharmonicities that are presently known for SF_6 . We calculate the thermal averages $\langle \Delta r \rangle$ and $\langle (\Delta r)^2 \rangle$ for V-C and C-O bonds in $\text{V}(\text{CO})_6^-$ ($^{13/12}\text{C}$, $^{18/16}\text{O}$) and also for Co-C and C-N bonds in $\text{Co}(\text{CN})_6^{3-}$ ($^{13/12}\text{C}$, $^{15/14}\text{N}$) for comparison.

The complete quadratic force field for the metal carbonyls $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ has been established by a comprehensive study of the vibrational spectra of the molecules $M(^{12}\text{C}^{16}\text{O})_6$, $M(^{13}\text{C}^{16}\text{O})_6$, and $M(^{12}\text{C}^{18}\text{O})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$).³ These studies lead to the important result that the interaction force constants are reasonably transferable from one $M(\text{CO})_6$ molecule to another. The force field for $\text{V}(\text{CO})_6^-$ has not been reported. Only the frequencies for the $^{12}\text{C}^{16}\text{O}$ species are known from the work of Abel et al.⁴ However, it has been shown that in the $M(\text{CO})_6$ series ($M = \text{Cr}, \text{Mo}, \text{W}$) most of the interaction force constants have equal or nearly equal magnitudes irrespective of M .³ Therefore, we will determine the force field for $\text{V}(\text{CO})_6^-$ with the assumption that these interaction force constants which are invariant in the Cr, Mo, and W hexacarbonyls can be used for $\text{V}(\text{CO})_6^-$ to establish the off-diagonal symmetry force constants. That is, we will use the same values for $f_{\text{MC,CO}}$, $f_{\text{MC,CO}}^{\text{is}}$, $f_{\text{MC,CO}}^{\text{c}}$, $f_{\text{CO,CO}}$, $f_{\text{CO,CO}}^{\text{is}}$, $f_{\text{CO,CO}}^{\text{c}}$, $f_{\text{MC,CO}}$, $f_{\text{MC,CO}}^{\text{is}}$, $f_{\text{MC,CO}}^{\text{c}}$, $f_{\alpha\beta}$, $f_{\alpha\beta}^{\text{is}}$, and $f_{\alpha\beta}^{\text{c}}$, as were reported for $\text{Cr}(\text{CO})_6$. The displacement coordinates are desig-

Table I. Valence Force Constants for $\text{V}(\text{CO})_6^-$

valence stretching force constants, mdyn \AA^{-1}		valence angle bending force constants, mdyn $\text{\AA} \text{rad}^{-1}$
f_{CO}	15.030	$f_{\beta} = 0.4595$
f_{MC}	2.160	$f_{\beta\beta'} = 0.1005$
$f_{\text{CO,CO}}^{\text{is}}$	0.285	$f_{\beta\beta''} = 0.0005$
$f_{\text{CO,CO}}^{\text{c}}$	0.180	$f_{\beta\beta'''} = -0.005$
$f_{\text{MC,MC}}^{\text{c}}$	-0.025	$(f_{\alpha} - f_{\alpha\alpha'}) = 0.50$
$f_{\text{MC,MC}}^{\text{is}}$	0.360	$(f_{\alpha\alpha'} - f_{\alpha\alpha''}) = 0.075$
$f_{\text{MC,CO}}^{\text{c}}$	0.683	$(f_{\alpha\alpha'} - f_{\alpha\alpha''}') = 0.01$
$f_{\text{MC,CO}}^{\text{is}}$	-0.052	
$f_{\text{MC,CO}}^{\text{c}}$	-0.097	

Table II. Symmetry Force Constants and Frequencies for $\text{V}(\text{CO})_6^-$

symmetry force constants ^a	frequencies, cm^{-1}					
	$\text{V}(^{12}\text{C}^{16}\text{O})_6^-$		$\text{V}(^{13}\text{C}^{16}\text{O})_6^-$	$\text{V}(^{12}\text{C}^{18}\text{O})_6^-$		
	obsd ^b	calcd	calcd	calcd		
A_{1g} \mathcal{F}_{11}	16.35	ω_1 2036	2034.5	1987.0	1989.1	
	\mathcal{F}_{22} 2.42	374	378.1	371.9	364.6	
	\mathcal{F}_{12} 0.38					
E_g \mathcal{F}_{33}	14.64	ω_3 1908	1907.7	1863.3	1864.8	
	\mathcal{F}_{44} 2.57	393	391.4	385.0	377.5	
	\mathcal{F}_{34} 0.69					
F_{1g} \mathcal{F}_{55}	0.358	356	356.1	345.4	351.6	
	F_{1u} \mathcal{F}_{66}	14.85	ω_6 1895	1897.9	1855.1	1853.2
		\mathcal{F}_{77} 1.80	650	655.1	643.1	651.9
\mathcal{F}_{88} 0.55		460	454.4	445.5	445.9	
\mathcal{F}_{99} 0.65	92	91.8	91.3	87.9		
\mathcal{F}_{67} 0.78						
\mathcal{F}_{68} 0						
\mathcal{F}_{69} 0						
\mathcal{F}_{78} -0.18						
\mathcal{F}_{79} -0.3						
\mathcal{F}_{89} -0.21						
F_{2g} $\mathcal{F}_{10,10}$	0.36	517	518.2	499.6	515.7	
	$\mathcal{F}_{11,11}$ 0.52	84	85.0	84.7	80.5	
	$\mathcal{F}_{10,11}$ -0.52					
F_{2u} $\mathcal{F}_{12,12}$	0.57	506	505.7	489.2	501.0	
	$\mathcal{F}_{13,13}$ 0.35	67.0	66.6	66.6	63.8	
	$\mathcal{F}_{12,13}$ -0.11					

^aUnits are mdyn \AA^{-1} except mdyn rad^{-1} for \mathcal{F}_{68} , \mathcal{F}_{69} , \mathcal{F}_{78} , and \mathcal{F}_{79} , and mdyn $\text{\AA} \text{rad}^{-2}$ for \mathcal{F}_{55} , \mathcal{F}_{88} , \mathcal{F}_{99} , \mathcal{F}_{89} , $\mathcal{F}_{10,10}$, $\mathcal{F}_{10,11}$, $\mathcal{F}_{11,11}$, $\mathcal{F}_{12,12}$, $\mathcal{F}_{12,13}$, and $\mathcal{F}_{13,13}$. The definitions of the symmetry coordinates are the same as in ref 3. ^bFrom ref 4. Only the frequencies for vibrations 1, 3, and 6 have been corrected for anharmonicity; that is, harmonic frequencies rather than observed frequencies are given for these vibrations only.

nated in the same way as in ref 3. The CMC angles are labeled α and the MCO angle is labeled β . The quadratic force constants (shown in Table I) are the second derivatives of the potential energy with respect to Δr_{MC} , ΔR_{CO} , $\Delta \alpha_{\text{CMC}}$, and $\Delta \beta_{\text{MCO}}$.

The fundamental frequencies for $\text{V}(\text{CO})_6^-$ are then used to determine the following force constants: f_{CO} , $f_{\text{CO,CO}}$, and $f_{\text{CO,CO}}^{\text{c}}$.

(1) Benedek, G. B.; Englman, R.; Armstrong, J. A. *J. Chem. Phys.* **1963**, *39*, 3349-3363. Jameson, C. J.; Rehder, D.; Hoch, M. *J. Am. Chem. Soc.*, following paper in this issue.

(2) Hoch, M.; Rehder, D. *Inorg. Chim. Acta* **1986**, *111*, L13. Näumann, F.; Rehder, D.; Pank, V. *J. Organomet. Chem.* **1982**, *240*, 363. McFarlane, H. C. E.; McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1976**, 1616.

(3) Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1969**, *8*, 2349-2363.

(4) Abel, E. W.; McLean, R. A. N.; Tyfield, S. P.; Braterman, P. S.; Walker, A. P.; Hendra, P. J. *J. Mol. Spectrosc.* **1969**, *30*, 29-50.

Table III. Evaluation of Approximate Cubic Force Constants for $M(\text{CO})_6$ -Type Molecules^a

F_{ijk}	term		$\text{V}(\text{CO})_6^-$	$\text{Co}(\text{CN})_6^{3-}$
f_{rrr}	Δr_1^3	$(1/r_{\text{MC}})(F_3 + 3F - 3F') - 3a_{\text{MC}}K_{\text{MC}}$	-11.313	-11.343
f_{rrr}'	$\Delta r_1^2 \Delta r_2$	$(1/4r_{\text{MC}})(F_3 - F + F')^b$	-0.093	-0.203
f_{aaa}	$(r\Delta\alpha)^3$	$(1/4r_{\text{MC}})(F_3 - 3F - F')$	-0.109	-0.236
f_{rra}	$\Delta r_1^2(r_1\Delta\alpha_{1j})$	$(1/4r_{\text{MC}})(F_3 + 3F - 3F')$	-0.056	-0.122
$f_{rr'a}$	$\Delta r_1\Delta r_2(r\Delta\alpha_{12})$	$(1/4r_{\text{MC}})(F_3 + F + 3F')$	-0.078	-0.170
f_{raa}	$\Delta r_1(r_1\Delta\alpha_{1j})^2$	$(1/4r_{\text{MC}})(F_3 + F - F')$	-0.075	-0.162
f_{RRR}	ΔR_1^3	$-3a_{\text{CO}}K_{\text{CO}}$ or $-3a_{\text{CN}}K_{\text{CN}}$	-108.9	-125.8

^a $F_{ijk} \equiv (\partial^3 V / \partial \mathcal{R}_i \partial \mathcal{R}_j \partial \mathcal{R}_k)$, all in $\text{mdyn } \text{\AA}^{-2}$, $F' \equiv (\partial V / \partial q_0) / q_0$, $F \equiv (\partial^2 V / \partial q^2)_0$, $F_3 \equiv q_0(\partial^3 V / \partial q^3)_0$. Note the typographical error in this term in eq 1 of ref 7.

from ω_1 , ω_3 , and ω_6 ; f_{MC} , $f_{\text{MC,MC}}$, and $f_{\text{MC,MC}}$, from ω_2 , ω_4 , and ω_7 ; f_{β} , $f_{\beta\beta}$, $f_{\beta\beta'}$, and $f_{\beta\beta''}$, from ω_5 , ω_8 , ω_{10} , and ω_{12} ; and finally the linear combinations $(f_{\alpha} - f_{\alpha''})$, $(f_{\alpha'} - f_{\alpha'''})$, and $(f_{\alpha\alpha'} - f_{\alpha\alpha''})$ from ω_9 , ω_{11} , and ω_{13} . Since ω_{13} was not observed, we used the same symmetry force constant $\mathcal{F}_{13,13}$ as in $\text{Cr}(\text{CO})_6$. This fixes the sum $(f_{\alpha} - f_{\alpha''}) - 2(f_{\alpha\alpha'} - f_{\alpha\alpha''})$. The complete set of force constants is given in Tables I and II. These are consistent with the set for Cr -, Mo -, and $\text{W}(\text{CO})_6$ in that the values for $\text{V}(\text{CO})_6^-$ are not drastically different and the relative magnitudes of cis vs. trans force constants and other such trends are preserved. The elements of the \mathbf{G}_S matrix have been given by Jones et al.⁵ Solution of the \mathbf{GF} matrix problem reproduces the fundamental frequencies of $\text{V}(\text{CO})_6^-$ to within $\pm 2 \text{ cm}^{-1}$. Frequencies for the ^{13}C and ^{18}O isotopomers calculated with this set of force constants are also given in Table II.

In order to calculate mean V-C and C-O bond displacements, we need some reasonable estimate of the anharmonicity of the bonds. Here we extend the method of Krohn and Overend for SF_6 ,⁶ which we have successfully applied to other molecules of this type (SeF_6 , TeF_6 , PtCl_6^{2-} , and PtBr_6^{2-}).⁷ We assume, as they did, that the anharmonicity can be described by a stretching Morse anharmonicity combined with nonbonded interactions. In this way we can derive the expressions for the cubic force constants as shown in Table III. The Morse parameters $a_{\text{VC}} = 1.711 \text{ \AA}^{-1}$ and $a_{\text{CO}} = 2.416 \text{ \AA}^{-1}$ are calculated by the method of Herschbach and Laurie⁸ using the bond lengths $r_e(\text{CO}) = 1.146 \text{ \AA}$ and $r_e(\text{VC}) = 1.931 \text{ \AA}$ in $\text{V}(\text{CO})_6^-$ from the X-ray crystal structure.⁹ $K_{\text{VC}} = 2.16 \text{ mdyn/\AA}$ and $K_{\text{CO}} = 15.03 \text{ mdyn/\AA}$ were estimated from the f_{MC} and f_{CO} values found in this vibrational analysis (see Table I). We neglect all contributions of nonbonded interactions to the cubic force constants involving the C-O stretch, so the entire anharmonicity of the CO bond is due to Morse anharmonicity. Terms other than those types shown in Table III are neglected. The nonbonded interaction constant $F(\text{C}\cdots\text{C})$ in Table III is obtained from the symmetry force constant $\mathcal{F}_{22} = K_{\text{MC}} + 4F$. For $\text{V}(\text{CO})_6^-$ $F = 0.065 \text{ mdyn/\AA}$ and F' and F_3 are taken to be -0.0065 and -0.65 mdyn/\AA according to the usual recipe in which $F' \approx -0.1F$, $F_3 \approx -10F$.

The vibrational contributions to the mean bond displacements are calculated using the method of Bartell¹⁰ as implemented in our previous work,¹¹ from which the following is easily derived:

$$\langle \partial V / \partial z_k \rangle = \sum_{j=1}^{12} F_{kj} \langle \mathcal{R}_j \rangle + \sum_{i=1}^{12} \sum_{j=13}^{36} -\frac{F_{ij}}{2r} \langle \mathcal{R}_i \mathcal{R}_j \rangle \epsilon_{kj} + \sum_{i=13}^{36} \sum_{j=13}^{36} -\frac{F_{ij}}{4r} \langle \mathcal{R}_i \mathcal{R}_j \rangle (\epsilon_{ki} + \epsilon_{kj}) + \sum_{i=1}^{36} \sum_{j=1}^{36} \frac{F_{kij}}{2} \langle \mathcal{R}_i \mathcal{R}_j \rangle$$

$$k = 1 \text{ to } 12 \quad (1)$$

Here \mathcal{R}_i stands for the curvilinear internal coordinates ΔR_{CO} or Δr_{MC} for $i = 1$ to 6 and $i = 7$ to 12, respectively, $\Delta\alpha$ for $i = 13$

Table IV. Mean Bond Displacements and Mean Square Amplitudes for the V-C Bond and the C-O Bond in $\text{V}(\text{CO})_6^-$ ^a

	T	$\langle \Delta r \rangle_{\text{vib}}$	$\langle \Delta r \rangle_{\text{rot}}$	$\langle \Delta r \rangle$	$\langle (\Delta r)^2 \rangle$
$\text{V}(^{12}\text{C}^{16}\text{O})_6^-$	300	11.6443	0.4432	12.0875	3.2451
$\text{V}(^{13}\text{C}^{16}\text{O})_6^-$	300	11.5170	0.4432	11.9602	3.2016
$\text{V}(^{12}\text{C}^{18}\text{O})_6^-$	300	11.6379	0.4432	12.0810	3.2380
$\text{V}(^{12}\text{C}^{16}\text{O})_6^-$	200	9.5167	0.2954	9.8122	2.7734
	240	10.3115	0.3545	10.6661	2.9453
	280	11.1844	0.4136	11.5980	3.1406
	320	12.1172	0.4727	12.5900	3.3535
	360	13.0960	0.5318	13.6278	3.5798
	400	14.1104	0.5909	14.7013	3.8167
		$\langle \Delta R \rangle_{\text{vib}}$	$\langle \Delta R \rangle_{\text{rot}}$	$\langle \Delta R \rangle$	$\langle (\Delta R)^2 \rangle$
$\text{V}(^{12}\text{C}^{16}\text{O})_6^-$	300	4.2967	0.1105	4.4073	1.2828
$\text{V}(^{13}\text{C}^{16}\text{O})_6^-$	300	4.2026	0.1105	4.3131	1.2549
$\text{V}(^{12}\text{C}^{18}\text{O})_6^-$	300	4.1904	0.1105	4.3009	1.2513
$\text{V}(^{12}\text{C}^{16}\text{O})_6^-$	200	4.2958	0.0737	4.3694	1.2817
	400	4.3077	0.1474	4.4551	1.2862

^a Δr refers to the V-C bond and ΔR to the CO bond; all are in 10^{-3} \AA .

to 24, and $\Delta\beta$ for $i = 25$ to 36. $r = r_e(\text{CO})$ for $k = 1$ to 6 and $r = r_e(\text{MC})$ for $k = 7$ to 12. $\epsilon_{kj} = 1$ if the bond to atom k is in the j th bond angle deformation; otherwise $\epsilon_{kj} = 0$. F_{ij} stands for $(\partial^2 V / \partial \mathcal{R}_i \partial \mathcal{R}_j)$ and F_{kij} for $(\partial^3 V / \partial \mathcal{R}_k \partial \mathcal{R}_i \partial \mathcal{R}_j)$, given in Tables I and III, respectively. As in previous work, in eq 7 we have neglected the averages $\langle \mathcal{R}_k \mathcal{R}_i \mathcal{R}_j \rangle$ and also set the sums over $\langle \Delta\alpha \rangle$ and $\langle \Delta\beta \rangle$ to zero. Upon setting $\langle \partial V / \partial z_k \rangle = 0$, i.e., applying Ehrenfest's theorem, we obtain the set of coupled equations:

$$\sum_{i=1}^{12} F_{ki} \langle \mathcal{R}_i \rangle = \Sigma_k \quad k = 1 \text{ to } 12 \quad (2)$$

Thus,

$$\langle \mathbf{R} \rangle = \mathbf{F}^{-1} \Sigma \quad (3)$$

The column vector $\langle \mathbf{R} \rangle$ contains the 12 desired mean displacements $\langle \mathcal{R}_i \rangle$ of the CO and the MC bonds. The vector Σ contains the elements

$$\Sigma_k = \sum_{i=1}^{12} \sum_{j=13}^{36} \frac{F_{ij}}{2r} \langle \mathcal{R}_i \mathcal{R}_j \rangle \epsilon_{kj} + \sum_{i=13}^{36} \sum_{j=13}^{36} \frac{F_{ij}}{4r} \langle \mathcal{R}_i \mathcal{R}_j \rangle (\epsilon_{ki} + \epsilon_{kj}) + \sum_{i=1}^{36} \sum_{j=1}^{36} \frac{-F_{kij}}{2} \langle \mathcal{R}_i \mathcal{R}_j \rangle \quad k = 1 \text{ to } 12 \quad (4)$$

All the mean square amplitudes $\langle \mathcal{R}_i \mathcal{R}_j \rangle$ such as $\langle \Delta r_1^2 \rangle$ or $\langle \Delta r_1 \Delta \alpha_{12} \rangle$, etc., including all cross-terms are evaluated as

$$\langle \mathcal{R}_i \mathcal{R}_j \rangle = \sum_s L_{is} \langle Q_s^2 \rangle L_{js} \quad (5)$$

where

$$\langle Q_s^2 \rangle = (h/8\pi^2 c \omega_s) \coth(hc\omega_s/2kT) \quad (6)$$

The above equations therefore allow us to calculate $\langle \Delta r_{\text{MC}} \rangle$ and $\langle \Delta R_{\text{CO}} \rangle$ as a function of temperature and masses. We need the inverse \mathbf{F}^{-1} of the force constant matrix for *stretches only*, for

(5) Jones, L. H. *J. Mol. Spectrosc.* **1962**, *8*, 105-120.

(6) Krohn, B. J.; Overend, J. J. *Phys. Chem.* **1984**, *88*, 564-574.

(7) Jameson, C. J.; Jameson, A. K. *J. Chem. Phys.* **1986**, *85*, 5484-5492.

(8) Herschbach, D. R.; Laurie, V. W. *J. Chem. Phys.* **1961**, *35*, 458-463.

(9) Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1974**, *96*, 7601-7602.

(10) Bartell, L. S. *J. Chem. Phys.* **1963**, *38*, 1827-1833; **1979**, *70*, 4581-4584.

(11) Jameson, C. J.; Osten, H. J. *J. Chem. Phys.* **1984**, *81*, 4915-4921, 4288-4292, 4293-4299, 4300-4305.

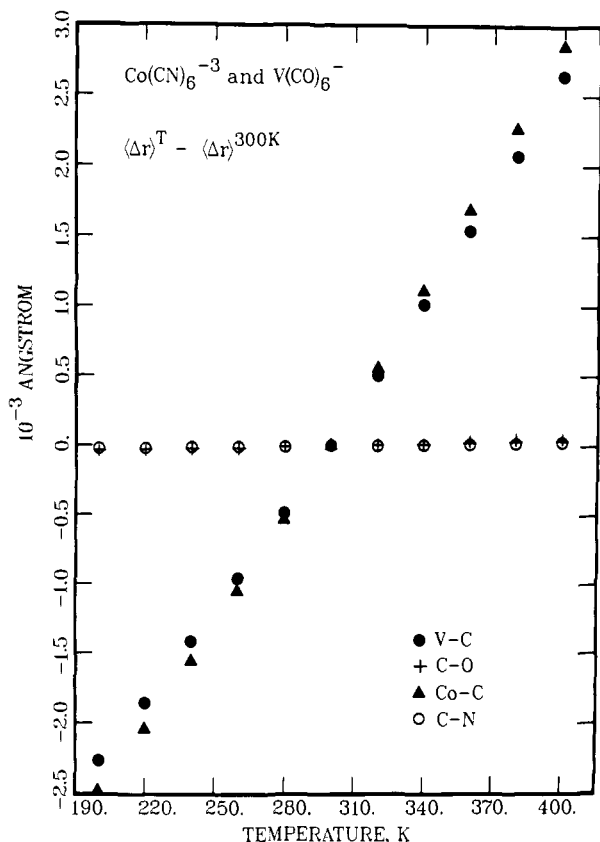


Figure 1. Mean bond displacements in $V(CO)_6^{3-}$ and $Co(CN)_6^{3-}$.

which the redundancy condition is not a problem. For $k = 1$ to 6 we obtain the same value of $\langle \Delta R_{CO} \rangle$, and for $k = 7$ to 12 we obtain the same value of $\langle \Delta r_{MC} \rangle$, as dictated by symmetry. The results of these calculations are given in Table IV. The rotational contributions to the mean bond displacements are calculated by the usual method.¹¹

We find the temperature dependence of $\langle \Delta R_{CO} \rangle$ and $\langle \Delta r_{VC} \rangle$ to be:

$$\langle \Delta R_{CO} \rangle^{400K} - \langle \Delta R_{CO} \rangle^{200K} = 1.20 \times 10^{-5} \text{ \AA} \text{ due to vibration} \\ \text{plus } 7.36 \times 10^{-5} \text{ \AA} \text{ due to rotation (86\% rotation)}$$

$$\langle \Delta r_{VC} \rangle^{400K} - \langle \Delta r_{VC} \rangle^{200K} = 4.59 \times 10^{-3} \text{ \AA} \text{ due to vibration plus} \\ 2.95 \times 10^{-4} \text{ \AA} \text{ due to rotation (only 6\% rotation)}$$

We have shown in Figure 1 the temperature dependence of the VC and CO bond displacements. The mass dependence of the V-C and C-O bond displacements at 300 K are given by:

$$\langle \Delta r \rangle^{51V-12C} - \langle \Delta r \rangle^{51V-13C} = 1.27 \times 10^{-4} \text{ \AA} \text{ for } ^{16}O \text{ isotopomers}$$

$$\langle \Delta r \rangle^{51V-12C(^{16}O)} - \langle \Delta r \rangle^{51V-12C(^{18}O)} = 6 \times 10^{-6} \text{ \AA}$$

$$\langle \Delta R \rangle^{12C-16O} - \langle \Delta R \rangle^{13C-16O} = 9.4 \times 10^{-5} \text{ \AA}$$

$$\langle \Delta R \rangle^{12C-16O} - \langle \Delta R \rangle^{12C-18O} = 1.06 \times 10^{-4} \text{ \AA}$$

We have applied the same theoretical calculation to the $Co(CN)_6^{3-}$ ion using the quadratic force field of Jones et al.¹² and using the molecular geometry from X-ray data: $r(Co-C) = 1.89 \text{ \AA}$ and $r(C-N) = 1.5 \text{ \AA}$.¹³ Morse parameters used are $a_{CoC} =$

Table V. Mean Bond Displacements and Mean Square Amplitudes for the Co-C Bond and the C-N Bond in $Co(CN)_6^{3-}$ ^a

	<i>T</i>	$\langle \Delta r \rangle_{vib}$	$\langle \Delta r \rangle_{rot}$	$\langle \Delta r \rangle$	$\langle (\Delta r)^2 \rangle$
$Co(^{12}C^{14}N)_6^{3-}$	300	12.2011	0.4158	12.6169	3.1316
$Co(^{13}C^{14}N)_6^{3-}$	300	12.0791	0.4158	12.4949	3.0896
$Co(^{12}C^{15}N)_6^{3-}$	300	12.1968	0.4158	12.6127	3.1264
$Co(^{12}C^{14}N)_6^{3-}$	200	9.8399	0.2772	10.1171	2.6831
	240	10.7228	0.3327	11.0554	2.8447
	280	11.6915	0.3881	12.0796	3.0311
	320	12.7246	0.4436	13.1681	3.2361
	360	13.8061	0.4990	14.3051	3.4551
	400	14.9247	0.5545	15.4791	3.6849
		$\langle \Delta R \rangle_{vib}$	$\langle \Delta R \rangle_{rot}$	$\langle \Delta R \rangle$	$\langle (\Delta R)^2 \rangle$
$Co(^{12}C^{14}N)_6^{3-}$	300	4.2865	0.1021	4.3886	1.2129
$Co(^{13}C^{14}N)_6^{3-}$	300	4.1986	0.1021	4.3006	1.1882
$Co(^{12}C^{15}N)_6^{3-}$	300	4.2168	0.1021	4.3189	1.1936
$Co(^{12}C^{14}N)_6^{3-}$	200	4.2949	0.0681	4.3630	1.2117
	400	4.2827	0.1361	4.4419	1.2152

^a Δr refers to the Co-C bond and ΔR to the C-N bond; all are in 10^{-3} \AA .

1.736 and $a_{CN} = 2.406 \text{ \AA}^{-1}$, respectively. K_{CoC} and K_{CN} are assigned the values 2.084 and $17.425 \text{ mdyn \AA}^{-1}$, estimated from f_{CoC} and f_{CN} given by Jones.¹² The nonbonded interaction constant $F(C \cdots C) = 0.138 \text{ mdyn/\AA}$ is obtained from $\mathcal{F}_{22} = K_{MC} + 4F$ using the experimental value of the symmetry force constant \mathcal{F}_{22} . The results are presented in Table V. We find the temperature dependence of $\langle \Delta R_{CN} \rangle$ to be very similar to that of $\langle \Delta R_{CO} \rangle$:

$$\langle \Delta R_{CN} \rangle^{400K} - \langle \Delta R_{CN} \rangle^{200K} = -1.2 \times 10^{-5} \text{ \AA} \text{ due to vibration} \\ \text{plus } 6.8 \times 10^{-5} \text{ \AA} \text{ due to rotation (120\% rotation)}$$

$$\langle \Delta r_{CoC} \rangle^{400K} - \langle \Delta r_{CoC} \rangle^{200K} = 5.08 \times 10^{-3} \text{ \AA} \text{ due to vibration} \\ \text{plus } 2.77 \times 10^{-4} \text{ \AA} \text{ due to rotation (5\% rotation)}$$

The mass dependence of the Co-C and C-N bonds at 300 K are given by:

$$\langle \Delta r \rangle^{59Co-12C} - \langle \Delta r \rangle^{59Co-13C} = 1.22 \times 10^{-4} \text{ \AA} \text{ for } ^{14}N \text{ isotopomers}$$

$$\langle \Delta r \rangle^{59Co-12C(^{14}N)} - \langle \Delta r \rangle^{59Co-12C(^{15}N)} = 4.2 \times 10^{-6} \text{ \AA}$$

$$\langle \Delta R \rangle^{12C-14N} - \langle \Delta R \rangle^{13C-14N} = 8.8 \times 10^{-5} \text{ \AA}$$

$$\langle \Delta R \rangle^{12C-14N} - \langle \Delta R \rangle^{12C-15N} = 6.9 \times 10^{-5} \text{ \AA}$$

It is worthwhile noting in Figure 1 that the temperature dependence of the M-C bond displacements is nearly two orders of magnitude larger than that of the CO or CN bond displacements, although the ¹³C-induced changes are only 1.4 times as large for the M-C bonds as for the CO or CN bonds. Since the electron distribution in transition metal complexes is known to be sensitive to the metal-ligand distance, these results indicate that the optical absorption bands of these complexes should exhibit a measurable temperature dependence. The change in the position of the ¹A_{1g} → ¹T_{1g} absorption maximum in the $Co(CN)_6^{3-}$ complex has been noted in aqueous solution, a change of about 4 nm in the range 0–90 °C.¹⁴

The observed temperature and mass dependence of ⁵¹V and ⁵⁹Co NMR chemical shifts in $V(CO)_6^{3-}$ and $Co(CN)_6^{3-}$ are interpreted in the following paper in terms of the calculated temperature and mass dependence of $\langle \Delta r_{VC} \rangle$, $\langle \Delta R_{CO} \rangle$, $\langle \Delta r_{CoC} \rangle$, and $\langle \Delta R_{CN} \rangle$.

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(12) Jones, L. H.; Memering, M. N.; Swanson, B. I. *J. Chem. Phys.* **1971**, *54*, 4666–4671.

(13) Curry, N. A.; Runciman, W. A. *Acta Crystallogr.* **1959**, *12*, 674.

(14) Juranic, N. *J. Chem. Phys.* **1981**, *74*, 3690–3693.