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Minimum Energy Coordinates. A Relationship between Molecular Vibrations and Reaction Coordinates

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Abstract: In the quadratic approximation, the molecular relaxation to a minimum energy configuration following a specific nuclear distortion is given by minimum energy coordinates, which are directly related to compliance constants. In the case of a fixed distortion of a bond stretching coordinate, the corresponding minimum energy coordinate provides a first-order approximation to the minimum energy path for unimolecular dissociation. In effect, the general quadratic potential function obtained from a detailed vibrational spectroscopic study can be used to estimate the reaction coordinate for unimolecular dissociation. Minimum energy coordinates also provide an approximation of the MEP for intramolecular rearrangement in fluxional molecules such as PF_5. The symmetry constraints imposed on reaction pathways via the minimum energy coordinate approximation are outlined. The implications with regard to the meaning of primary force and compliance constants are discussed.

Minimum Energy Coordinates

General quadratic potential functions (force and compliance constants) determined from vibrational spectroscopic data provide invaluable information concerning interatomic forces in molecules and external forces in crystalline lattices.[1] The molecular vibrational problem has generally been modeled in terms of force constants and displacement coordinates using the Wilson **GF** formalism.[2] However, the alternative compliance constant formalism[3,4] which has recently been discussed by Decius[5] and Jones and Ryan[6] offers several advantages to the usual force constant approach. A comparison of the two different formalisms has recently been discussed by Jones and Swanson.[1]

While primary force and compliance constants have distinctly different meanings, both provide a measure of coordinate strength for a molecule in its equilibrium configuration. The interaction constants, on the other hand, provide information about mutual interactions of the various coordinates. Primary constants are usually stressed in any discussion of quadratic potential functions; however, interaction constants can help to clarify bonding concepts as they are the direct result of changes in the molecular electronic structure following nuclear distortion. The meaning of interaction force and compliance constants can be conveniently discussed in terms of the interaction displacement coordinates introduced by Jones.[7]

Interaction displacement coordinates, which are directly related to interaction compliants via $(j)_i = C_{ij}/C_{ii}$,[6] measure the change in coordinate j required to minimize the potential energy following a fixed distortion of coordinate i. For example, in CO_2 the quantity $(R_2)_{R_1}$ measures the change in the C–O_2 bond which minimizes potential energy as C–O_1 is stretched a unit amount. In bonding terms, $(R_2)_{R_1}$ measures the change in the C–O_2 bond strength which results from weakening the C–O_1 bond. As pointed out by Machida and Overend,[8] the interaction displacement coordinate relating AB and BC stretch coordinates for a triatomic, ABC, provides a measure of the bond length change in the diatomic fragment following cleavage of the AB or BC bonds. Thus, $(i)_j$ not only provides useful bonding information but also contains information concerning geometric changes accompanying molecular dissociation. It should be noted that interaction displacement coordinates are not molecular vibrations, but rather reflect localized bonding changes which accompany a specific nuclear distortion. The implications of interaction displacement coordinates with regard to bonding in metal carbonyls and metal cyanides have been discussed in some detail.[1]

A more complete picture of the relaxation in molecular structure which results from a specific nuclear distortion is provided by minimum energy coordinates. The total change in molecular structure required to minimize potential energy following a localized fixed distortion is given by the minimum energy coordinate

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

Here, $\{R_i\}$ is the internal coordinate basis set, n is the number of internal coordinates, and $\{(j)_i\}$ are the interaction displacement coordinates. In a sense, $\mathcal{R}_i$ provides a picture in internal coordinate space of how the coordinate strengths change as one coordinate is weakened.

This result was first obtained by Machida and Overend who considered polyatomics where the molecular fragments following bond dissociation possess more than one degree of in-

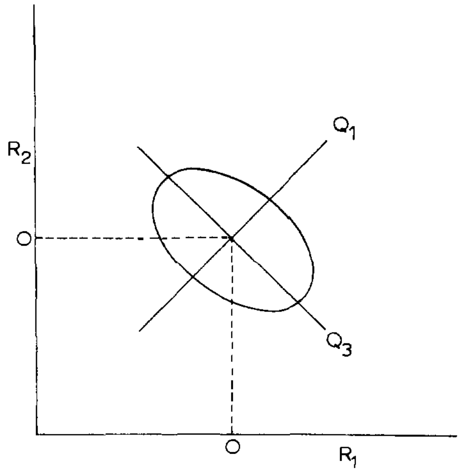

Figure 1. Quadratic potential energy surface and normal mode directions for CO_2 ($R_1 = r_1 - r_1{}^e$, where $r_1{}^e$ denotes the equilibrium C-O$_1$ bond lengths). The eliptical nature of the quadratic surface has been exaggerated for the purpose of illustration.

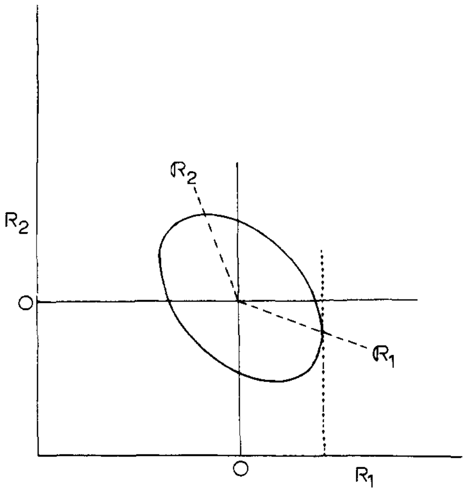

Figure 2. Minimum energy coordinates directions for CO_2. Again, the eliptical nature of the quadratic surface has been exaggerated.

ternal freedom. These authors were primarily interested in the relationship between the signs of the various interaction potential constants and the molecular geometry changes which accompany bond cleavage. What is stressed here is that there is a direct relationship between minimum energy coordinates and the minimum energy path or reaction coordinate for dissociation reactions involving a single bond.

The minimum energy coordinate $\mathcal{R}_i$ is defined by minimizing the potential energy with respect to coordinates R_j when coordinate R_i is constrained to a unit distortion,

$$(\delta V/\delta R_j)_{R_i=1} = 0 \text{ for } j = 1, n \text{ and } j \neq i \tag{2}$$

For a unimolecular dissociation, where R_i is the bond stretching coordinate for the bond which is broken, the MEP may be defined in precisely the same way. Both the MEP and $\mathcal{R}_i$ define the locus of minimum energy points in the potential energy surface as a function of distortion of a specific coordinate. The MEP and $\mathcal{R}_i$ differ only in that the former is defined with respect to the "true" potential energy surface, while $\mathcal{R}_i$ refers only to the quadratic potential energy surface. Thus, $\mathcal{R}_i$ is a path in internal coordinate space which can be evaluated from vibrational data and can provide a crude estimate of an important static feature of any potential surface, the reaction coordinate.

It is constructive to consider a simple example: the two C-O bond stretches in CO_2. Contours of equal energy in the potential surface plotted in R_1, R_2 space ($R_1 = r_1 - r_1{}^e$ where $r_1{}^e$ is the equilibrium C-O$_1$ bond length) are elipses as shown in Figure 1. The two C-O stretching coordinates transform as $\Sigma_g{}^+$ or $\Sigma_u{}^+$ ($D_{\infty h}$). As there are no other internal coordinates of $\Sigma_g{}^+$ or $\Sigma_u{}^+$ symmetry, the symmetry coordinates $S_1(\Sigma_g{}^+)$ and $S_3(\Sigma_u{}^+)$ are the normal coordinates

$$Q_1{}^{\Sigma_g{}^+} = 1/\sqrt{2}\,(R_1 + R_2)$$
$$Q_3{}^{\Sigma_u{}^+} = 1/\sqrt{2}\,(R_1 - R_2) \tag{3}$$

corresponding to the major and minor axes of the equipotential elipses given in Figure 1. Consider now the potential energy as a function of nuclear distortion. As r_1 is stretched, r_2 will compress so as to minimize potential energy; the fractional compression of r_2 is given by the interaction displacement coordinate. Essentially, vertical sections are being cut through the potential energy surface perpendicular to the particular internal coordinate of interest. In the case of CO_2, $\mathcal{R}_1$ corresponds to the tangential intersection of a line perpendicular to R_1 (passing through $r^e + \Delta r$), with the eliptical contours of equipotential (see Figure 2). It is only at this intersection that the potential energy is minimized; this then specifies the change required in R_2 to minimize potential energy with $R_1 = r^e + \Delta r$.

For CO_2 the minimum energy coordinate

$$\mathcal{R}_1 = R_1 - 0.077R_2 \tag{4}$$

indicates that r_2 will compress 7.8% of the amount that r_1 is stretched in order for CO_2 to relax to a minimum of potential energy. It is important to note that minimum energy coordinates are not the same as normal coordinates, but rather are linear combinations of the various normal coordinates; see Figures 1 and 2 for comparison of $\mathcal{R}_1\mathcal{R}_2$ and Q_1Q_2. However, a given minimum energy coordinate may involve predominantly one normal mode of vibration as is the case for unimolecular dissociation of $M(CO)_6$ (where M = Cr, Mo, W) to form $M(CO)_5$ and CO.[1]

It is appropriate to ask whether the minimum energy coordinate, which is determined in the limit of small nuclear distortions, provides a useful approximation to the true MEP. Unfortunately, it is not possible to test this approximation in any exact way, since the MEP for reactions more complex than $H_2 + H$ are not known. Perhaps a more meaningful question is whether or not the minimum energy coordinate can tell us anything about the true reaction pathway in terms of how the molecular structure changes during the course of reaction. The test here involves a comparison of $\mathcal{R}_i$ with the actual structural changes for a system where the structures of both the initial molecule and the final molecular fragment are known. In these cases, the general features of the MEP are intuitively known

Consider the reaction of CO_2 to give CO + O. In the limit of breaking the C-O$_1$ bond, r_2 must approach the equilibrium bond length in CO. Thus, during the course of the reaction r_2 will compress slightly ($\Delta r_2 = -0.04$ Å). The minimum energy coordinate $\mathcal{R}_1$ (eq 4) exhibits the same general feature. Machida and Overend considered several triatomic molecules where the MEP's for bond dissociation can be estimated from structural data for both the triatomic and diatomic fragments.[8] With one exception (SO_2) the sign of the interaction force constants led to the correct prediction as regards the change in the B-C bond length as the A-B bond is broken in ABC. What is needed now are additional studies on molecules with more than three atoms.

It is interesting to note that in CO_2 the normal mode of vibration possessing the lowest force constant, Q_3, is a rather poor approximation of the MEP (eq 3). For a bound system with a well defined potential minimum it is erroneous to equate the MEP with one given normal mode direction. The MEP is

Table I. Symmetry Potential Constants for PF_5[a]

F_{11}	7.15[b]	C_{11}	0.1430
F_{22}	5.09[b]	C_{22}	0.201
F_{12}	0.9[b]	C_{12}	−0.0253
F_{33}	4.10[b]	C_{33}	0.256
F_{44}	2.999[d]	C_{44}	0.349
F_{34}	0.75[b]	C_{34}	−0.064
F_{55}	4.19[c]	C_{55}	0.239
F_{66}	0.28[c]	C_{66}	3.99
F_{77}	4.19[c]	C_{77}	0.267
F_{56}	0[c]	C_{56}	0.14
F_{57}	−0.18[c]	C_{57}	0.012
F_{67}	−0.35[c]	C_{67}	0.334
F_{88}	1.457[d]	C_{88}	0.686

[a] The units for F_{11}, F_{22}, F_{12}, F_{33}, and F_{55} are mdyn/Å, those for F_{44}, F_{66}, F_{67}, and F_{88} are (mdyn Å/rad^2, and those for F_{34}, F_{56}, and F_{57} are mdyn/rad. The units for compliants are the reciprocal of those of the corresponding force constants. [b] Taken from ref 14. [c] Taken from ref 13. [d] Taken from ref 12.

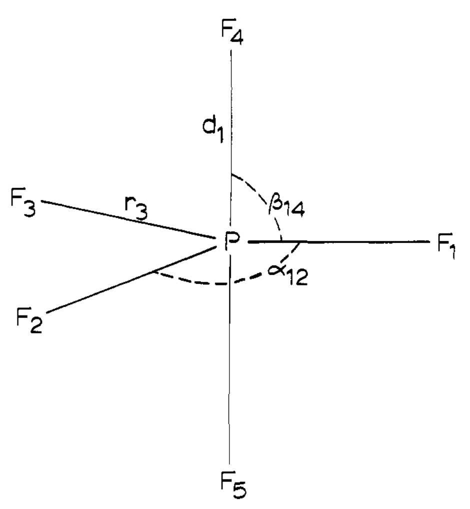

Figure 3. Internal coordinates for PF_5.

Table II. Valence Compliants and Interaction Displacement Coordinates for PF_5[a]

Valence Compliants

$C_r = 0.207$
$C_d = 0.228$
$C_\alpha = 2.659$
$C_\beta = 0.376$
$C_{rr} = -0.032$
$C_{dd} = -0.027$
$C_{rd} = -0.010$
$C_{d\beta} = C_{r_4\beta_{14}} = -0.018$
$C_{d\beta}' = C_{r_4\beta_{15}} = 0.018$

$C_{\alpha\alpha} = -1.329$
$C_{\beta\beta} = C_{\beta_{14}\beta_{24}} = -0.101$
$C_{\beta\beta}' = C_{\beta_{14}\beta_{15}} = -0.198$
$C_{\beta\beta}'' = C_{\beta_{14}\beta_{25}} = 0.012$
$C_{\alpha\beta} = C_{\alpha_{23}\beta_{24}} = -0.079$
$C_{\alpha\beta}' = C_{\alpha_{23}\beta_{14}} = 0.157$
$C_{r\alpha} = C_{r_1\alpha_{12}} = 0.005$
$C_{r\alpha}' = C_{r_1\alpha_{23}} = -0.010$
$C_{r\alpha} = C_{r_1\beta_{14}} = 0.005$
$C_{r\beta}' = C_{r_1\beta_{24}} = -0.003$

Interaction Displacement Coordinates[b]

$(r)_r = -0.154$
$(d)_d = -0.120$
$(r)_d = -0.050$
$(d)_r = -0.045$
$(\alpha)_\alpha = -0.500$
$(\beta)_\beta = -0.269$
$(\beta)_\beta' = -0.526$
$(\beta)_\beta'' = 0.032$
$(\alpha)_\beta = -0.209$
$(\beta)_\alpha = -0.030$
$(\alpha)_\beta' = 0.418$

$(\beta)_\alpha' = 0.059$
$(r)_\alpha = 0.002$
$(\alpha)_r = 0.023$
$(r)_\alpha' = -0.003$
$(\alpha)_r' = -0.046$
$(r)_\beta = 0.014$·
$(\beta)_r = 0.026$
$(r)_\beta' = -0.007$
$(\beta)_r' = -0.013$
$(d)_\beta = -0.049$
$(\beta)_d = -0.081$
$(d)_\beta' = 0.049$
$(\beta)_d' = 0.081$

[a] See Figure 3 for a description of the internal coordinates. [b] The coordinates $(\text{stretch})_{\text{stretch}}$ and $(\text{bend})_{\text{bend}}$ are unitless while the units for $(\text{bend})_{\text{stretch}}$ and $(\text{stretch})_{\text{bend}}$ are rad/Å and Å/rad, respectively.

equivalent to a particular normal mode Q_i only when the potential surface is flat with respect to Q_i. In this case Q_i corresponds to the hypothetical normal mode of zero frequency. The only real systems for which the MEP (and in these cases, the actual reaction pathway) and a given normal mode are identical are solids undergoing a second-order phase change.[9]

Intramolecular Rearrangement in Fluxional Molecules

Five-coordinate complexes have drawn considerable attention over the past 10 years.[10] Part of the interest in five-coordinate complexes stems from their central role in ligand substitution mechanisms for four- and six-coordinate complexes. Both SN2 mechanisms for four-coordinate complexes and SN1 mechanisms for six-coordinate complexes proceed through five-coordinate intermediates. It seemed possible, then, that structural characterization of stable five-coordinate molecules could shed some light on the nature of the transient five coordinate intermediate in ligand substitution reactions.

One of the interesting structural properties generally exhibited by five-coordinate complexes is stereochemical nonrigidity. The D_{3h} symmetry PF_5 molecule where axial and equatorial fluorines undergo rapid exchange on the NMR time scale is typical. Several mechanisms have been proposed to model the intramolecular exchange in five-coordinate molecules. Of these, the pseudorotation mechanism first proposed by Berry[11] seems to be the best from the standpoint of barrier energies[10] and its appealing simplicity. However, since the axial equatorial exchange proceeds via intramolecular rearrangement, it seems appropriate to model the exchange using minimum energy coordinates. That is, the minimum energy coordinate associated with a unit decrease in the F_{ax}-P-F_{ax} angle ($0.5\beta_{14} + 0.5\beta_{15}$ in Figure 3) should provide some insight as to how intramolecular rearrangement proceeds. The idea here is that axial equatorial exchange must involve a decrease in the F_{ax}-P-F_{ax} angle, irrespective of the details of the actual mechanism. What is of interest is how the various angles and bond lengths change as F_{ax}-P-F_{ax} is decreased from 180°.

From the standpoint of vibrational analysis, PF_5 is one of the best studied five-coordinate molecules.[12-15] Unfortunately, there is still considerable question as to the quadratic force field for PF_5. The main difficulty with PF_5 is the absence of isotopic shift data which could be used to pinpoint the interaction constants. Fortunately, Coriolis constants ζ_5 and ζ_6 determined from band contour analysis[12] help in fixing two of the interaction potentials in the E' block.[13] Also, Raman intensities have been used to calculate bond polarizability derivatives which help to evaluate stretch-stretch interactions.[14] Thus, in taking the E' potentials from Levin's work,[13] the A_1' symmetry potentials from the Raman intensity study,[14] and the remaining symmetry constants from Lord and Hoskins study,[12] we arrive at the best estimate for the quadratic force field. This symmetry force constants matrix was then inverted and the resulting symmetry compliance constants (Table I) used to calculate valence compliants and the related interaction displacement coordinates (Table II). It is clear that the valence compliants so obtained in no way represent the unique solution to the potential function. However, it is felt that while the magnitude of the various compliants may deviate from the unique solution, their signs are probably correct. Thus, the minimum energy coordinates should give some idea of the general directions of the intramolecular rearrangement as well as unimolecular dissociation.

The minimum energy coordinate associated with a unit decrease in the F_{ax}-P-F_{ax} angle

$$\mathcal{R}(0.5\beta_{14} + 0.5\beta_{15}) = 0.5(\beta_{14} + \beta_{15}) + 0.418\alpha_{23} - 0.209(\alpha_{12} + \alpha_{13}) - 0.237(\beta_{24} + \beta_{34} + \beta_{25} + \beta_{35}) \quad (5)$$

is consistent with the pseudorotation mechanism.[16] As F_{ax}–P–F_{ax} is decreased, the in plane angle α_{23} increases. At first glance one might expect a unit decrease in α_{23}, since in the limit of interconversion between the two D_{3h} structures the total angle changes in F_{ax}–P–F_{ax} and F_2–P–F_3 are the same. However, the relative change in α_{23} of 41.8% of the change in F_{ax}–P–F_{ax} simply indicates that the C_{4v} intermediate is more pyramidal (i.e., the F_{eq}–P–F_{eq} angles in the intermediate are less) than that obtained by equal magnitude changes in F_2–P–F_3 and F_{ax}–P–F_{ax}.

The minimum energy coordinates for a fixed distortion of the axial bond length

$$\mathcal{R}(d) = d_1 - 0.120d_2 - 0.05(r_1 + r_2 + r_3) - 0.081(\beta_{14} + \beta_{24} + \beta_{34}) + 0.081(\beta_{15} + \beta_{25} + \beta_{35}) \quad (6)$$

indicates that the remaining axial and equatorial P–F bonds strengthen as d_1 is stretched. The angular changes show that the three equatorial fluorines bend up toward the leaving fluorine. Both the angle and bond length changes suggest a nearly tetrahedral PF_4 fragment in the limit of breaking the P–F_4 bond. Note that the axial bond compresses more than the equatorial bonds thereby reducing the P–F_{ax}, P–F_{eq} bond length differences as P–F_4 is stretched (P–F_{ax} = 1.577 Å and P–F_{eq} = 1.534 Å in PF_5[17]). The coordinate $\mathcal{R}(d)$ looks remarkably like what might be expected for an intermediate transition state species decaying into a tetrahedral complex in an SN2 ligand substitution reaction!

The minimum energy coordinate corresponding to a distortion of one of the P–F_{eq} bonds is quite different,

$$\mathcal{R}(r) = r_1 - 0.154(r_2 + r_3) - 0.045(d_1 + d_2) - 0.046\alpha_{23} + 0.023(\alpha_{12} + \alpha_{13}) + 0.026(\beta_{14} + \beta_{15}) - 0.013(\beta_{24} + \beta_{34} + \beta_{25} + \beta_{35}) \quad (7)$$

As was the case with $\mathcal{R}(d)$, the remaining P–F bonds all compress as P–F_1 is stretched. However, in this case the equatorial bonds compress more than the axial bonds thereby increasing the disparity between P–F_{ax} and P–F_{eq}. Surprisingly, the two remaining equatorial fluorines get closer together as evidenced by a decrease in α_{23}. The axial fluorines also bend slightly away from the leaving group. The overall geometry change suggests a PF_4 fragment similar to SF_4 where S–F_{eq} = 1.542 Å, S–F_{ax} = 1.643 Å, F_{eq}–S–F_{eq} = 103.8°, and F_{ax}–S–F_{ax} = 176.8°.[18]

The paths $\mathcal{R}(r)$ and $\mathcal{R}(d)$ are surprisingly different suggesting the possibility of two distinctly different conformations for PF_4. It should be noted that the path $\mathcal{R}(r)$ leads to a distorted trigonal-bypyramidal geometry for the PF_4 radical as is consistent with recent calculations of Higuchi[19] and the general evidence of an SF_4 type structure for the tetravalent phosphoranyl radicals.[20] Again, it is stressed that the magnitudes of the various changes should not be considered hard numbers in view of the uncertainty of the potential function and the known anharmonicity in PF_5. However, these preliminary results are intriguing and point to the need of obtaining unique quadratic potential functions for PF_5 and related fluxional molecules.

Symmetry Considerations

It is useful to know the point symmetry for a molecule as it traverses the reaction coordinate. In the approximation that the MEP is given by the minimum energy coordinate, the molecular symmetry is determined by the symmetry of $\mathcal{R}_i$. The minimum energy coordinate, and the MEP, will always transform as the totally symmetric representation in the point symmetry of the distorted molecule, K. Thus, those operations in the nondistorted molecule symmetry group, H, which remain invariant with respect to a distortion along $\mathcal{R}_i$ (that is, the kernel or cokernel of $\Gamma_{(\mathcal{R}_i)}$)[21] comprise the operations of the group K. As $\mathcal{R}_i$ is determined using a quadratic potential energy function, the group K is specified by a localized distortion of the bond being broken. Essentially, the quadratic compliants which determine the path of minimum energy do not lower the molecular symmetry formed by a localized bond stretch. For octahedral MX_6 systems, the symmetry along $\mathcal{R}_{MX}$, corresponding to breaking one M–X bond, is C_{4v}; for tetrahedral MX_4 compounds, a distortion along $\mathcal{R}_{MX}$ results in C_{3v} symmetry. In this approximation the symmetry will change when a maximum or minimum of potential energy is reached. In a distortion of PF_5 along $\mathcal{R}(0.5\beta_{14} + 0.5\beta_{15})$ the molecular symmetry is initially C_{2v}, and then becomes C_{4v} at the point where F_{ax}–P–F_{ax} = F_{eq}–P–F_{eq}.

It is clear that the quadratic approximation severely limits the molecular symmetry along the MEP. This is graphically illustrated inthe case of $CO_2 \rightarrow CO + O$ where the minimum energy coordinate involves no OCO bend since there is no interaction potential between OCO deformation and C–O stretch. The symmetry along the true MEP will depart from that along $\mathcal{R}_i$ only as a result of higher order terms in the potential energy function.

The symmetry properties of $\mathcal{R}_i$ in the point group of the nondistorted molecule are also useful. The subgroup K may be subduced given the group H and the symmetry species of the distortion along $\mathcal{R}_i$.[22] This is not particularly illuminating, as the group K can easily be determined by inspection. However, the symmetry of the MEP in H must be the same as that of the first excited state according to the second-order Jahn-Teller theorem in order for the integral $\langle \Psi_0 | \partial H/\partial S | \Psi_i \rangle$ to be nonzero (here Ψ_0 and Ψ_i are the ground and excited state wave functions and S is the displacement along the MEP). Thus, the minimum energy coordinate for unimolecular dissociation and the first excited electronic state must transform the same. This may have importance for systems such as D_{3h} MX_5 where unimolecular dissociation could involve either axial or equitorial M–X bonds. In D_{3h} $\mathcal{R}_{M-X_{ax}}$ transforms as A_2'' while $\mathcal{R}_{M-X_{eq}}$ has symmetry E'. Thus, a knowledge of the symmetry of the lowest unoccupied electronic state could help specify the reaction direction, $\mathcal{R}_{M-X_{eq}}$ or $\mathcal{R}_{M-X_{ax}}$.

The Meaning of Primary Force and Compliance Constants

As pointed out earlier, normal mode calculations have generally been carried out in terms of the force constant formalism. However, there are limiting problems associated with using force constants to discuss bonding.[1,23] While these problems have been well documented,[12,22] the most insidious difficulty should be mentioned here. Force constants depend on what coordinate set is selected to describe the system. Even in the case of the simple water molecule this dependence on coordinate selection can be misleading. If the two O–H bonds and the H–O–H angle were used (the general valence quadratic force field, GVQFF) the valence O–H stretching constant is ca. 0.7 mdyn/Å lower than that determined using the general central quadratic force field (GCQFF) where the two O–H bonds and the H–H nonbonded distance are used. Clearly, it is advantageous to have a bonding parameter which is invariant to coordinate selection.

The mathematical difficulties associated with the force constant description can be obviated by using the alternative compliance constant scheme.[5,6] However, at first glance the compliance description is confusing since coordinate strength is inversely proportional to the magnitude of the primary compliant. With the aid of minimum energy coordinates and the relaxed force constant first introduced by Jones,[23] the distinction between primary force and compliance constants is clarified. The relaxed force constant, the reciprocal of the primary compliance constant $\Upsilon_{ii} = 1/c_{ii}$, measures the force required to distort coordinate i while allowing the remaining coordinates to relax so as to minimize potential energy,

$$\Upsilon_{ii} = \left(\frac{\partial^2 V}{\partial R_i^{\,2}}\right)_{\substack{\mathcal{F}_j = 0 \\ j \neq i}} \tag{8}$$

The term "relaxed" is appropriate since the constant Υ_{ii} is defined with respect to a distortion in R_i while constraining the generalized forces on the remaining coordinates, $\mathcal{F}_j$, to zero. The regular, or rigid, force constant measures the force required to distort coordinate i while fixing the remaining coordinates to zero displacement

$$F_{ii} = \left(\frac{\partial^2 V}{\partial R_i^{\,2}}\right)_{\substack{R_j = 0 \\ j \neq i}} \tag{9}$$

As both Υ_{ii} and F_{ii} are defined with respect to coordinate distortion, both are graphically presented in Figure 2 for CO_2. The path given by the minimum energy coordinate $\mathcal{R}_i$ is the path taken in defining the relaxed force constant, while the path along the internal coordinate direction R_i defines the regular force constant F_{ii}. As Υ_{ii} follows a minimum of potential energy while F_{ii} does not, the relaxed constant is always less than or equal to the regular rigid force constant. That is $F_{ii} \geq \Upsilon_{ii}$ since following the direction R_i corresponds to climbing the side of the potential energy "hill" in coordinate space. Effectively, part of the value of the regular force constant can be attributed to the force required to constrain the remaining coordinates as R_i is distorted.

Figure 2 also helps in understanding why regular force constants vary in magnitude from one coordinate set to the next, while compliants and relaxed force constants are invariant. If the coordinate set is changed, the force required to constrain coordinates R_j as R_i is deformed may vary dramatically. For H_2O, more force is required to constrain r_2 and D (the H–H nonbonded distance) as r_1 is stretched (the GCQFF model) than to constrain r_2 and α (the GVQFF approximation). If the coordinate set is changed, a different path up the potential energy hill is chosen. The relaxed constants Υ_{ii} do not change since the minimum energy coordinates are invariant to what coordinates are chosen to describe the system (this follows from the invariance of the compliance constants themselves). There are only certain minimum energy directions in coordinate space and they are not dependent on which coordinate set is selected.

It is felt that the relaxed force constant is a more chemically meaningful bond strength parameter than the regular constant, since the path taken in defining Υ_{ii} is closer to the true MEP than the individual internal coordinate directions used to define F_{ii}. In any real system it is artificial to constrain all other coordinates R_j while deforming coordinate R_i so as to measure the strength of coordinate R_i. When R_i is deformed, the remaining coordinates simultaneously relax to a minimum energy configuration. Essentially Υ_{ii} is the best approximation to the force constant corresponding to unimolecular dissociation. As the MEP is the adiabatic reaction pathway, it is appropriate to term the relaxed force constant an adiabatic bond strength parameter and the rigid force constant a nonadiabatic bond strength parameter.

The minimum energy coordinates themselves provide useful bonding information as they describe the molecular relaxation which accompanies coordinate distortion. The tie between $\mathcal{R}_i$'s and our current bonding models is obvious. The relaxed force constant and minimum energy coordinates together provide a more complete description of bonding than the regular force field description alone.

The connection between reaction dynamics and quadratic potential functions, via minimum energy coordinates, is intriguing. Chemists have an intuitive feeling for the relationship between bonding and reaction pathways. Certainly there is a great body of literature which represents an effort to evaluate MEP's using theoretical bonding models.[24] While many experimental methods have been used to focus on the qualitative aspects of reaction pathways, there has been no consistent relationship between experiment and the quantitative aspects of the MEP.[25] The minimum energy coordinate does provide such an empirical relationship. It is stressed here that the minimum energy coordinate is a first-order approximation to the MEP with the usual limitations of the quadratic approximation. Furthermore, $\mathcal{R}_i$ is an estimate of a static feature of the potential surface, and, as such, it may say nothing about true reaction pathways which are nonadiabatic. However, minimum energy coordinates at the very least have pedagogic significance in that they provide a conceptually simple tie between interatomic forces and reaction coordinates.

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