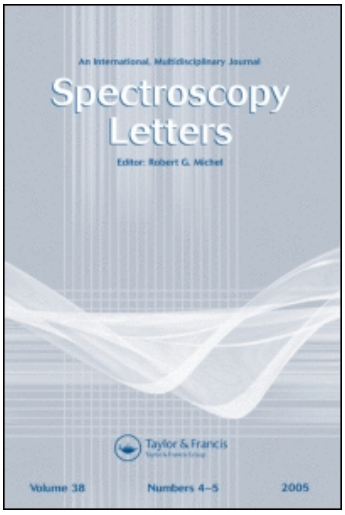

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Generalized Approach to Relaxed Force Constants

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Generalized Approach to Relaxed Force Constants

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The main purpose of potential constants, *i.e.*, force and compliance constants, is to provide a quantitative understanding of bonding relationships. Compliance constants have been shown to possess several mathematical advantages over conventional force constants.[1-3] Compliance constants, however, are parameters which decrease in magnitude as bond strength increases; consequently, their use as bond strength parameters is not particularly satisfying. The desirability of a measure of bond strength which increases in magnitude as the bond becomes stronger, and at the same time possesses all the advantages of compliance constants is self evident. For this reason, the relaxed force constant $\tau_{ii}=1/C_{ii}$ was introduced by Jones some time ago.[4] In the present communication, this approach is generalized to include relaxed interaction force constants. A brief discussion of their meaning is also presented.

In a recent paper, Jones and Swanson[3] have discussed the meaning of primary and interaction potential constants in both the force and compliance constant formalisms. They also discussed a more chemically meaningful bond strength parameter--the relaxed force constant,[4] given by

$$T_{ii} = \left(\frac{\partial^2 V}{\partial R_i^2}\right)_{\substack{\mathcal{F}_j = 0, \\ j \neq i,}} \tag{1}$$

where the $\mathcal{F}_j$ are generalized forces applied to the various internal coordinates R_j. The relaxed force constant, which is the reciprocal of the corresponding compliance constant, is a measure of the force required to distort coordinate R_i while the remaining coordinates are allowed to relax to a minimum energy configuration. On the other hand, the conventional primary force constant, which is given by

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

measures the force required to distort coordinate R_i while the remaining coordinates are constrained to zero displacement.

In this paper, the minimum energy approach is extended to define a relaxed interaction force constant as follows:

$$T_{ij} = \left(\frac{\partial^2 V}{\partial R_i \partial R_j}\right)_{\substack{\mathcal{F}_k = 0, \\ k \neq i,j.}} \tag{3}$$

Since

$$R_i = -\sum_{\ell} C_{\ell i} \mathcal{F}_{\ell} , \tag{4}$$

T_{ij} can be expressed in terms of compliance constants. It is given by

$$T_{ij} = -C_{ij}/C_{ii}C_{jj}. \tag{5}$$

This general expression, of course, also gives the primary relaxed force constant when i=j.

While the meaning of the conventional interaction force constant

$$F_{ij} = \left(\frac{\partial^2 V}{\partial R_i \partial R_j}\right)_{\substack{R_k = 0, \\ k \neq i,j}} \tag{6}$$

is not clear unless the entire force field has been determined,[5-7] the meaning of the relaxed interaction force constant can be discussed in terms of interaction displacement constants since

$$-T_{ij}/T_{jj} = C_{ij}/C_{ii} = (j)_i. \tag{7}$$

Here, $(j)_i$ is defined as the rate of change of coordinate R_j with respect to changes of R_i, with the constraint that the potential remain a minimum.[2] Thus, the relaxed interaction force constant proposed here has a simple physical interpretation--T_{ij} *is a measure of the force on coordinate* R_i *caused by a distortion of coordinate* R_j, *when* R_i *is allowed to relax to an equilibrium configuration.* By the definition of interaction displacement constants, R_i is given by

$$R_i = (i)_j R_j \tag{8}$$

when coordinate R_j is distorted. Expressing $(i)_j$ in terms of generalized relaxed force constants in this equation, rearranging, and changing the sign of both sides, one obtains

$$-T_{ii} R_i = T_{ij} R_j. \tag{9}$$

The term on the left is the restoring force resulting from the extension or compression of coordinate R_i as it relaxes to a new equilibrium. The term on the right can be thought of as the force on coordinate R_i caused by the change in coordinate R_j. In other words, as R_j is distorted, a force $(f_i)_j = T_{ij} R_j$ acts upon coordinate R_i. In order to balance this force and reach equilibrium, R_i must change until the restoring force $(f_i)_i = -T_{ii}R_i$ matches $(f_i)_j$.

Let us consider the water molecule as an example. The relevant potential constants are given in Table 1. If R_1, that is, the $O\text{-}H_1$ bond, is now stretched by 0.1 Å, a force $(f_{R_2})_{R_1} = T_{RR} R_1 = -0.0171$ mdyn will be exerted

Table 1

Valence Compliance and Generalized Relaxed Force Constants of H_2O[a,b]

C_R	0.119	T_R	8.403
C_{RR}	0.00242	T_{RR}	-0.171
C_α	1.461	T_α	0.684
$C_{R\alpha}$	-0.0386	$T_{R\alpha}$	0.222

a) The units for C_R and C_{RR} are Å/mdyn, those for C_α are rad^2/mdyn Å, and those for $C_{R\alpha}$ are rad/mdyn. The units for the relaxed force constants are the reciprocal of those of the corresponding compliance constants.
b) Compliance constants taken from Ref. 6. C_R and C_α are the primary stretching and angle deformation compliants, respectively, while C_{RR} and $C_{R\alpha}$ are the stretch-stretch interaction, and stretch-bend interaction compliants, respectively.

upon R_2, the $O\text{-}H_2$ bond. In order to counteract this force, R_2 must change from zero up to a certain value such that $(f_{R_2})_{R_2} = -T_R R_2 = -0.0171$ mdyn. Clearly, R_2 must be equal to 0.00203 Å, which is the same result obtained from $R_2 = (C_{RR}/C_R) R_1$. Similarly, one finds that the $H_1\text{-}O\text{-}H_2$ angle decreases as a result of the stretch of the $O\text{-}H_1$ bond.

Since generalized force constants are expressed in terms of compliance constants, it immediately follows that the former are invariant with respect to the coordinate set chosen to describe the molecular configuration, and that all primary and interaction relaxed force constants can be evaluated independently, even when redundant coordinates occur. This is not true of conventional force constants. For example, in the case of planar XY_3-type molecules, redundancy conditions can be used to obtain all the primary and interaction valence compliance constants such as C_R, C_α, C_{RR}, $C_{R\alpha}$, and $C'_{R\alpha}$ (and consequently T_R, T_α, T_{RR}, $T_{R\alpha}$, and $T'_{R\alpha}$) while F_R and F_{RR} are the only individual force constants which can be obtained explicitly from the in-plane symmetry relations of this type of molecule.[8] Similarly, no valence

force constants involving angle deformation coordinates can be evaluated explicitly for tetrahedral XY_4, octahedral XY_6, and other molecular models. All of the corresponding generalized force constants can be easily obtained in terms of compliance constants. Thus, the T_{ij} provide valuable bonding information whose interpretation is straightforward, and which is sometimes impossible to obtain in terms of conventional force constants.

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