

On the Rotational Contributions to the Dipole-Moment Derivatives

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In order to get dipole-moment derivatives, $\partial \mu / \partial S_j$, that are free from rotational contributions, we used Crawford's method applied to a new type of reference molecule. The agreement with earlier calculated rotational correction terms is good, the applicability of the new reference molecule is wider. The rotational contributions to the $\partial \mu / \partial S_j$ -quantities are presented for a number of C_{2v} - and C_{3v} -type molecules.

INTRODUCTION

It is useful to interpret the experimental infrared absorption intensities in terms of dipole-moment derivatives with respect to the symmetry coordinates.

In the case of a molecule with a nonvanishing permanent moment, the motions represented by those symmetry species that include a molecular rotation produce $\partial \mu / \partial S_j$ -quantities containing a contribution from the rotation of the permanent dipole moment.

In comparing data on different isotopic species or on closely related compounds, the only appropriate intensity parameters are those which are corrected for rotational contributions.

This contribution arises from the condition that the angular and linear momentum of the entire molecule is conserved in a perturbation of the equilibrium configuration under vibration. This requires any alteration in the angular or linear momentum, resulting from a symmetry distortion, to be exactly compensated by an amount of rotation or translation of the whole molecule with the same frequency. Since translational motions do not affect the dipole moment of a molecule, only the rotational motions need be considered. As we know from pure rotational spectra, a molecular rotation contributes to the absorption intensity if the molecule has a permanent moment.

In the derivation of the intensity sum rules Crawford (1) has given the mathematical framework to calculate the difference in rotational contribution between two isotopic molecules. Subsequently Dickson, Mills and Crawford (2) proposed a method to obtain the absolute rotational correction for $\partial \mu / \partial S$ -quantities. However, the choice of the rotational free reference molecule needed for such a calculation leads to difficulties in some cases.

Here we present a new type of reference molecule, with a wider applicability.

THE ROTATIONAL CORRECTION

The experimental integrated intensity, A_i , of the i th fundamental absorption band is related to the square of the dipole derivative, $\partial \mu / \partial Q_i$, with respect to the i th normal

coordinate, Q_i , by

$$A_i = (N_0 \pi g_i / 3c^2) (\partial \mathbf{u} / \partial Q_i)^2 \quad (1)$$

in the harmonic-oscillator-linear-dipole approximation (3). In Eq. (1) N_0 is Avogadro's number, c the speed of light, \mathbf{u} the molecular dipole-moment vector, and g_i the degree of degeneracy of the i th fundamental.

The normal coordinates are defined in terms of a set of internal coordinates, \mathbf{R} , through the \mathbf{L} -matrix: $\mathbf{R} = \mathbf{LQ}$ (4). Thus we can write

$$\frac{\partial \mathbf{u}}{\partial Q_i} = \sum_j L_{ji} \frac{\partial \mathbf{u}}{\partial R_j},$$

or in matrix notation,

$$(\partial \mathbf{u} / \partial \mathbf{Q}) = \tilde{\mathbf{L}} (\partial \mathbf{u} / \partial \mathbf{R}), \quad (2)$$

$\tilde{\mathbf{L}}$ being the transposed \mathbf{L} -matrix.

In the interpretation of intensity data one usually determines the dipole-moment derivatives with respect to symmetry coordinates (5), which are taken as linear combinations of the internal coordinates, $\mathbf{S} = \mathbf{UR}$, leading to

$$(\partial \mathbf{u} / \partial \mathbf{Q}) = \tilde{\mathbf{L}} \tilde{\mathbf{U}} (\partial \mathbf{u} / \partial \mathbf{S}). \quad (3)$$

Our aim is to separate the contribution originating from the compensating rotation accompanying a vibration from the dipole-moment derivatives, obtained from Eq. (2) or (3). This requires the availability of a reference molecule in which vibration produces no compensating rotatory motion. The definition of such a reference molecule is given in the following section.

The dipole-moment derivatives obtained from Eq. (3) will be denoted by $(\partial \mathbf{u} / \partial \mathbf{S})_A$, where the subscript A refers to the actual molecule under consideration. The theoretical quantity needed will be denoted by $(\partial \mathbf{u} / \partial \mathbf{S})_R$, where the subscript R stands for the reference molecule. The difference between these two parameters is the rotational correction, or in formula:

$$(\partial \mathbf{u} / \partial \mathbf{S})_R = (\partial \mathbf{u} / \partial \mathbf{S})_A - \mathbf{V}_{AR}. \quad (4)$$

The columnvector, \mathbf{V}_{AR} , can be evaluated with the help of two additional coordinate sets:

\mathbf{X} : the vector of the $3N$ Cartesian displacement coordinates (N is the number of atoms in the molecule).

$\boldsymbol{\varrho}$: the external coordinates (the six translations and rotations). The transformation matrices between $\boldsymbol{\varrho}$, \mathbf{R} , \mathbf{S} , and \mathbf{X} are defined as follows.

$$\begin{aligned} \mathbf{R} &= \mathbf{BX}, & \mathbf{B} &= (\partial \mathbf{R} / \partial \mathbf{X}), & \mathbf{A}^* &= (\partial \mathbf{X} / \partial \mathbf{R})^*, \\ \mathbf{S} &= \mathbf{UBX}, & \mathbf{UB} &= (\partial \mathbf{S} / \partial \mathbf{X}), & \mathbf{A}^* \tilde{\mathbf{U}} &= (\partial \mathbf{X} / \partial \mathbf{S})^*, \\ \boldsymbol{\varrho}^* &= \boldsymbol{\beta}^* \mathbf{X}, & \boldsymbol{\beta}^* &= (\partial \boldsymbol{\varrho}^* / \partial \mathbf{X}), & \boldsymbol{\alpha}^* &= (\partial \mathbf{X} / \partial \boldsymbol{\varrho}^*). \end{aligned} \quad (5)$$

The matrices and vectors marked with an asterisk are isotope-dependent. The properties of these transformation matrices for a given isotope are:

$$\begin{aligned} \mathbf{B} \boldsymbol{\alpha}^* &= \mathbf{O}, & \boldsymbol{\beta}^* \mathbf{A}^* &= \mathbf{O}, & \mathbf{B} \mathbf{M}^{*-1} \tilde{\mathbf{B}} &= \mathbf{G}^*, \\ \mathbf{B} \mathbf{A}^* &= \mathbf{E}_{3N-6}, & \boldsymbol{\beta}^* \boldsymbol{\alpha}^* &= \mathbf{E}_6, & \boldsymbol{\beta}^* \mathbf{M}^{*-1} \tilde{\boldsymbol{\beta}}^* &= \mathbf{N}^*, \\ \mathbf{A}^* \mathbf{B} + \boldsymbol{\alpha}^* \boldsymbol{\beta}^* &= \mathbf{E}_{3N}, & \tilde{\boldsymbol{\alpha}}^* \mathbf{M}^* \boldsymbol{\alpha}^* &= \mathbf{N}^{*-1}, \end{aligned} \quad (6)$$

where \mathbf{G} is Wilson's kinetic-energy matrix (4), \mathbf{M} is the diagonal matrix of the atomic masses, and \mathbf{N} is a 6×6 diagonal matrix containing the reciprocals of both the molecular mass and the principal moments of inertia.

Crawford (1) derived a relation between the \mathbf{A} -matrices of two different isotopes. For the \mathbf{A} -matrix of the reference molecule this relation reads

$$\mathbf{A}_R = \mathbf{A}_A - \alpha_R \beta_R \mathbf{A}_A, \quad (7)$$

where the subscripts have the meaning as defined above.

From Eq. (7) one easily obtains

$$\mathbf{U} \tilde{\mathbf{A}}_R (\partial \mathbf{u} / \partial \mathbf{X}) = \mathbf{U} \tilde{\mathbf{A}}_A (\partial \mathbf{u} / \partial \mathbf{X}) - \mathbf{U} \tilde{\mathbf{A}}_A \beta_R \tilde{\alpha}_R (\partial \mathbf{u} / \partial \mathbf{X}), \quad (8)$$

which is equivalent to Eq. (4). So the column vector of the rotational corrections can be written as

$$\mathbf{V}_{AR} = \{\mathbf{U} \tilde{\mathbf{A}}_A \beta_R\} \{\tilde{\alpha}_R (\partial \mathbf{u} / \partial \mathbf{X})\}. \quad (9)$$

Since translational motions do not change \mathbf{u} , we may rewrite the second part of \mathbf{V}_{AR} (1), giving

$$\tilde{\alpha}_R \frac{\partial \mathbf{u}}{\partial \mathbf{X}} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ (\mu_0)_y \mathbf{k} - (\mu_0)_z \mathbf{j} \\ (\mu_0)_z \mathbf{i} - (\mu_0)_x \mathbf{k} \\ (\mu_0)_x \mathbf{j} - (\mu_0)_y \mathbf{i} \end{bmatrix}, \quad (10)$$

where $(\mu_0)_x$ denotes the x -component of the permanent dipole moment and \mathbf{i} , \mathbf{j} , and \mathbf{k} are the Cartesian unit direction vectors. In the case of symmetry this column vector

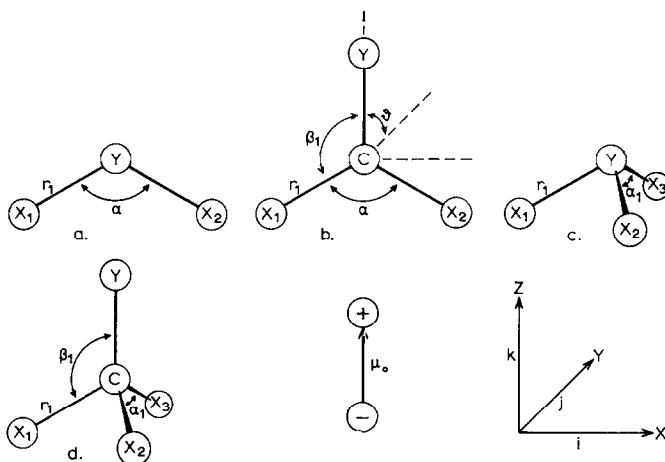


FIG. 1. Definition of internal coordinates in (a) bent X_2Y molecules, (b) X_2CY molecules, (c) pyramidal X_3Y molecules, (d) X_3CY molecules. Definition of dipole-moment direction and Cartesian coordinate axes.

Table I. Rotational corrections and symmetry coordinates in methyl halides.^a

$S_{4x} = 6^{-\frac{1}{2}}(2\Delta r_1 - \Delta r_2 - \Delta r_3)$ $S_{5x} = 6^{-\frac{1}{2}}(2\Delta \alpha_1 - \Delta \alpha_2 - \Delta \alpha_3)$ $S_{6x} = 6^{-\frac{1}{2}}(2\Delta \beta_1 - \Delta \beta_2 - \Delta \beta_3)$							
X_3CY	μ_o (D)	Reference molecule with $m_X = 0$			Reference molecule with $m_C, m_Y \times 1000$		
		v_{4x}	v_{5x}	v_{6x}	v_{4x}	v_{5x}	v_{6x}
H ₃ CF	-1.81	+0.0798	+0.0894	-0.2085	+0.0797	+0.0892	-0.2082
D ₃ CF	-1.81	+0.1123	+0.1312	-0.3220	+0.1120	+0.1310	-0.3214
H ₃ CCl	-1.87	+0.0711	+0.0685	-0.1310	+0.0710	+0.0684	-0.1308
D ₃ CCl	-1.87	+0.1073	+0.1052	-0.2073	+0.1071	+0.1050	-0.2069
H ₃ CBr	-1.80	+0.0651	+0.0586	-0.1003	+0.0650	+0.0586	-0.1002
D ₃ CBr	-1.80	+0.1009	+0.0914	-0.1587	+0.1007	+0.0913	-0.1584
H ₃ CI	-1.62	+0.0542	+0.0471	-0.0755	+0.0541	+0.0471	-0.0754
D ₃ CI	-1.62	+0.0850	+0.0742	-0.1199	+0.0849	+0.0740	-0.1197
^a Geometrical parameters are the same as in Ref. 12.							

often reduces to a very simple form, e.g., in the case of C_{2v} or C_{3v} symmetry there is only a nonzero component of the permanent moment along the main axis of symmetry.

The $U\tilde{A}_R\tilde{\beta}_R$ term gives the translation and rotation set up in the reference molecule, when its atoms execute the displacements appropriate to a symmetry distortion S in the actual molecule. The A_A -matrix can be calculated from (1)

$$A_A = M_A^{-1}\tilde{B}G_A^{-1}. \quad (11)$$

The β_R -matrix can be written easily.

Thus, after defining an appropriate reference molecule the calculation of the rotational contributions is straightforward.

THE REFERENCE MOLECULE

The determination of the rotational corrections is only possible if we can define a reference molecule (a hypothetical molecule, being an isotope of the original one), which possesses rotation-free internal coordinates.

Table II. Definition of symmetry coordinates and rotational contributions in $\text{Br}_3\text{CH/D}$.^a

$S_{4x} = 6^{-\frac{1}{2}}(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)$ $S_{5x} = 6^{-\frac{1}{2}}(2\Delta r_1 - \Delta r_2 - \Delta r_3)$ $S_{6x} = 6^{-\frac{1}{2}}(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)$						
$\mu_o(\text{D})$	Reference molecule with $m_{\text{Br}}=0$			Reference molecule with $m_{\text{C}}, m_{\text{H/D}} \times 100\,000$		
	V_{4x}	V_{5x}	V_{6x}	V_{4x}	V_{5x}	V_{6x}
Br_3CH +0.99	+0.8049	+0.1251	-0.0104	+0.8011	+0.1251	-0.0097
Br_3CD +0.99	+0.8014	+0.1229	-0.0123	+0.7994	+0.1229	-0.0119
^a Geometrical parameters from Ref. 13.						

The only rotation-free molecule known in the literature is a molecule in which isotopes of zero mass are introduced for atoms which are not situated on the main molecular symmetry axis. For example, in the case of X_2CY -molecules (2, 6), where $X, Y = \text{H, D, F, Cl, Br, and I}$, one has used as a reference molecule the isotopic molecule containing zero X -masses. During all vibrations of such a reference molecule the CY -bond will maintain a fixed direction and thus there is no compensating rotational motion. Also

Table III. Bent triatomic molecules X_2Y .

$S_3 = 2^{-\frac{1}{2}}(\Delta r_1 - \Delta r_2)$					
X_2Y	$r_{XY}(\text{\AA})$	$\alpha(^{\circ})$	Ref.	$\mu_o(\text{D})$	$V_3(\text{D/\AA})$ $m_j \times 1000$
H_2O	0.9584	104.45	14	-1.85	-0.0771
D_2O	0.9584	104.45	14	-1.85	-0.1436
H_2S	1.34	92.33	15	-0.97	-0.0156
D_2S	1.34	92.33	15	-0.97	-0.0302
O_2S	1.433	119.33	15	+1.47	+0.1810

Table IV. Definition of symmetry coordinates and rotational contributions
in X_2CY -molecules.

$S_4 = 2^{-\frac{1}{2}}(\Delta r_1 - \Delta r_2)$ $S_5 = 2^{-\frac{1}{2}}(\Delta \rho_1 - \Delta \rho_2)$ $S_6 = \Delta \theta$ (out-of-plane)								
X_2CY	$r_{CX}(\text{\AA})$	$r_{CY}(\text{\AA})$	$\alpha(^{\circ})$	Ref.	$\mu_0(D)$	Reference molecule ($m_C, m_Y \times 10\ 000$)		
						V_4	V_5	V_6
H_2CO	1.09	1.213	120	16	-2.33	+0.1188	-0.3419	-0.2279
D_2CO	1.09	1.213	120	16	-2.33	+0.1619	-0.5152	-0.3575
F_2CO	1.312	1.174	108.0	17	-0.95	-0.0385	-0.4750	-0.3959
Cl_2CO	1.746	1.166	111.3	7	-1.18	-0.1244	-0.7109	-0.6010
Br_2CO	2.05	1.13	110	7	-1.38	-0.2166	-0.9010	-0.7967
F_2CS	1.312	1.56	108.0	10	-0.05	+0.0020	-0.0186	-0.0157
Cl_2CS	1.746	1.56	111.3	10	-0.28	-0.0079	-0.1400	-0.1111

in the case of X_2CY (7-II) molecules ($X = H, D, F, Cl, Br; Y = O, S$) the introduction of an X -isotope of zero mass provides a usable reference molecule.

However, this procedure cannot be followed in bent X_2Y - or pyramidal X_3Y -molecules. Introduction of an X -isotope with zero mass in such molecules leads to indefinite elements of the β_R -matrix, thus prohibiting the calculation of the rotational corrections (see Eq. (9)).

In order to overcome these difficulties, we propose the following reference molecule. Replace the atoms of the actual molecule which are situated on the main symmetry axis by isotopes that are a factor of a thousand or more heavier than the original atoms.¹ In such a reference molecule, the compensating rotational motions are negligible, because of the large masses of the substituted isotopes. This is also valid in the case of X_2Y - and X_3Y -molecules, while no difficulties arise in the calculation of the elements of β_R . In the case of X_3CY -molecules (see Fig. 1d) with $X = H$ or D and Y a halogen atom, a multiplication factor of 1000 for the C and Y atom is very satisfactory, due to the low X -masses. It can be seen from Table I that the use of this reference molecule leads to results which agree within 1% with those obtained using a reference molecule with zero X -masses.

If the X -atom has a large mass e.g., Br_3CH , the multiplication factor must be 10 000 or even more (see Fig. 2 and Table II).

¹ If three or more atoms are situated on the main symmetry axis, only two adjacent nonterminal atoms must be replaced by heavy isotopes (e.g., the two C atoms in methylcyanide).

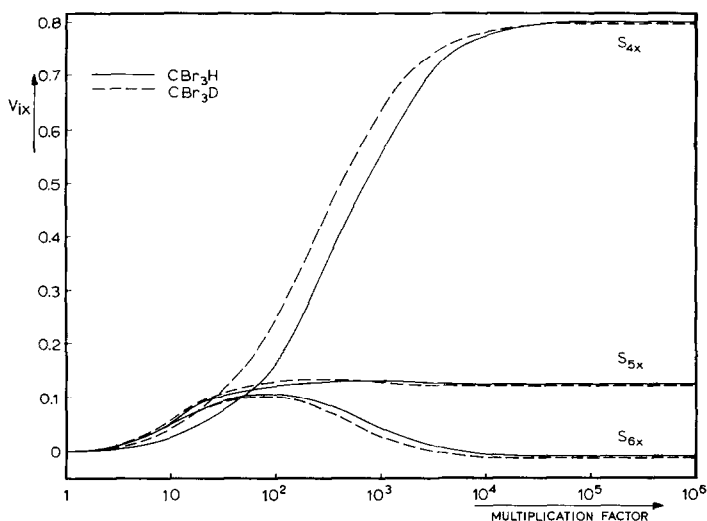


FIG. 2. Rotational correction terms V_{ix} for $\text{Br}_3\text{CH/D}$ as a function of the factor by which the atoms on the main symmetry axis (C and H/D) were multiplied. S_{4x} , S_{5x} , and S_{6x} are symmetry coordinates as defined in Table II.

REMARKS ON THE CALCULATION OF ROTATIONAL CONTRIBUTIONS

In order to ensure that the rotational correction terms can be interpreted unambiguously, it will be necessary that clear definitions are used with respect to:

1. *The dipole-moment direction.* The dipole-moment vector is directed from the center of the negative charges to the center of the positive charges. $(\partial\mu_\xi/\partial S)$ and V_ξ -values are positive when positive charge is displaced in the positive ξ -direction ($\xi = x, y, \text{ or } z$).

2. *The Cartesian coordinate axes.* The Cartesian coordinate axes are defined so as to form a right-hand coordinate system (see Fig. 1) $\mathbf{i} \times \mathbf{j} = \mathbf{k}$, and so on, cyclically.

3. *The direction of rotation.* A rotation about the ξ -axis is defined as positive when its rotation-vector ω_ξ points along the positive ξ -axis. As a consequence the general form of the β -matrix elements can be given as follows.

$$\begin{array}{lll}
 \rho_1(T_x): \beta_{1,3i-2} = m_i/m_{\text{tot}}, & \beta_{1,3i-1} = 0, & \beta_{1,3i} = 0, \\
 \rho_2(T_y): \beta_{2,3i-2} = 0, & \beta_{2,3i-1} = m_i/m_{\text{tot}}, & \beta_{2,3i} = 0, \\
 \rho_3(T_z): \beta_{3,3i-2} = 0, & \beta_{3,3i-1} = 0, & \beta_{3,3i} = m_i/m_{\text{tot}}, \\
 \rho_4(R_x): \beta_{4,3i-2} = 0, & \beta_{4,3i-1} = -m_i z_{0i}/I_{xx}, & \beta_{4,3i} = m_i y_{0i}/I_{xx}, \\
 \rho_5(R_y): \beta_{5,3i-2} = m_i z_{0i}/I_{yy}, & \beta_{5,3i-1} = 0, & \beta_{5,3i} = -m_i x_{0i}/I_{yy}, \\
 \rho_6(R_z): \beta_{6,3i-2} = -m_i y_{0i}/I_{zz}, & \beta_{6,3i-1} = m_i x_{0i}/I_{zz}, & \beta_{6,3i} = 0,
 \end{array}$$

where $i = 1, 2, \dots, N$

ξ_{0i} = the equilibrium ξ distance of atom i to the center of mass ($\xi = x, y, z$).

I_{xx} , I_{yy} , I_{zz} are the principal moments of inertia.

4. *The symmetry coordinates.* The symmetry coordinates are built up from internal coordinates (e.g., Δr_i , $\Delta \alpha_i$). The internal coordinates are taken as increments in bond-length and interbondangles. If scaled symmetry coordinates are used, the scaling factors must be clearly indicated. The scaling factors influence some of the U -matrix elements and consequently the rotational correction terms (see Eq. (9)).

Table V. Pyramidal X_3Y molecules.

$S_{3x} = 6^{-\frac{1}{2}}(2\Delta r_1 - \Delta r_2 - \Delta r_3)$ $S_{4x} = r_{XY}6^{-\frac{1}{2}}(2\Delta \alpha_1 - \Delta \alpha_2 - \Delta \alpha_3)$						
X_3Y	$r_{XY}(\text{\AA})$	$\alpha(^{\circ})$	$\mu_o(D)$	Ref.	Reference molecule ($m_Y \times 1000$)	
					$v_{3x}(D/\text{\AA})$	$v_{4x}(D/\text{\AA})$
H_3N	1.014	106.78	-1.47	15	-0.0670	-0.0375
D_3N	1.014	106.78	-1.47	15	-0.1174	-0.0657
F_3N	1.371	102.15	+0.235	15	+0.0500	+0.0273
H_3P	1.419	93.5	-0.55	15	-0.0103	-0.0053
D_3P	1.419	93.5	-0.55	15	-0.0196	-0.0101
F_3P	1.563	96.9	+1.03	18	+0.1635	+0.0864
Cl_3P	2.043	100.10	+0.78	15	+0.1120	+0.0604
H_3As	1.523	92	-0.22	15	-0.0016	-0.0008
D_3As	1.523	92	-0.22	15	-0.0032	-0.0016
F_3As	1.712	100	+2.59	15	+0.2136	+0.1152
Cl_3As	2.161	98.42	+1.59	15	+0.1548	+0.0826
H_3Sb	1.712	91.5	-0.12	15	-0.0005	-0.0003
D_3Sb	1.712	91.5	-0.12	15	-0.0010	-0.0005
Cl_3Sb	2.325	99.5	+3.00	15	+0.2004	+0.1077

Table VI. X_3CY molecules.^a

Symmetry coordinates as in Table II.

X_3CY	$r_{CX}(\text{\AA})$	$r_{CY}(\text{\AA})$	$\alpha(^{\circ})$	$\mu_O(D)$	Rotational corrections		
					Reference molecule ($m_C, m_Y \times 100\ 000$)		
					V_{4x}	V_{5x}	V_{6x}
F_3CH	1.332	1.098	108.80	+1.65	+1.3021	+0.2640	-0.0710
F_3CD	1.332	1.098	108.80	+1.65	+1.2629	+0.2385	-0.0820
Cl_3CH	1.767	1.073	108.40	+1.01	+0.8140	+0.1473	-0.0250
Cl_3CD	1.767	1.073	108.40	+1.01	+0.8061	+0.1415	-0.0292
^a Geometrical parameters as in Ref. 19.							

CALCULATIONS AND CONCLUDING REMARKS

Using the reference molecule as proposed here, rotational contributions were calculated for the following types of molecules. Bent X_2Y molecules: C_{2v} (see Table III and Fig. 1a); X_2CY molecules: C_{2v} (see Table IV and Fig. 1b); pyramidal X_3Y molecules: C_{3v} (see Table V and Fig. 1c); and X_3CY molecules: C_{3v} (see Table VI and Fig. 1d).

It is evident from Table I that the results obtained with our reference molecule are the same as those obtained with Crawford's reference molecule. The reference molecule as proposed here leads to correct rotational contributions for all small molecules, with the exception perhaps of triatomic linear ones and molecules in which no n -fold axis ($n \geq 2$) is present. In the case of those molecules difficulties arise, by applying a Crawford's type reference molecule as well as our type of reference molecule. The choice of a rotational free molecule is not quite clear in such cases, which leads to some arbitrariness in the absolute rotational contribution.

However, if the molecular symmetry is C_s or lower a sensible choice can sometimes be made (e.g., the C and O atoms in methanol, the C-O bond being almost a 3-fold axis). In "large" molecules (eight or more atoms) the rotational contributions can be ignored.

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