J|A|C|S
COMMUNICATIONS

Published on Web 08/12/2006

The Interpretation of Compliance Constants and Their Suitability for Characterizing Hydrogen Bonds and Other Weak Interactions

Jon Baker* and Peter Pulay*

Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701

Received March 30, 2006; E-mail: baker@uark.edu; pulay@uark.edu

The concepts of bond strength and bond order are of major importance in chemistry. Over the years, various attempts have been made to define bond order quantitatively, going back to early work by Pauling[1] and Coulson[2] in the 1930s. Most theoretical definitions involve both the density and overlap matrices and can be considered as an extension to a standard population analysis, as defined, for example, by Mulliken[3] or Löwdin.[4] Such definitions, although certainly useful, have well-known weaknesses; several of these were subsequently pointed out by Mulliken himself.[5] For example, the addition of diffuse functions to the basis set can have a very adverse affect on a Mulliken population analysis and on all related quantities, such as bond orders.[6]

A more experimental definition of bond order might have advantages which would supplement the theoretical treatments. In 1946, Walsh proposed a definition based on ionization potentials.[7] A more intuitive measure of bond strength might be to use the force constant between the two atoms involved. Although they are not very direct experimental quantities, force constants can be determined indirectly from experimental measurements (unlike bond orders based on population analysis), and they can also be directly computed. An even better quantity to use as a bond strength descriptor would appear to be compliance constants.

Compliance constants are elements of the inverse force constant matrix. The compliance matrix has two advantages over the regular force constant (Hessian) matrix. First, a particular compliance constant depends only on the definition of the two internal coordinates pertaining to it and is independent of the definition of all other coordinates.[8−10] Although still not widely appreciated, force constants depend, in principle, on the definition of *all* internal coordinates. This is quite evident, for example, in ring compounds where the values of the ring stretching force constants depend on the definition of the deformational coordinates. A second advantage is that compliance constants, unlike force constants, can be readily defined for redundant coordinate systems, that is, when the number of coordinates exceeds the number of degrees of freedom.[11] The invariant nature of compliance constants has recently been reviewed by Grunenberg et al.[12]

A minor disadvantage of compliance constants is that they are inversely proportional to the bond strength, and their units are the reciprocal of those of force constants. By inverting the diagonal elements of the compliance matrix, the *relaxed force constants* are obtained. A diagonal force constant can be visualized as the force required to distort the molecule by a unit amount along a coordinate while holding all other coordinates fixed in their equilibrium positions. The relaxed force constant, on the other hand, measures the force required to distort the coordinate a unit amount while allowing all other coordinates to relax to a new minimum energy configuration.[11] Thus a regular stretching force constant can be considered as a measure of bond strength with the rest of the system constrained, while a relaxed stretching force constant measures bond strength, allowing the rest of the molecule to relax so as to minimize the potential energy. Under normal circumstances, involving a well-defined, nonredundant set of internal coordinates, standard force constants and relaxed force constants have similar values (with the latter all generally slightly smaller than the former, as expected from their definition). Relaxed force constants have the units and magnitude of force constants and are more convenient to use than compliance constants but carry the same information.

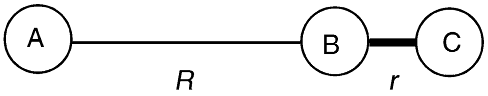

Figure 1. A model for the relaxed force constant of two atoms not directly connected by a bond.

In this communication, we use both model systems and real molecular complexes to arrive at a qualitative understanding of the factors determining the magnitude of relaxed force constants (and the corresponding compliance constants), in particular, those between weakly bound atoms. As the subsequent examples will show, relaxed force constants between atoms measure the effects of both the direct bonding interaction and indirect interactions through other atoms that the two atoms are connected to. For atoms connected by a normal bond, the direct interaction is usually dominant. However, for weakly bonded or nonbonded atoms, the indirect contribution usually overwhelms the direct through-bond interaction. This can be seen from the simplest model system, a linear triatomic molecule shown in Figure 1.

In this model, atom A is bound by a weak force constant f and long bond R to atom B. The latter is bound by a strong force constant F and short bond r to atom C. There is no direct interaction between A and C, and all forces are assumed to be harmonic. The potential energy V is given by $2V = fR^2 + Fr^2 = f(X - r)^2 + Fr^2$, where R, r, and $X = R + r$ are displacement coordinates for the A−B, B−C, and A−C bonds. Minimizing this energy expression with respect to r at a given X gives $r = fX/(F + f)$. Substituting this back in the energy expression gives $2V = Ff/(F + f)X^2$. The relaxed force constant for X is the coefficient of X^2 in this expression, $Ff/(F + f) = f/(1 + f/F)$. As $F \gg f$, this is approximately equal to f, *even though there is no direct interaction between A and C*. This finding can be readily generalized to two rigid molecules M and N, held together by weak intermolecular forces. In this case, *all* relaxed force constants between two atoms, one in M and one in N, are expected to be of the same order of magnitude and close to the force constant corresponding to rigid-body motion between the two centers of mass. Some variation may arise from the fact that the two molecules not only can translate relative to each other but can also rotate. However, this does not affect the main conclusion that compliance constants (or relaxed force constants) between two atoms located on different subsystems are measures of the overall interaction between the subsystems and *not* the bonding—if any—between specific atoms.

10.1021/ja0618503 CCC: $33.50 © 2006 American Chemical Society

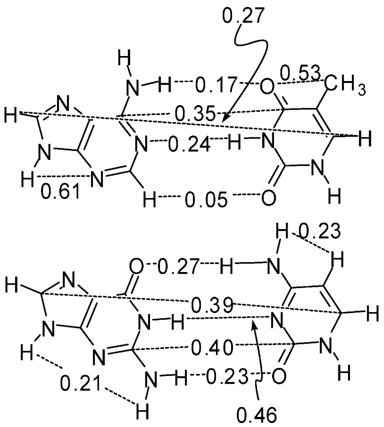

Figure 2. Some relaxed force constants in the adenine−thymine base pair (top) and the guanine−cytosine base pair (bottom), in aJ/Å^2.

A different example for the importance of indirect interactions is given by the water molecule. This is normally described in terms of two O−H bond lengths and an H−O−H bond angle. In terms of distance coordinates, the bond angle is replaced by an H−H stretch. An increase in the latter is essentially equivalent to a bend and requires a significant effort, which is reflected in the fairly large value of the H−H stretching force constant (1.714 aJ/Å^2 at the B3LYP/6-311G** level), even though the two hydrogen atoms are not bonded. The large value of a relaxed force constant between two atoms which are obviously not bonded makes the identification of genuine bonding interactions, such as hydrogen bonds, based on the relative magnitudes of relaxed force constants or compliance constants highly problematic.

To further illustrate this point, we consider the relaxed force constants in the Watson−Crick base pairs adenine−thymine (AT) and guanine−cytosine (GC). In a recent article in this journal, Grunenberg has proposed using distance-only compliance constants as unique bond strength descriptors for hydrogen bonds and other weak interactions.[13] He looked at the six principal hydrogen-bonding intermolecular interactions in these base pairs and ordered them in terms of their bond strengths based on the magnitudes of the computed compliance constants. We have reproduced Grunenberg's calculations by optimizing the geometries of these two base-pair dimers at the B3LYP/6-311++G** level and computing the force constants at the converged geometry analytically. These were used to calculate the compliance matrix and relaxed force constants. All calculations were done with the PQS program package.[14] Planarity was enforced, but the vibrational analysis indicates that both structures are minima anyway. Relaxed force constants for the hydrogen bonds and for some selected pairs of atoms are shown in Figure 2.

As this figure shows, relaxed force constants between atoms that are clearly not bonded are of the same order of magnitude as relaxed force constants for genuine hydrogen bonds. For instance, the relaxed force constant between two distant (>12.0 Å) hydrogen atoms on the opposite ends of the AT complex has a larger value (0.27 aJ/Å^2) than the genuine N−H···O=C and N···H−N hydrogen bonds (0.17 and 0.24 aJ/Å^2, respectively). On the basis of the triatomic molecule model, this is to be expected as the relaxed force constant measures the force constant holding together the two fragments, *not* individual bond contributions. Intramolecular relaxed force constants—between atoms in the same base—are even larger, for instance, 0.61 aJ/Å^2 between a nitrogen and a nonbonded hydrogen in the γ position (Figure 2, top left).

We have calculated compliance constants for a number of supramolecular systems, and they all show the same pattern.[15] On this basis, we conclude that compliance constants (or relaxed force constants) measure the total interaction between fragments, but not individual bonding interactions, and are therefore not useful diagnostics of the strength of weak interatomic interactions.

Acknowledgment. This work was supported in part by NSF Grant CHE-0515922. We thank Professor Neil T. Allison for useful assistance.

References

(1) Pauling, L.; Brockway, L. O.; Beach, J. Y. *J. Am. Chem. Soc.* **1935**, *57*, 2705−2709.
(2) Lennard-Jones, J. A.; Coulson, C. A. *Trans. Faraday Soc.* **1939**, *35*, 811−823.
(3) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833−1840.
(4) Löwdin, P. O. *Phys. Rev.* **1955**, *97*, 1474.
(5) Mulliken, R. S. *J. Chem. Phys.* **1962**, *36*, 3428−3439.
(6) Baker, J. *Theor. Chim. Acta* **1985**, *68*, 221−229.
(7) Walsh, A. D. *Trans. Faraday Soc.* **1946**, *42*, 779−789.
(8) Taylor, W. T.; Pitzer, K. S. *J. Res. Natl. Bur. Stand.* **1947**, *38*, 1−17.
(9) Maslov, P. G. *Dokl. Akad. Nauk SSSR* **1949**, *67*, 819−822.
(10) Decius, J. C. *J. Chem. Phys.* **1963**, *38*, 241−248.
(11) Jones, L. H.; Swanson, B. I. *Acc. Chem. Res.* **1976**, *9*, 128−134.
(12) Grunenberg, J.; Streubel, R.; Frantzius, G. von; Marten, W. *J. Chem. Phys.* **2003**, *119*, 165.
(13) Grunenberg, J. *J. Am. Chem. Soc.* **2004**, *126*, 16310−16311.
(14) *PQS*, version 3.2; Parallel Quantum Solutions, 2013 Green Acres Road, Suite A, Fayetteville, AR 72703; see http://www.pqs-chem.com.
(15) Baker, J. *J. Chem. Phys.* **2006**, *125*, 014103/1−014103/6.

JA0618503