

Chimia 49 (1995) 408–410
 © Neue Schweizerische Chemische Gesellschaft
 ISSN 0009–4293

Comment on the Chemical Relevance of Force-Field Models

Edgar Müller*

Introduction

In his recent article (*Chimia* 1995, 49, 153), Dr. Daniel Huber offered a convincing introduction to the physics of Newton's equation of motion and its application to vibrating molecules. Presentday availability of powerful desktop computers allows the modelling of the dynamic behaviour of a complex molecular system almost in real time, giving the chemist a direct visual impression of the atomic processes which are supposed to take place in the test tube. The temptation to substitute test tube and spectrometer by computer is irresistible indeed, but there is still a *Caveat* which should be taken into account.

Newton's equation of motion, together with the mathematical methods for its solution, are generally valid principles, and their application to molecular reality is permitted as long as the electron-core-separability (*Born-Oppenheimer* approximation) holds, which is generally the case. The major difficulty in applying it to the molecular world arises from the insufficient knowledge we have of the molecular potential functions, needed in turn for the solution of the equations of motion. This difficulty is not trivial as will be shown by the following example.

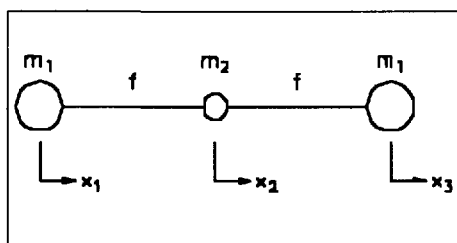
Linear Symmetric Three-Atomic Molecules

As mentioned, the solutions of the vibrational equations of motion (in *Cartesian*, mass-weighted displacement coordinates $q = M^{-1/2} \cdot x$) are obtained as **eigenvectors** and **eigenvalues** of $(M^{-1/2} \cdot F \cdot M^{-1/2})$,

where M is a diagonal matrix of atomic masses, and F is the so-called **Hessian matrix** of the second partial derivatives of the total energy (= potential function) with respect to the *Cartesian* displacement coordinates x : ($f_{ij} = \partial^2 V / (\partial x_i \cdot \partial x_j)$).

In the case of a linear, three-atomic molecule of the A–B–A type, where the atoms are represented by masses and the chemical bonds by springs (we shall call this a 'mechanical' model, in contrast to the later defined 'chemical' model), we obtain a system of three masses and two springs, with a potential function $V(x)$ given by:

$$V(x) = 1/2 \cdot f \cdot (x_1 - x_2)^2 + 1/2 \cdot f \cdot (x_2 - x_3)^2$$



(the origins of the coordinate and energy scales are hereby chosen at the equilibrium conformation of the molecule, where the potential gradient vanishes)

The matrices M and F are then:

$$M = \begin{pmatrix} m_1 & 0 & 0 \\ 0 & m_2 & 0 \\ 0 & 0 & m_1 \end{pmatrix} \quad F = \begin{pmatrix} f & -f & 0 \\ -f & 2f & -f \\ 0 & -f & f \end{pmatrix}$$

and the solutions of the equations (eigenvalues λ) are:

symmetric stretching vibration:
 $\lambda_1 = \omega_1^2 = f / m_1$

asymmetric stretching vibration:
 $\lambda_2 = \omega_2^2 = f \cdot (2m_1 + m_2) / (m_1 \cdot m_2)$

translation:
 $\lambda_3 = \omega_3^2 = 0$

The frequency ratio r between symmetric and asymmetric stretching vibration is independent of the force constant and comes out as:

$$r = \omega_1 / \omega_2 = (m_2 / (2m_1 + m_2))^{1/2}$$

which should always be less than 1. The asymmetric stretching vibration ($\bar{\nu}_a$) should, therefore, in the framework of our model, always appear at higher frequency than the symmetric one ($\bar{\nu}_s$). This is indeed the case for most linear molecules of the type mentioned, as shown by the example of CO_2 and its isoelectronic relatives (*Table 1*).

There are, however, some linear trihalogenide anions showing a *reversed pattern*: i.e. the asymmetric stretching vibration is observed at a lower frequency than the symmetric one (*Table 2*).

Other trihalogenides again show an apparently 'normal' situation (*Table 3*).

But even in these latter examples, there is a considerable discrepancy between the experimental data and the predictions of the 'mechanical' model. From a chemical point of view, this can be understood as follows: in a molecule, the valence-electron cloud reacts to the motions of the nuclei in such a way that the stretching of one bond influences the force constants of the other bonds, especially those which emanate from the same atom as the perturbed bond. Analog relationships hold for the other deformation coordinates like angles and dihedral angles. Generally, the valence electrons enhance some of the molecule's normal vibrations (co-operative effects), while they tend to impede others (anti-operative effects). The interplaying of these effects is at the origin of the concerted chemical reactions!

In order to account for the mutual influence of the bond stretches in our example, we can introduce an augmented 'chemical' potential expression, of the form:

$$V(x) = 1/2 \cdot f \cdot (x_1 - x_2)^2 + 1/2 \cdot f \cdot (x_2 - x_3)^2 + k \cdot (x_1 - x_2) \cdot (x_2 - x_3)$$

with an explicit coupling term k between the two bond elongations.

The *Hessian* matrix evaluates then as:

$$F = \begin{pmatrix} f & -f+k & -k \\ -f+k & 2(f-k) & -f+k \\ -k & -f+k & f \end{pmatrix}$$

with the solutions of the equations (eigenvalues λ of $M^{-1/2} \cdot F \cdot M^{-1/2}$):

$$\lambda_1 = \omega_1^2 = (f+k)/m_1$$

*Correspondence: Dr. E. Müller
 28 av. de Florimont
 CH-1006 Lausanne

$$\lambda_2 = \omega_2^2 = (f-k)/m_1 + 2(f-k)/m_2$$

$$\lambda_3 = \omega_3^2 = 0$$

From the two observable values λ_1 and λ_2 , we can determine f and k exactly (μ being the reduced mass $(m_1 \cdot m_2)/(2m_1 + m_2)$) (Table 4).

This leads to the chemically reasonable result given in Table 5.

The force constant f can be taken as a measure of the strength of a bond, whereas the coupling constant k is a measure of the 'chemical effect', i.e. a measure of how much the lengthening of one bond influences the force constant of the other bond.

The same analysis can be extended to other linear molecules; in this way we obtain for CO₂ and F-H-F⁻ the values listed in Table 6).

The solutions of the eigenvalue problem (*vide supra*) lead (with $\omega_s = \omega_1$ and $\omega_a = \omega_2$) to the inequality:

$$\omega_a \geq \omega_s \text{ if } (k/f) \cdot (1 + m_2/m_1) \leq 1$$

which in turn leads to the conclusion that the reversal of the order of the normal vibrations in trihalogenide anions does not only depend on the ratio k/f , but also on the mass ratio m_2/m_1 ; this latter being the decisive term (Table 7).

The Case of More Complicated Molecules

The importance of the coupling terms in the quadratic potential of the harmonic approximation is, therefore, clearly put in evidence. In principle, a coupling term may arise for every internal coordinate pair of a molecule, and in consequence, it is not sufficient to define a force field only in terms of bond, angle, and dihedral angle force constants. The number of required parameters increases with the square of the coordination number of an atom. Whereas the stretching vibrations of a linear A-B-A molecule could be fully described with the help of only two parameters (f and k), a coordination number of 4 (e.g. for an organic C-atom), requires already:

- 4 bond-stretching force constants
- 5 angle-deformation force constants (one of the six angles being linearly dependent upon the other ones)
- 36 coupling terms (corresponding to the $(9 \cdot 8)/2$ nondiagonal elements of the symmetric 9×9 F -matrix)

i.e., a total of 45 parameters. Whereas the bond and angle parameters are more or less transferable from one situation to another, the coupling terms are not, due to their strong dependency upon the actual

Table 1

	$\bar{\nu}_s$ exp.	$\bar{\nu}_a$ exp.	$\bar{\nu}_s/\bar{\nu}_a$ exp.	$\bar{\nu}_s/\bar{\nu}_a$ calc.
CO ₂	1337 cm ⁻¹	2349 cm ⁻¹	0.569	0.522
NO ₂ ⁺	1396 cm ⁻¹	2360 cm ⁻¹	0.591	0.552
CS ₂	658 cm ⁻¹	1533 cm ⁻¹	0.429	0.397
CSe ₂	364 cm ⁻¹	1303 cm ⁻¹	0.279	0.266

(with $\bar{\nu} = \omega/(2 \cdot \pi \cdot c)$ where c is the speed of light).

Table 2

	$\bar{\nu}_s$ exp.	$\bar{\nu}_a$ exp.	$\bar{\nu}_s/\bar{\nu}_a$ exp.	$\bar{\nu}_s/\bar{\nu}_a$ calc.
Cl-Br-Cl ⁻	278 cm ⁻¹	225 cm ⁻¹	1.236	0.728
Cl-I-Cl ⁻	269 cm ⁻¹	226 cm ⁻¹	1.190	0.801

Table 3

	$\bar{\nu}_s$ exp.	$\bar{\nu}_a$ exp.	$\bar{\nu}_s/\bar{\nu}_a$ exp.	$\bar{\nu}_s/\bar{\nu}_a$ calc.
Br-Br-Br ⁻	164 cm ⁻¹	191 cm ⁻¹	0.859	0.577
I-I-I ⁻	114 cm ⁻¹	145 cm ⁻¹	0.786	0.577

Table 4

$$f = 1/2 \cdot (\lambda_1 \cdot m_1 + (\lambda_2 \cdot m_1 \cdot m_2)/(2m_1 + m_2)) = 1/2 \cdot (\lambda_1 \cdot m_1 + \lambda_2 \cdot \mu)$$

$$k = 1/2 \cdot (\lambda_1 \cdot m_1 - (\lambda_2 \cdot m_1 \cdot m_2)/(2m_1 + m_2)) = 1/2 \cdot (\lambda_1 \cdot m_1 - \lambda_2 \cdot \mu)$$

Table 5

	$\bar{\nu}_s$ exp.	$\bar{\nu}_{as}$ exp.	f (mdyn/Å)	k (mdyn/Å)
Cl-Br-Cl ⁻	278 cm ⁻¹	225 cm ⁻¹	1.088	0.528
Cl-I-Cl ⁻	269 cm ⁻¹	226 cm ⁻¹	1.099	0.413
Br-Br-Br ⁻	164 cm ⁻¹	191 cm ⁻¹	0.917	0.345
I-I-I ⁻	114 cm ⁻¹	145 cm ⁻¹	0.748	0.224

Table 6

	$\bar{\nu}_s$ exp.	$\bar{\nu}_{as}$ exp.	f (mdyn/Å)	k (mdyn/Å)
O=C=O	1337 cm ⁻¹	2349 cm ⁻¹	15.497	1.335
F-H-F ⁻	596 cm ⁻¹	1450 cm ⁻¹	2.289	1.682

Table 7

	k/f	m_2/m_1	$(k/f) \cdot (1+m_2/m_1)$
Cl-Br-Cl	0.485	2.25	1.58
Cl-I-Cl	0.376	3.58	1.72
Br-Br-Br	0.376	1.00	0.75
I-I-I	0.299	1.00	0.60
F-H-F	0.735	0.0526	0.77
O=C=O	0.0861	0.75	0.0646

coordination geometry. Furthermore, there are considerable experimental difficulties in the determination of the complete parameter set, as there are only nine experimentally accessible IR frequencies. Even with isotopic experiments there is a lack of data in the absence of symmetry.

An even more difficult situation is present in coordination compounds, which combine, in general, high coordination numbers, variable geometries (remember that the change of a bond length may not only change the force constants of the remaining bonds and angles, but also their equilibrium values!), and an incomplete electronic shell at the central atom. This impedes in most cases a workable empiric parametrization of the force field. Good

quantum chemical calculations (including experimental scaling) are required in order to obtain useful parameters in such cases. The limited transferability of the force field requires furthermore the parameters to be recalculated for every significant change of the equilibrium geometry (*i.e.*, for every stable conformation).

Force-field parameters are also increasingly used in molecular dynamics simulations, *e.g.* to obtain information about the steric course of a chemical reaction. In this context it has to be noted that the quadratic force field, even under valid *Born-Oppenheimer* approximation, only holds in the neighbourhood of the energy minimum for which it was derived. One cannot expect, in consequence, to obtain much use-

ful information about the steric/electronic course of organic or metallo-organic chemical reactions from this type of simulation, unless potential models are used which do account explicitly for the influence of the nuclear motions on the valence-electron system.

In spite of these shortcomings, modern force-field calculations have their advantages too, especially because they allow a rapid and inexpensive calculation of energies and equilibrium structures of stable molecules, given that the necessary parameters are available. Their speed has also permitted most successful applications in the fields of conformational analysis of macromolecules, as well as for the exploration of molecular host/guest relationships. Future development efforts should unambiguously be directed towards more generally valid potential models, which could eventually permit a successful simulation of organic and metallo-organic reaction mechanisms.

Prof. H. Huber, University of Basle, is cordially acknowledged for his critical comments and valuable suggestions.

Bibliography

K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', 3rd edn., John Wiley, New York, 1978.