# Molecular Vibrations and Reaction Pathways. Minimum Energy Coordinates and Compliance Constants for Some Tetrahedral and Octahedral Complexes

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**Abstract:** General quadratic compliance constants have been evaluated for $UF_6$, $WF_6$, $RuO_4$, $OsO_4$, and $XeO_4$ using normal and isotopic frequency data and Coriolis coupling constants. Minimum energy coordinates determined from these unique compliance functions are used to discuss the structure changes which accompany dissociation. In the case of $XeO_4$, where both the initial $XeO_4$ and final $XeO_3$ structures are known, the minimum energy coordinate ($\mathcal{R}_{XeO}$) correctly models the structural change in the $XeO_3$ fragment as regards the direction of the O–Xe–O and Xe–O bond length changes. In addition, the relative magnitudes of the angle and bond length changes as modeled by $\mathcal{R}_{XeO}$ are correct. The minimum energy coordinates for $Ni(CO)_4$, $Zn(CN)_4{}^{2-}$, and $M(CO)_6$ (M = Cr, Mo, W) are compared with those of the tetroxides and hexafluorides. With the exception of $UF_6$, the minimum energy coordinates for these complexes compare favorably with the molecular structure relaxation expected from bonding considerations.

General quadratic potential functions obtained from detailed vibrational analysis have been used extensively to discuss interatomic forces in molecules.[1] As pointed out by Machida and Overend,[2] the signs of the various interaction potential constants can also give us information about geometry changes accompanying unimolecular dissociation. Recently it was shown that the minimum energy path of reaction dynamics can be approximated by minimum energy coordinates which are directly related to compliance constants.[3]

The minimum energy coordinate

$$\mathcal{R}_i = r_i + \sum_{\substack{j=1\\ j\neq i}}^{n} (C_{ij}/C_{ii})r_j \qquad (1)$$

provides a measure of the change in internal coordinates $R_j$ required to minimize potential energy when coordinate $R_i$ is constrained to a unit distortion. Here $C_{ii}$ and $C_{ij}$ are primary and interaction compliants, $n$ gives the number of internal coordinates, and $r_i$ denotes a unit vector along the internal coordinate direction $R_i$.[4] Since $\mathcal{R}_i$ is defined by minimizing potential energy following a localized distortion in internal coordinate $R_i$

$$\left(\frac{\partial V}{\partial R_j}\right)_{R_i=+1} = 0 \qquad (2)$$

$$j = 1, n; j \neq i$$

it provides an approximation to the minimum energy path (MEP) for unimolecular dissociation where $R_i$ is the bond stretching coordinate for the bond being broken. In the quadratic approximation, $\mathcal{R}_i$ and the MEP are identical. As pointed out in ref 3, the minimum energy coordinates corresponding to angle deformation coordinates may be used to model the MEP for intramolecular exchange in fluxional molecules. Symmetry constraints to the MEP and implications concerning the meaning of primary force and compliance constants which arise from the minimum energy coordinate approximation are discussed in ref 3.

Minimum energy coordinates contain two kinds of information. They represent a molecular structure response function which arises when one coordinate is slightly distorted from its equilibrium configuration. Any change in molecular structure which accompanies a fixed distortion is determined by interatomic forces and molecular electronic structure which determines these forces. For small distortions near equilibrium, the bonding changes implied by $\mathcal{R}_i$ should faithfully reflect those changes expected from our bonding models. That is, near equilibrium the quadratic part of the potential function should dominate the higher order terms in determining bonding changes. The bonding implications of $\mathcal{R}_i$ are really no different than that obtained from the individual interaction displacement coordinates; the utility of interaction coordinates in discussing bonding has been demonstrated for several $\pi$ acceptor complexes.[1]

Minimum energy coordinates, by virtue of their direct relationship to the MEP, also contain potential information concerning structural changes which occur during reaction. Since $\mathcal{R}_i$ are evaluated from quadratic potential functions, there is question about their reliability as a model of the MEP at large distortions. Certainly, the true MEP can only be obtained from an anharmonic potential function; the higher order terms describe the deviation from the linear pathway given by $\mathcal{R}_i$. In spite of this obvious limitation there is some indication that minimum energy coordinates are in agreement with known structural changes for dissociation reactions. Machida and Overend have made comparisons of $\mathcal{R}_i$ for triatomic ABC species with known bond length changes of the AB diatom following cleavage of the B–C bond.[2] With one exception ($SO_2$; however, see ref 5) the minimum energy coordinates correctly predict the change evaluated from the known structures. While the results for triatomic species are encouraging, there is a clear need to know whether or not $\mathcal{R}_i$ model reaction pathways for more complex systems. This report concerns the unique compliance functions for some four- and six-coordinate compounds where comparisons can be made with the molecular relaxation expected from current bonding models, or where the actual structural change is known.

Minimum energy coordinates are determined by interaction compliance constants. These constants are usually constrained in underdetermined least-squares calculations of quadratic potential functions. However, it is essential that uniquely determined compliance functions be used in evaluating $\mathcal{R}_i$. The molecules discussed here, $MF_6$ (M = W, U)[6,7] and $MO_4$ (M = Xe, Os, Ru),[8-10] are ideal in that their high symmetry and the availability of isotopic data and Coriolis coupling constants ensure that the unique compliance functions can be obtained. These molecules are perhaps the best studied four- and six-coordinate complexes from the standpoint of their quadratic potentials. The compliance functions obtained here for the tetroxides and hexafluorides will be compared with those obtained earlier for $Ni(CO)_4$,[11] $Zn(CN)_4{}^{2-}$,[12] $Co(CN)_6{}^{3-}$,[13] and $M(CO)_6$ (M = Cr, Mo, W).[14] Finally, the reaction

Table I. Compliance Constants for Tetroxides

| | $XeO_4$ | $RuO_4$ | $OsO_4$ |
|---|---|---|---|
| A. Symmetry Compliance Constants[a] | | | |
| $C_{11} = C_r + 3C_{rr}$ | 0.1626 (29)[b] | 0.1334 (14) | 0.1117 (11) |
| $C_{22} = C_\alpha - 2C_{\alpha\alpha} + C_{\alpha\alpha'}$ | 1.430 (52) | 1.027 (38) | 0.913 (30) |
| $C_{33} = C_r - C_{rr}$ | 0.1553 (4) | 0.1467 (2) | 0.1237 (2) |
| $C_{44} = C_\alpha - C_{\alpha\alpha'}$ | 0.9297 (75) | 0.8449 (34) | 0.7337 (45) |
| $C_{34} = (2(C_{r\alpha} - C_{r\alpha'}))^{1/2}$[d] | 0.0291 (26) | −0.024 (2) | −0.0156 (17) |
| B. Valence Compliance Constants[a] | | | |
| $C_r$ | 0.157 (1) | 0.1434 (5) | 0.1207 (4) |
| $C_{rr}$ | 0.0018 (8) | −0.0033 (4) | −0.0030 (3) |
| $C_\alpha$ | 0.942 (21) | 0.765 (15) | 0.671 (13) |
| $C_{\alpha\alpha}$ | −0.239 (8) | −0.171 (6) | −0.152 (5) |
| $C_{\alpha\alpha'}$ | 0.013 (21) | −0.08 (2) | −0.062 (13) |
| $C_{r\alpha}$[e] | 0.010 (1) | −0.0085 (5) | −0.0055 (6) |
| $C_{r\alpha'}$ | −0.010 (1) | 0.0085 (5) | 0.0055 (6) |
| C. General and Relaxed Valence Force Constants[a] | | | |
| $f_r$ | 6.40 (10)[c] | 6.99 (4)[c] | 8.32 (6)[c] |
| $\Upsilon_r$ | 6.36 (4) | 6.975 (24) | 8.285 (14) |
| $\Upsilon_\alpha$ | 1.062 (24) | 1.307 (25) | 1.490 (29) |

[a] For compliance constants, units are Å mdyn$^{-1}$ for pure stretching constants, rad$^2$ Å$^{-1}$ mdyn$^{-1}$ for pure bending constants, and rad mdyn$^{-1}$ for stretch-bend interactions. For force constants the units are inverse of compliance constant units. [b] Numbers in parentheses are standard deviations in units of last digit given for compliance and force constants. [c] Values taken from McDowell et al.'s articles. [d] Relations for symmetry compliants pertaining to redundant coordinates are $(6(C_{r\alpha} + C_{r\alpha'}))^{1/2} = 0$ and $C_\alpha + 4C_{\alpha\alpha} + C_{\alpha\alpha'} = 0$. [e] $C_{\alpha\alpha}$ refers to interaction between adjacent angles, while $C_{\alpha\alpha'}$ is for opposite angles. $C_{r\alpha}$ refers to angle deformation with bond stretch where the bond forms one side of the angle. $C_{r\alpha'}$ is the interaction between bond stretch and angle deformation where the bond does not form one side of the angle.

pathways for unimolecular dissociation of four-coordinate complexes as approximated by $\mathcal{R}_i$ will be compared with that proposed by Bürgi and Dunitz.[15]

Table II. Compliance Constants for Hexafluorides

| | $UF_6$ | $WF_6$ |
|---|---|---|
| A. Symmetry Compliance Constants[a,d] | | |
| $C_{11} = C_r + 4C_{rr} + C_{rr'}$ | 0.198 (3)[b] | 0.143 (4) |
| $C_{22} = C_4 - 2C_{rr} + C_{rr'}$ | 0.307 (7) | 0.186 (4) |
| $C_{33} = C_r - C_{rr'}$ | 0.261 (1) | 0.202 (1) |
| $C_{44} = C_\alpha + 2C_{\alpha\alpha} - 2C_{\alpha''\alpha} - C_{\alpha'''\alpha}$ | 1.636 (10) | 1.137 (2) |
| $C_{34} = 2(C_{r\alpha} - C_{r\alpha''})$ | 0.032 (10) | −0.077 (2) |
| $C_{55} = C_\alpha - 2C_{\alpha'\alpha} + C_{\alpha'''\alpha}$ | 2.234 (14) | 0.977 (57) |
| $C_{66} = C_\alpha - 2C_{\alpha\alpha} + 2C_{\alpha''\alpha} - C_{\alpha'''\alpha}$ | 2.195 (19) | 2.86 (54) |
| B. Valence Compliance Constants[a] | | |
| $C_r$ | 0.266 (2) | 0.187 (2) |
| $C_{rr}$ | −0.018 (1) | −0.007 (3) |
| $C_{rr'}$ | 0.005 (2) | −0.015 (3) |
| $C_{r\alpha}$ | 0.008 (3) | −0.019 (1) |
| $C_{r\alpha''}$ | −0.008 (3) | 0.019 (1) |
| $C_\alpha$ | 1.516 (85) | 1.25 (14) |
| $C_{\alpha\alpha}$ | −0.070 (24) | −0.22 (7) |
| $C_{\alpha'\alpha}$ | −0.558 (35) | −0.244 (13) |
| $C_{\alpha''\alpha}$ | 0.070 (24) | 0.22 (7) |
| $C_{\alpha'''\alpha}$ | −0.40 (7) | −0.76 (13) |
| C. General and Relaxed Valence Force Constants[a] | | |
| $f_r$ | 3.85 (5)[c] | 5.50 (7)[c] |
| $\Upsilon_r$ | 3.76 (3) | 5.35 (4) |
| $\Upsilon_\alpha$ | 0.659 (36) | 0.80 (9) |

[a] Units are the same as in Table I. [b] Numbers in parentheses are standard deviations in units of last digit given for compliance and force constants. [c] Values taken from McDowell et al.'s articles. [d] Relations for symmetry compliants pertaining to redundant coordinates are $C_{r\alpha} + C_{r\alpha''} = 0$, $C_\alpha + 4C_{\alpha\alpha} + 2C_{\alpha'\alpha} + 4C_{\alpha''\alpha} + C_{\alpha'''\alpha} = 0$, and $C_\alpha - 2C_{\alpha\alpha} + 2C_{\alpha'\alpha} - 2C_{\alpha''\alpha} + C_{\alpha'''\alpha} = 0$.

## Evaluation of Compliance Constants

McDowell et al. have reported general quadratic force fields for the tetroxides and hexafluorides.[6-10] As these reported force fields are uniquely determined from Coriolis and frequency data, the compliance matrices may be obtained by simply inverting the reported force constant matrices. However, in order to better estimate the errors for the valence compliance constants,[16] the $F_2$ and $F_{1u}$ symmetry compliance constants for the four- and six-coordinate complexes respectively were recalculated using the least-squares compliance constant perturbation program COMPLY.[17]

For tetroxides $C_{33}$, $C_{44}$, and $C_{34}$ were refined simultaneously to fit the normal and ${}^{18}O$ substituted frequency data and the Coriolis constants $\zeta_{33}$ and $\zeta_{44}$. In the case of $XeO_4$, both ${}^{129}Xe$ and ${}^{132}Xe$, and for $RuO_4$, ${}^{96}Ru$ and ${}^{102}Ru$, isotopic frequency data were also used. For $WF_6$, frequency data and $\zeta_{33}$ and $\zeta_{44}$ were fitted simultaneously in evaluating $C_{33}$, $C_{44}$, and $C_{34}$ while for $UF_6$ both ${}^{235}U$ and ${}^{238}U$ isotopic frequency data were employed along with the observed $\zeta$ constants. Harmonic frequencies calculated by McDowell et al. were used in the calculations. Since the errors in the calculated harmonic frequencies are large (due to large uncertainties in the anharmonicity corrections), emphasis was given in the refinements on fitting the harmonic isotopic shift data. The frequency data were weighted as $(\nu_i{}^6/\sigma^2(\nu_i))$ where $\nu_i$ is the frequency (cm$^{-1}$) of the $i$th normal mode and $\sigma(\nu_i)$ is the estimated error in the observed frequency.[17] $\zeta$ constants were weighted as $1/\sigma^2(\zeta_i)$, where $\sigma(\zeta_i)$ is the estimated error of the observed $\zeta$ constant $i$, and the relative weight of frequency and $\zeta$ constant data was taken as unity.

The refinements in all cases converged readily to give errors of less than 0.2 cm$^{-1}$ in the frequency data and less than 4% in all $\zeta$ constants. The refined compliance constants show little cross correlation[18] as is reflected in their low least-squares error estimates. The remaining symmetry compliants and their estimated errors were obtained directly from the corresponding symmetry force constants published by McDowell et al.[6-10] The symmetry compliants and their errors are presented in Tables I and II along with the valence compliants and relaxed force constants. In Tables III and IV the interaction displacement coordinates are presented for all the molecules

Table III. Interaction Coordinates for Tetroxides,[a] $Zn(CN)_4^{2-}$ and $Ni(CO)_4$

| IC | $XeO_4$ | $RuO_4$ | $OsO_4$ | IC | $Zn(CN)_4^{2-}$ [b] | $Ni(CO)_4$ [b] |
|---|---|---|---|---|---|---|
| $(r)_r = (r_1)_{r_2}$ | 0.012 (4)[c] | −0.023 (3) | −0.025 (3) | $(CN)_{C'N'}$ | 0.00 | −0.01 |
| $(r)_\alpha = (r_1)_{\alpha_{12}}$ | 0.011 (1) | −0.011 (1) | −0.008 (1) | $(MC)_{CN}$ | 0.02 | −0.30 |
| $(r)_{\alpha'} = (r_1)_{\alpha_{23}}$ | −0.011 (1) | 0.011 (1) | 0.008 (1) | $(MC)_{c'N'}$ | −0.05 | 0.07 |
| $(\alpha)_\alpha = (\alpha_{12})_{\alpha_{13}}$ | −0.253 (15) | −0.224 (13) | −0.227 (12) | $(MC)_{MC'}$ | −0.09 | −0.07 |
| $(\alpha)_{\alpha'} = (\alpha_{12})_{\alpha_{34}}$ | 0.013 (22) | −0.105 (22) | −0.092 (21) | $(CN)_{MC}$ | 0.00 | −0.01 |
| $(\alpha)_r = (\alpha_{12})_{r_1}$ | 0.066 (7) | −0.059 (3) | −0.046 (5) | $(B_{21})_{MC_1}$ | 0.26 | −0.03 |
| $(\alpha)_{r_1} = (\alpha_{12})_{r_3}$ | −0.066 (7) | 0.059 (3) | 0.046 (5) | $(\alpha_{12})_{MC_1}$ | −0.46 | −0.51 |

[a] The quantities are dimensionless for $(\text{stretch})_{\text{stretch}}$ and $(\text{bend})_{\text{bend}}$. The dimensions are rad/Å and Å/rad for $(\text{bend})_{\text{stretch}}$ and $(\text{stretch})_{\text{bend}}$. [b] Values for $Zn(CN)_4^{2-}$ and $Ni(CO)_4$ taken from ref 1. [c] Numbers in parentheses are standard deviations in units of last digit given for the interaction coordinates.

Table IV. Interaction Coordinates for Hexafluorides,[a] $Co(CN)_6^{3-}$ and $M(CO)_6$ (M = Cr, Mo, W)

| | $UF_6$ | $WF_6$ | | $CO(CN)_6^{3-}$ [b] | $M(CO)_6$ [b] |
|---|---|---|---|---|---|
| $(r)_r = (r_1)_{r_2}$ | −0.068 (3) | −0.038 (5) | $(CN)^t_{C'N'}$ | −0.003 | −0.013 |
| $(r)_{r'} = (r_1)_{r_4}$ | 0.017 (8) | −0.081 (8) | $(CN)^t_{C'N'}$ | 0.005 | −0.014 |
| $(r)_\alpha = (r_1)_{\alpha_{12}}$ | 0.005 (1) | −0.015 (2) | $(MC)_{CN}$ | −0.104 | −0.401 |
| $(r)_{\alpha''} = (r_1)_{\alpha_{34}}$ | −0.005 (1) | 0.015 (2) | $(MC)^c_{C'N'}$ | −0.007 | 0.037 |
| $(\alpha)_\alpha = (\alpha_{12})_{\alpha_{23}}$ | −0.046 (16) | −0.176 (70) | $(MC)^t_{C'N'}$ | −0.002 | 0.164 |
| $(\alpha)_{\alpha'} = (\alpha_{12})_{\alpha_{24}}$ | −0.368 (27) | −0.19 (2) | $(MC)^c_{MC'}$ | −0.013 | −0.008 |
| $(\alpha)_{\alpha''} = (\alpha_{12})_{\alpha_{34}}$ | 0.046 (16) | 0.176 (70) | $(MC)^t_{MC'}$ | −0.23 | −0.23 |
| $(\alpha)_{\alpha'''} = (\alpha_{12})_{\alpha_{45}}$ | −0.264 (41) | −0.61 (73) | $(CN)^c_{MC'}$ | −0.001 | 0.004 |
| $(\alpha)_r = (\alpha_{12})_{r_1}$ | 0.030 (19) | −0.102 (4) | $(CN)^t_{MC'}$ | 0.018 | 0.019 |
| | | | $(\beta_{21})_{MC_1}$ | | 0.21 |
| $(\alpha)_{r''} = (\alpha_{12})_{r_5}$ | −0.030 (19) | 0.102 (4) | $(\alpha_{12})_{MC_1}$ | | 0.16 |

[a] Units are the same as given in Table III. [b] Values for $Co(CN)_6^{3-}$ and $M(CO)_6$ taken from ref 12.

discussed. It is stressed that all of the valence compliance constants may be calculated uniquely since the symmetry compliants which involve the redundant coordinates are defined as zero (see expressions in Tables I and II). In contrast, valence force constants involving angle deformations cannot be evaluated independently, but only as linear combinations, since symmetry force constants which involve the redundant deformation coordinates are indeterminate.

## Results and Discussion

**Four-Coordinate Complexes.** It is interesting to compare the M-O and O-M-O coordinate strengths in the tetroxides as manifest by the relaxed and regular force constants.[3] As has been pointed out in ref 3, the relaxed force constant, $\Upsilon_i = 1/C_{ii}$, provides an adiabatic measure of coordinate strength since the pathway in coordinate distortion space which defines $\Upsilon_i$, the minimum energy coordinate direction, is the quadratic approximation to the true reaction coordinate. The regular or rigid force constant can be considered a nonadiabatic measure of coordinate strength as the pathway followed in defining $f_{ii}$ is simply the internal coordinate direction $R_i$. Essentially, in defining $\Upsilon_i$, the molecular geometry is allowed to change so as to minimize potential energy as $R_i$ is distorted, while for $f_{ii}$ all other coordinates $R_j$ are constrained as $R_i$ is distorted. One result of this distinction between relaxed and regular force constants is that $\Upsilon_i$ are always less than $f_{ii}$ since additional force is required to constrain coordinates $R_j$ in the case of the regular force constant. These differences are illustrated in $f_{MO}$ and $\Upsilon_i$ for the tetroxides. Again, it should be noted that the use of the compliant formalism and relaxed force constants allow a measure of the angle deformation strengths for these systems even though a redundancy condition exists among the internal coordinates.

The M-O and O-M-O coordinate strengths vary Os > Ru > Xe and the differences in all cases are statistically significant. The increase in the M-O bond strength going down the iron group is in agreement with Gray's[19] statement that the M-O covalent interaction in tetroxide ions $MO_4^-$ (M = Mn, Tc, Re) and other transition metal tetroxides increases in going from 3d → 4d → 5d. Also, the increase in the O-M-O deformation strength presumably arises from this increase in M-O covalent character.

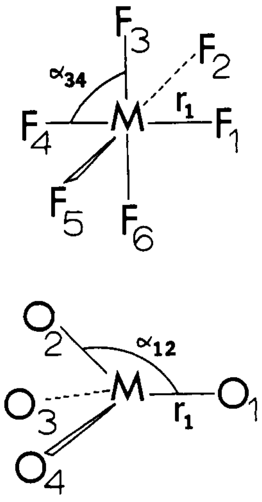

Figure 1. Internal coordinates for $MF_6$ and $MO_4$ complexes.

The minimum energy coordinates corresponding to a weakening of the M-O bond in $RuO_4$ and $OsO_4$ (Table IV) are essentially the same.

$$\mathcal{R}_{Ru\text{-}O_1} = r_1 - 0.023(r_2 + r_3 + r_4) - 0.06(\alpha_{12} + \alpha_{13} + \alpha_{14}) + 0.06(\alpha_{23} + \alpha_{24} + \alpha_{34}) \quad (3)$$

(see Figure 1 for a schematic of the internal coordinates). Thus, as the M-$O_1$ bond is cleaved, the remaining $MO_3$ fragment becomes less pyramidal (O-M-O > tetrahedral angle) and the remaining M-O bonds are strengthened. The minimum energy coordinates for bond dissociation in the tetroxides follow the same general direction as has been observed for the tetrahedral $\pi$-acceptor complexes $Ni(CO)_4$ and $Zn(CN)_4{}^{2-}$. However, the magnitudes of bond length and angle changes are much larger in the case of $\pi$-acceptor complexes; for example, in $Zn(CN)_4{}^{2-}$

$$\mathcal{R}_{Zn-C_1} = r_1 - 0.09(r_2 + r_3 + r_4) - 0.46(\alpha_{12} + \alpha_{13} + \alpha_{14}) + 0.46(\alpha_{23} + \alpha_{24} + \alpha_{34}) \quad (4)$$

This difference may result in part from the significant difference in M–L bond strengths between these two types of complexes (the M–O bonds are much stronger than M–C bonds in cyanides and carbonyls).

The minimum energy coordinate for cleavage of the $Xe-O_1$ bond in $XeO_4$

$$\mathcal{R}_{Xe-O_1} = r_1 + 0.0114(r_2 + r_3 + r_4) + 0.066(\alpha_{12} + \alpha_{13} + \alpha_{14}) - 0.066(\alpha_{23} + \alpha_{24} + \alpha_{34}) \quad (5)$$

is in direct contrast to those observed for the other tetroxides. As $Xe-O_1$ is weakened, the $XeO_3$ fragment becomes *more* pyramidal and the remaining bonds *weaken* slightly. While the singular behavior of $XeO_4$ may at first glance appear confusing, this difference is in agreement with the structure change expected using the valence shell electron pair repulsion theory.[20] If we assume dissociation of $XeO_4$ proceeds via homolytic cleavage, the $XeO_3$ fragment will possess a stereochemically active lone pair. As lone pairs are expected to repel more strongly than bonding electron pairs, the $XeO_3$ fragment should become more pyramidal. Furthermore, increased $e^-$–$e^-$ repulsion in $XeO_3$ should result in weaker XeO bonds. Thus, VSEPR theory provides a simple explanation for the unusual minimum energy coordinate observed for $XeO_4$. In this case, we have an additional test in that the structures of $XeO_4$[21] and $XeO_3$[22] are both known. The known structural change is in agreement with the minimum energy coordinate.

It is useful to probe whether or not $\mathcal{R}_i$ provide any information about the relative bond length and angle changes and the magnitude of the structure change. As $\mathcal{R}_i$ describes a linear path (this stems directly from the quadratic approximation), it is necessary to determine a cut-off point for distortion of the bond being broken. That is, we must come up with an approximate $Xe-O_1$ bond distance at which the Xe–O bond is assumed to be broken. Intuition suggests that the van der Waals distance would be appropriate. Thus, the bond length change in going from the equilibrium Xe–O distance in $XeO_4$ to the van der Waals distance for a Xe–O nonbonded interaction provides the multiplicative factor required to estimate the overall structural change in the remaining $XeO_3$ fragment. Surprisingly, the observed structural change and that obtained using $\mathcal{R}_{Xe-O}$ and the van der Waals approximation are the same.

The exact agreement between the known structural change and that evaluated by distorting XeO along $\mathcal{R}_i$ to the van der Waals distance for $Xe-O_1$ is, no doubt, fortuitous. Certainly, the high errors associated with the $XeO_3$ structure,[22] the difficulty in evaluating accurate van der Waals distances, and the obvious limitations of the quadratic approximation make such an approach foolhardy. It is significant, however, that the *relative* angle and bond length changes given by $\mathcal{R}_{Xe-O_1}$ are correct.

It is interesting to compare the reaction coordinates for dissociation of four-coordinate complexes discussed here with the structure correlation approach used by Bürgi and Dunitz.[23] The general direction of the structural changes in the $ML_3$ fragments discussed here for $RuO_4$, $OsO_4$, $Ni(CO)_4$, and $Zn(CN)_4{}^{2-}$ is in agreement with the results of Burgi and Dünitz. For these four molecules the $ML_3$ fragment becomes less pyramidal and the M–L bonds strengthen as $M-L_1$ is weakened. Burgi and Dünitz results suggest that the reaction coordinate is invariant from one molecule to the next (the nature of the central atom and the ligands do not influence the structure change). The minimum energy coordinates, on the other hand, indicate that the reaction coordinate is strongly influenced by the nature of the molecule. There are significant differences in the minimum energy coordinates of the tetroxides and the $\pi$-acceptor complexes. Equally important, $\mathcal{R}_{Xe-O}$ for $XeO_4$ does not follow the general reaction coordinate direction obtained using the structure correlation method. It is possible that the invariance of the reaction coordinate to molecular make-up observed by Bürgi and Dunitz is an artifice of the set of molecules which they studied.

**Six-Coordinate Complexes.** The relaxed force constants for the M–F stretch indicate that the W–F bond is significantly stronger than the U–F bond. Similarly, the F–U–F angle is much easier to deform than the corresponding F–W–F angle in $WF_6$. The above are indicative of the stronger directional forces in $WF_6$ relative to those in $UF_6$. This is in agreement with the observations that the $UF_6$ octahedron is significantly distorted in the solid state.[24] In general, the crystal structures of rare earth fluorides appear to be dominated by F–F repulsions; indeed, these structures have been described in terms of a fluorine lattice with metal atoms occupying interstitial sites.[25]

The minimum energy coordinates corresponding to a distortion in the $M-F_1$ bonds in $WF_6$ and $UF_6$ also exhibit interesting differences. For the sake of comparison, the interaction displacement coordinates for the hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) are tabulated along with those of $UF_6$ and $WF_6$ in Table IV. The coordinate

$$\mathcal{R}_{U-F_1} = r_1 + 0.017r_4 - 0.068(r_2 + r_3 + r_5 + r_6) + 0.03(\alpha_{12} + \alpha_{13} + \alpha_{15} + \alpha_{16}) - 0.03(\alpha_{24} + \alpha_{34} + \alpha_{45} + \alpha_{46}) \quad (6)$$

shows that the U–F bond trans to $U-F_1$ weakens slightly while the cis U–F bonds get significantly stronger (see Figure 1 for a description of the internal coordinates). In contrast, the corresponding coordinate for $WF_6$

$$\mathcal{R}_{W-F_1} = r_1 - 0.081r_4 - 0.038(r_2 + r_3 + r_5 + r_6) - 0.102(\alpha_{12} + \alpha_{13} + \alpha_{15} + \alpha_{16}) + 0.102(\alpha_{23} + \alpha_{24} + \alpha_{45} + \alpha_{46}) \quad (7)$$

shows the opposite behavior as regards the trans W–F bond. If one assumes an ionic model for the M–F interactions in hexafluorides, it is reasonable to expect that both the cis and trans M–F bonds should strengthen as $M-F_1$ is weakened. The fact that the trans W–F bond strengthens more than the cis bonds is suggestive of covalent character in $WF_6$. The observation that the trans bond in $UF_6$ weakens as $UF_1$ is stretched is inconsistent with an ionic model. For the lack of any better explanation, we are tempted to attribute this unusual behavior of $UF_6$ to the directional nature of the actinide f orbitals.

$$\mathcal{R}_{M-C_1O_1} = r_1 - 0.228r_4 - 0.013(r_2 + r_3 + r_5 + r_6) + 0.16(\alpha_{12} + \alpha_{13} + \alpha_{15} + \alpha_{16}) - 0.16(\alpha_{24} + \alpha_{34} + \alpha_{45} + \alpha_{46}) \quad (8)$$

The situation for the hexacarbonyls is distinctly different. In this case, the bond strength changes as $M-C_1O_1$ is weakened are almost entirely trans directed in contrast to what might be expected from orbital participation arguments.[26] This unusual behavior has been discussed in ref 1.

The angle changes as $M-L_1$ is lengthened are also interesting. In the case of $WF_6$, the $F_1-W-F_i$ angles where $F_i$ is cis to $F_1$ decrease as $W-F_1$ is weakened. That is, the cis fluorines collapse onto the leaving fluorine to produce a more isotropic distribution of fluorines in the limit of breaking the $W-F_1$ bond. This is what is expected if F–F repulsion plays an important role in $WF_6$.

Both $UF_6$ and $M(CO)_6$ show the opposite behavior. As $M{-}L_i$ is lengthened, the cis ligands bend away from the leaving group. For $UF_6$, the change in the angles is quite small. However, it is significant that they do not collapse onto the leaving group as would be consistent with F–F repulsions being an important factor. Indeed, the features of the minimum energy coordinate for $UF_6$ are perplexing and point to the possible importance of f orbitals in determining internal forces in actinide fluorides.

The angle changes in the hexacarbonyls are surprising in view of the propensity for stable five-coordinate complexes of transition metals to adopt trigonal bipyramidal structures. Certainly, if the $M(CO)_5$ fragments adopt a $D_{3h}$ structure we would expect the cis ligands to collapse onto the leaving group.[27] It is inappropriate to attach too much significance to the angle changes predicted by $\mathscr{R}_i$ for the hexacarbonyls since minimum energy coordinates do not always give the correct structure change at large distortions from the equilibrium configuration. However, it should be noted that recent matrix isolation studies of $M(CO)_5$ fragments formed by in situ photolysis of an inert gas matrix containing $M(CO)_6$ show that the fragments possess $C_{4v}$ symmetry.[28] Also, molecular orbital calculations indicate that a $C_{4v}$ geometry is favored for an isolated $M(CO)_5$ fragment; indeed, the preferred geometry seems to be one in which the $CO^{cis}{-}M{-}CO^{trans}$ angles are approximately 90°.[29] The minimum energy coordinates are in support of these observations and lend further credence to the suggestion that the stable gas phase geometry for $M(CO)_5$ fragments of Cr, Mo, and W is $C_{4v}$. The geometry change given by $\mathscr{R}_{M\text{-}CO}$ is in agreement with the observation that ligand substitutions in metal carbonyls proceed via dissociative mechanisms. That is, $\mathscr{R}_{M\text{-}CO}$ for $M(CO)_6$ indicates that the pentacarbonyl fragments produced by removal of one CO group are amenable to attack by an incoming ligand. While the availability of a site is not a sufficient condition for dissociative ligand substitution mechanisms, it is necessary.

## Conclusion

The results given here for $XeO_4$, along with those reported earlier for triatomic molecules, suggest that minimum energy coordinates can be used to obtain the final structure of fragments formed upon dissociation. It should be noted, however, that there are molecules for which the minimum energy coordinates do not correctly model the known structure change.[5] For these latter systems there appears to be a curve crossing of the ground and an excited electronic state such that the initial and final pathways are quite different. Accordingly, caution must be taken in inferring too much about the final fragment geometries using this quadratic approach. More work is needed before we understand the systematics well enough to know where this formalism will break down as regards the prediction of fragment geometries. Nonetheless, $\mathscr{R}_i$ appear to correctly model the initial part of a dissociative pathway and this information tells us something about the potential energy surface and changes in bonding which accompany a small distortion from equilibrium configuration.

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## References and Notes

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(4) In ref 3 the minimum energy coordinate was defined as

$$\mathscr{R}_i = R_i + \sum_{\substack{j=1 \\ j\neq i}}^{n} (C_{ij}/C_{ii})R_j$$

As pointed out by a referee this notation is confusing when expressed in terms of internal coordinates and is more properly expressed in terms of unit vectors along the various internal coordinate directions. It should be noted that $\mathscr{R}_i$ is a linear pathway in internal coordinate space and that the actual structure change for a nonunit distortion of $R_i = X$ is given by $X\mathscr{R}_i$.

(5) Machida and Overend assume that dissociation of $SO_2$ leads to the formation of neutral SO. It is possible that the initial path is toward formation of the ions $SO^+$ and $O^-$ and that the S–O bond length change in going from $SO_2$ to $SO^+$ would provide a more appropriate comparison. The possibility of the initial pathway going toward ion formation rather than neutral fragments is also seen in the compliance functions for $BF_3$ and $SO_3$. (J. J. Rafalko and B. I. Swanson, unpublished result.) Recent NDDO calculations for $BF_3$ also support this suggestion (H. S. Rzepa and M. J. S. Dewar, unpublished results).

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(27) As discussed in ref 3, the symmetry constraint imposed on the reaction pathway in the minimum energy coordinate approximation requires a $C_{4v}$ symmetry $M(CO)_5$ fragment. This constraint can be violated only by virtue of higher order terms in the potential energy function and will occur when a maximum or minimum of potential energy is reached. Thus, an octahedral system where the cis ligands collapse onto the leaving group might be expected to deviate in symmetry at large distortions of the $M{-}L_1$ bond.

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