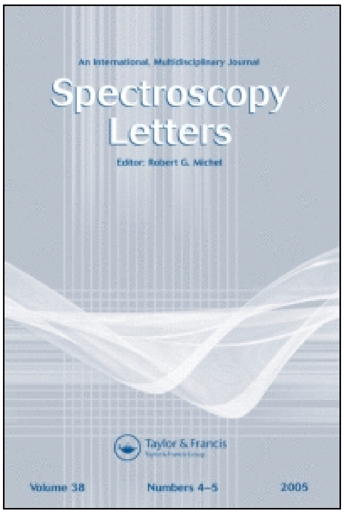

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OUT-OF-PLANE VIBRATIONS OF BENZENE: A VALENCE FORCE FIELD CALCULATION USING CORRECT TORSIONAL COORDINATES

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Normal coordinate calculations are widely used by spectroscopists either to check the assignment of the fundamental vibrations or to derive a potential function representing the observational data of the molecules investigated.

The first step in such a calculation is the construction of the inverse kinetic energy matrix, or G matrix. This is readily performed by using the B matrix whose elements define the transformation from cartesian to internal coordinates; as known, it is of most physical significance to state the force constants in terms of the latter coordinates. The B matrix is in turn evaluated using $\underline{s}$ vectors, which are defined for any internal coordinate, e.g. bond stretch, valence angle bend, out-of-plane wag, linear valence angle bend and torsion (1). As far as the torsional coordinates are concerned, the $\underline{s}$ vectors were defined in the past considering a hydrogen-peroxide-like molecule (2). Later, for those molecules in which more than one alternative in choosing hydrogen-peroxide-like torsion may exist,a linear combination of them was proposed (3).

Recently, some papers (4-6) have dealt with a correct derivation of these $\underline{s}$ vectors for torsional internal coordinates (for example, a complete treatment on torsions has been presented in Ref. (5)). The use of the new defined s vectors clearly leads to different G matrix elements and therefore these torsional internal coordinates bear in turn to a set of force constants quite different from those calculated in the previous way.

In spite of what mentioned, only few studies of such new torsional coordinates are reported at present in the literature and all of them are referred to alkanes (3-5). Since the aromatic molecules make an important class of organic compounds and many authors are interested in determining suitable molecular potential functions for those, we have calculated a valence force field for the out-of--plane vibrations of benzene using the correct torsional internal coordinates above mentioned.

In order to do that, it was written a subroutine "TORS" (7) which calculates the B matrix elements relative to the torsional internal coordinates using the formulas given in Ref. (5); such a subroutine, which incidentally is completely general and therefore applicable to molecules of any geometry and complexity,can be easily inserted in programs which compute the G matrix by means of the s vector method.

As said above, the torsional internal coordinates of benzene were previously selected as a linear combination of two hydrogen--peroxide-like torsions; for example, the torsion z_1 around the bond connecting atoms 1 and 2 (see Fig. 1) was defined as:

$$\Delta z_1 = 1/\sqrt{2}(\Delta z_{7-1-2-3}+\Delta z_{6-1-2-8})$$

and the s vectors were thus calculated for the atoms 1,2,3,6,7 and 8. Following the correct derivation of torsion (see Ref. (5)) the same internal coordinate is:

$$\Delta z_1 = \Delta z_{(6,7)-1-2-(3,8)}$$

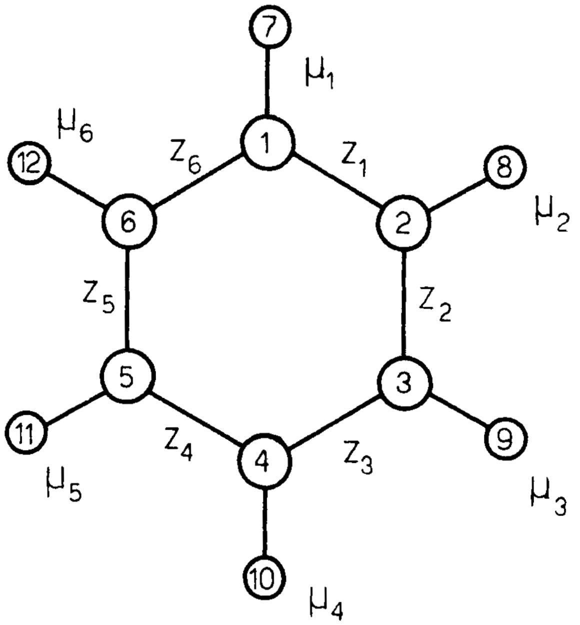

FIG. 1

Out-of-Plane Internal Coordinates for Benzene.

and the s vectors are now calculated for the groups (6,7) and (3,8), and for the atoms 1 and 2.

Computations were carried out on a CDC Cyber 76 computer; the experimental frequencies and the force constants related to the out-of-plane bending vibrations were taken from Ref. (8). The structural parameters used in the calculations are the following: i) bond length: C-C = 1.39 Å, C-H = 1.08 Å; ii) angles: all 120°; iii) atomic masses: see Ref. (9). Since our interest is mainly concerned with torsions, the force constants (diagonal and interactions) which are only connected with the out-of-plane bending coordinates (H_μ and f^o_μ, f^m_μ, f^p_μ) were constrained to be constants, while those related to the torsional coordinates were refined. Few iterations were performed to obtain a set of force constants which presents a close fit

TABLE I

Force Field for Out-of-Plane Benzene Vibrations [a]

Force constant [b]	Ref. (8)	This work	
		Value	Standard error
H_μ	0.3237	0.3237	-
H_z	0.1190	0.2575	0.0014
f^o_μ	0.0184	0.0184	-
f^m_μ	-0.0235	-0.0235	-
f^p_μ	-0.0227	-0.0227	-
$f^o_{z\mu}$	0.0273 [c]	-0.0381	0.0003
$f^m_{z\mu}$	-	-	-
$f^p_{z\mu}$	-	-	-
f^o_z	-0.0388	-0.0777	0.0015
f^m_z	-	0.0260	0.0009
f^p_z	-	-	-

[a] Units in Mdyn. Å/rad^2.

[b] Force constants are labelled as in Ref. (8).

[c] In Ref. (8), the interaction force constants $f^o_{z\mu}(z_i,\mu_i)$ and $f^{o'}_{z\mu}(z_i,\mu_{i+1})$ were calculated separately; according to Wilson (1) we have assumed here $f^o_{z\mu} = -f^{o'}_{z\mu}$.

TABLE II

Observed and Calculated Frequencies (cm^{-1}) for Out-of-Plane Vibrations of Benzene

SYMMETRY SPECIES	$^{12}C_6H_6$ OBS.[a]	$^{12}C_6H_6$ CALC.	$^{13}C_6H_6$ OBS.[a]	$^{13}C_6H_6$ CALC.	C_6D_6 OBS.[a]	C_6D_6 CALC.
B_{2g}	989	989	981	981	830	828
	703	705	680	683	599	596
A_{2u}	670	674	669	672	496	495
E_{2u}	966	968	958	956	789	793
	404	404	392	392	351	348
E_{1g}	849	850	842	843	664	661

[a] Taken from Ref. (8).

between observed and calculated frequencies; the results are reported in Tables I and II. In respect of the force field of Ref. (8), the additional interaction term f_z^m, which is supported by the results of the Jacobian, variance-covariance and correlation matrices, has been here introduced.

In conclusion we propose a new force field for the out-of-plane benzene vibrations as function of the G matrix derived from a correct set of $\underline{s}$ vectors. We feel that such a force field can be transferred with benefit to other molecules containing phenyl-rings for which the evaluation of a molecular potential function is of interest.

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