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DEFINITION AND SYMBOLISM OF MOLECULAR FORCE CONSTANTS

Recommendations (1978)

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DEFINITION AND SYMBOLISM OF MOLECULAR FORCE CONSTANTS

(RECOMMENDATIONS, 1978)

COMMISSION ON MOLECULAR STRUCTURE AND SPECTROSCOPY[†]

Definitions and notations for force constants often vary between different authors. This arises from the fact that force constant problems have wide varieties and different aims in their applications. At the same time the whole subject is still constantly changing. Therefore it seems unwise to attempt to fix all minor details at the present stage. For these reasons, some conventions of fundamental importance will be given below as general guidelines, minor details being left to each person, who should fit them to the specific problem to be studied in conformity with the suggested guidelines as far as possible. This document deals principally with harmonic force constants. Anharmonic force constants are mentioned in an Appendix.

Force constants are the coefficients in an expansion of the intramolecular potential function in terms of a definite set of coordinates the values of which define the deformation of the molecule away from its equilibrium configuration. In order to define force constants, one has to indicate both the definition of each coordinate and the expansion of the potential.

1. The definitions and symbols of force constants used should always be clearly defined in each paper.

This self-evident comment must be the first recommendation, because confusion always results from the unspecified use of definitions and notations.

Often the same notation is used with different meanings by different authors, and hence the particular notation used in a paper should be clearly defined even when the variation is small, perhaps only in the coefficients or in the numbering.

2. Among various kinds of force field, the most important is the general force field, GFF, which is expressed in terms of 3N-6 basis coordinates:

$$V = \frac{1}{2} \sum_{ij} f_{ij} \ (or \ F_{ij}) \cdot S_i \cdot S_j \tag{1}$$

We recommend that the force constants in this force field be denoted by f or F (preferably by f). The basis coordinates S (or sometimes s) may be internal symmetry coordinates, local symmetry coordinates or any others most suitable to the problem, but the number of the coordinates has to be reduced to 3N-6 (3N-5 for linear molecules), N being the number of atoms in the molecule.

Since many kinds of basis coordinate systems are possible for the GFF of a molecule, the distinction should be made clear by the use of subscripts or superscripts.

The choice of coordinate in the GFF strongly depends on the symmetry of the molecule, but it is not uniquely given by the symmetry alone. This is easily illustrated by the simple example that the most suitable coordinates are not always the same for CH_3D and CH_3I or for CH_2D_2 and CH_2I_2, although the two molecules belong to the same symmetry group.

3. • *The other extreme and fundamental force field is the internal valence force field, IVFF, which is expressed in terms of bond-stretching, angle-bending, torsional and other displacements directly connected to the structural parameters of the molecule. We recommend that the force constants of this molecular field be denoted by k or K (preferably by k) in the form of*

$$V = \frac{1}{2} \sum_{ij} k_{ij} \ (or \ K_{ij}) \cdot R_i \cdot R_j \ , \tag{2}$$

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where R denotes the internal valence coordinates. When the internal valence force field itself is the GFF, either k (or K) or f (or F) can be used for the force constant.

The notations R may be replaced by other specified symbols, such as Δr, $\Delta \phi$ or others. Subscripts or superscripts are used for defining minor details of the coordinates and the force constants, in the same manner as for f or F described in paragraph 2.

The most conspicuous difference between the IVFF and the GFF lies in the fact that the former suffers from redundancy such as among the bending coordinates of the bond angles around an atom, or among the stretching and bending coordinates in a ring structure. Therefore not all the force constants of the IVFF can be determined, unless assumptions are made about the force constants related to the redundancy (an example is shown in Appendix 3).

For molecules with no angle redundancies (e.g. H_2O, NH_3) the IVFF representation is a possible choice for the GFF representation. In such cases it is open to the author to use either the symbol k or the symbol f for his force constants.

4. Between the two extremes of the IVFF and the GFF described above, there might be a number of intermediate systems which consist of more than 3N-6 coordinates. The force constants in these systems should be expressed by k or K with appropriate subscripts or superscripts, in the sense that it is a modified IVFF which is not yet reduced to a GFF.

The intermediate systems described above can be derived from, or can be correlated with, the IVFF by an orthogonal transformation. The number of coordinates in the system is reduced from that of the IVFF by the number of redundant coordinates considered.

5. We recommend that the force constants for the Urey-Bradley force field, UBFF, be denoted by upper-case letters, K, H, F and Y for bond-stretching, angle-bending, nonbonded repulsive and torsional motions, respectively.

When there is danger of confusion between the force constants in the UBFF and those in other force fields, it is advisable to use lower-case letters, f or k, for the latter. When F or K is used, the definition should be clearly stated in the paper.

6. We recommend that the geometry of the molecule used in the calculation of force constants be clearly shown in the paper.

Some of the force constants are independent of the geometry, whereas others are clearly related with the geometry and their numerical values have meanings only when the geometry is clearly specified. Bond lengths, bond angles and other molecular parameters used in the calculation should therefore be mentioned in the paper, when necessary. When the value of the equilibrium distance is not known, an estimated value may be used. In any case, the value used in the calculation should clearly be mentioned.

7. The force constants for angle variation depend upon the choice of the coordinates, for which the following definitions are recommended:

(i) For the coordinate of angle-bending, the deformation of bond angle itself is taken, namely $\Delta \phi$ but not $r\Delta \phi$, though the latter has often been used in the past.

(ii) For the coordinate of out-of-plane bending:

$$\Delta \theta_{i-jkl} = \frac{\Delta z_j}{r_{eij}} \sin \Phi_{kil} \qquad (3)$$

instead of

$$\Delta \theta_{i-jkl} = \frac{\Delta z_j}{r_{eij}} \qquad (4)$$

where the numbering of the atoms is given in Fig. 1. Φ_{kil} denotes the angle between the bonds ik and il, Δz_j the perpendicular distance of the atom j from the instantaneous plane ikl and r_{eij} the equilibrium length of the bond ij.

(iii) For the coordinate of torsion:

$$\Delta t = \sum_{N} \Delta \tau_{ijkl} / N , \qquad (5)$$

where $\Delta \tau$ denotes the change in the torsional angle between the bonds ji and kl belonging to the two rotating groups (See Fig. 2); τ_{ijkl} is thus the dihedral angle between planes ijk
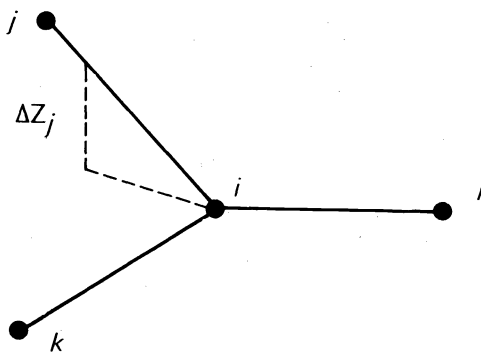
$$\Delta Z_j$$

Fig. 1

and jkl. N is the number of torsional angles formed by the possible combinations of the bonds adjacent to the torsional axis (e.g. N is 2 for NH_2-OH and 4 for NH_2-NH_2).

The designation of angle coordinates by $\Delta\phi$ has the disadvantage that the dimensions of the force constants are different from those of bond-stretching force constants, whereas it has the advantages that the redundancy is more easily treated with these coordinates and moreover that an arbitrary choice of the value of r, when the adjacent bonds are inequivalent, can be avoided.[*]

The definition of the out-of-plane bending coordinates described above has the advantage that the bending displacement is defined uniquely, independently of the choice of the j numbering of the surrounding atoms.
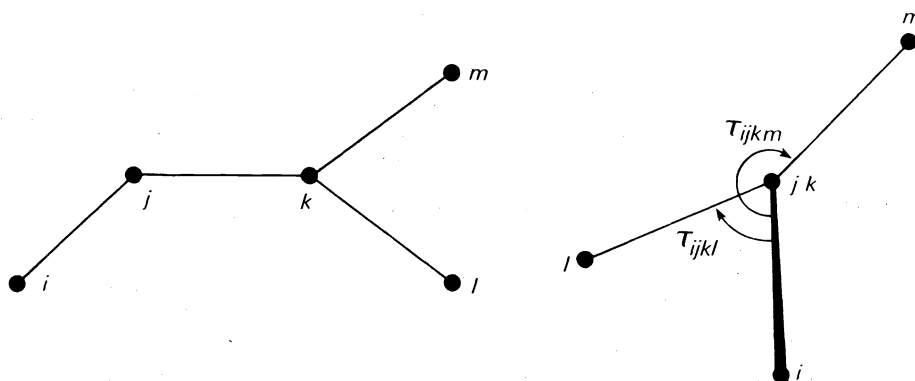

Figure 2

8. The signs of the coordinates in the molecular force field of any type should be defined clearly, because they are indispensable for the assignment of the signs of the interaction force constants with other coordinates.

(i) With the atoms arranged as in Figure 2, viewed along the bond jk with the atom j nearer to the observer than atom k, the sign of the torsional coordinate $\Delta\tau_{ijkl}$ is taken to be positive if the torsional angle τ_{ijkl} increases, where τ_{ijkl} is defined as the angle from the projection of bond ij to the projection of bond kl, traced in the clockwise sense. Thus $\Delta\tau_{ijkl} = \Delta\tau_{lkji}$.

(ii) The sign of the out-of-plane bending coordinate is defined by the direction of the vector Δz_j, which is taken from the plane ikl to the atom j, as shown in Fig. 1: thus

$$\Delta\theta_{i-jkl} = -\Delta\theta_{i-kjl} .$$

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[*] In molecules of type XY_n, where the Y atoms are symmetrically equivalent and all are attached to the X atom, so that all the X-Y distances are equal (e.g., CO_2, H_2O, NH_3, CH_4 and SF_6), the force constants can be obtained from the frequencies even when we have no knowledge of the bond length, if we use $r\Delta\phi$ for the bending coordinate instead of $\Delta\phi$. In such cases $r\Delta\phi$ may be used as an exception to recommendation no. 7.

(iii) The sign of the CH_2 rocking, wagging or twisting coordinate of the XCH_2Y-part of a large molecule is taken to be positive if, viewing the XCH_2Y-group from the direction perpendicular to the HCH plane, with the atom X nearer to the observer, as shown in Fig. 3, the HCH group rotates in the clockwise direction (for rocking), the H atoms move away from the X atom to increase the XCH angles (for wagging), or the H atom on the right comes nearer and the H atom on the left moves away (for twisting). In other words, viewing from above, with the X atom nearer to the observer, the HCH group rotates in the clockwise direction for the twisting coordinate. Thus it should be noted that

$$S_{XCH_2Y}^{rock} = -S_{YCH_2X}^{rock}, \qquad S_{XCH_2Y}^{wag} = -S_{YCH_2X}^{wag}, \qquad S_{XCH_2Y}^{twist} = S_{YCH_2X}^{twist}$$

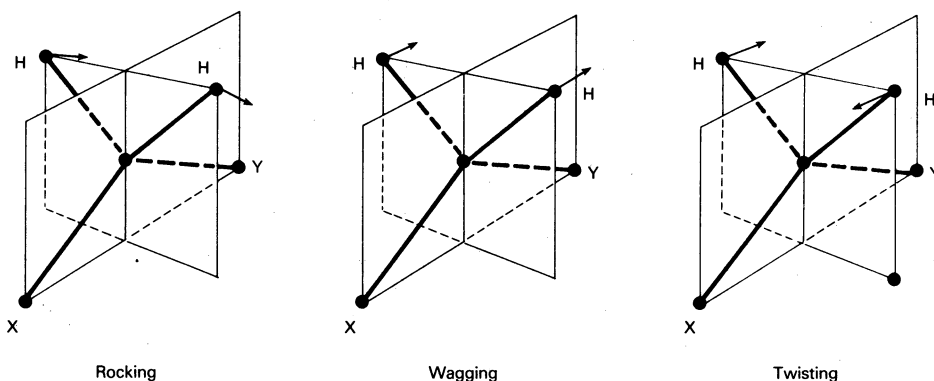Rocking   Wagging   Twisting

Figure 3

(iv) The following definitions of the symmetry coordinates of the CH_3 degenerate stretching (ds), degenerate deformation (dd), and degenerate rocking (dr) modes are recommended:

In the CH_3XY molecule shown in Fig. 4, the H atom located at the <u>trans</u> position relative to Y is numbered as 1. The H atoms 2 and 3 are numbered in the <u>clockwise</u> direction, viewing the atoms along the bond XC with the atom X nearer to the observer than C. Two components of the ds, dd, and dr symmetry coordinates are then expressed as:

$$S_{ds} = \Delta(2r_1 - r_2 - r_3)/\sqrt{6}$$
$$S'_{ds} = \Delta(r_2 - r_3)/\sqrt{2}$$
$$S_{dd} = \Delta(2\alpha_{23} - \alpha_{31} - \alpha_{12})/\sqrt{6}$$
$$S'_{dd} = \Delta(\alpha_{31} - \alpha_{12})/\sqrt{2}$$
$$S_{dr} = \Delta(2\beta_1 - \beta_2 - \beta_3)/\sqrt{6}$$
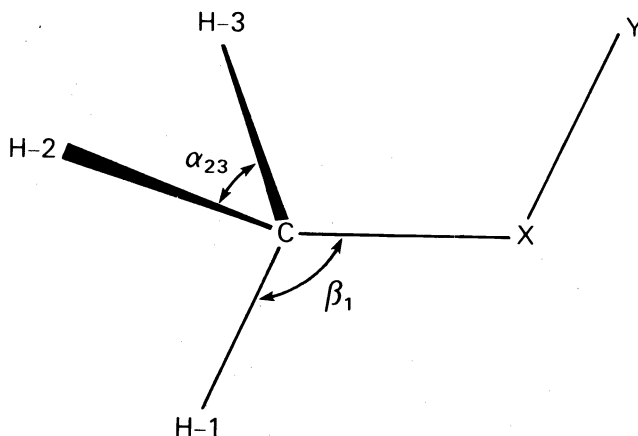$$S'_{dr} = \Delta(\beta_2 - \beta_3)/\sqrt{2}$$

Fig. 4

APPENDIX

1. For the specification of force fields of molecules it is inevitable that the definitions and symbols of anharmonic force constants be considered, in addition to the quadratic force constants described above. The expansion of the anharmonic potential function can be carried out in an unrestricted Taylor series or in a restricted sum in which each cross term appears only once. The problem has been considered by several authors and is left for further exploration. The definitions in the foregoing recommendations for harmonic force constants are closely connected to the unrestricted expansion of the anharmonic potential function in the form of the Taylor series.

2. An attempt to make the dimensions of all the force constants identical by the use of dimensionless coordinates $\Delta r/r$ has been pursued with promising results. Considering, however, that there still are a number of points to be examined, this suggestion should be more thoroughly explored before it is recommended as an IUPAC standard.

3. An illustrative example:

The following example will illustrate the relation between the IVFF and the GFF through redundancy. In the in-plane vibrations of the H_2CO molecule the IVFF for angle deformation is expressed by (See Fig. 5)

$$V = \frac{1}{2}k_{11}(\Delta\phi_1)^2 + \frac{1}{2}k_{22}[(\Delta\phi_2)^2 + (\Delta\phi_3)^2] + k_{12}(\Delta\phi_1\Delta\phi_2 + \Delta\phi_1\Delta\phi_3) + k_{23}\Delta\phi_2\Delta\phi_3 \qquad (6)$$
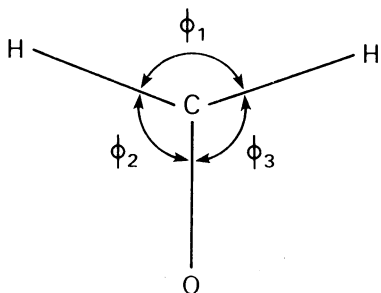

Fig. 5

On the other hand, by the use of symmetry coordinates

$$S_1 = (2\Delta\phi_1 - \Delta\phi_2 - \Delta\phi_3)/\sqrt{6}$$
$$S_2 = (\Delta\phi_2 - \Delta\phi_3)/\sqrt{2} \qquad (7)$$

and a redundant coordinate

$$S_3 = (\Delta\phi_1 + \Delta\phi_2 + \Delta\phi_3)/\sqrt{3} \qquad (8)$$

the potential function Eq. (5) is transformed to

$$V = \frac{1}{2}f_{11}S_1^2 + \frac{1}{2}f_{22}S_2^2 + \frac{1}{2}f_{33}S_3^2 + f_{13}S_1S_3 \qquad (9)$$

where

$$f_{11} = (2k_{11} + k_{22} - 4k_{12} + k_{23})/3$$
$$f_{22} = k_{22} - k_{23} \qquad (10)$$
$$f_{33} = (k_{11} + 2k_{22} + 4k_{12} + 2k_{23})/3$$
$$f_{13} = (k_{11} - k_{22} + k_{12} - k_{23})\left(\frac{\sqrt{2}}{3}\right).$$

Since S_3 is zero by the redundancy, the third and the fourth terms of Eq. (9) drop out automatically from the potential function and the remaining part becomes precisely the GFF of the molecule. It must be emphasized that the force constants f_{33} and f_{13} cannot be obtained by experiment. In other words, it is impossible to evaluate the force field expressed by Eq. (6), unless some assumptions are made on f_{33} and f_{13}. A similar situation is encountered whenever redundancy is involved in the coordinates.