On the Ambiguity of Molecular Complexes Formed by Two Molecules

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We present a general consideration how many structural conformers are compatible with *one* set of rotational constants if one rotational spectrum of a dimer is investigated. A selection of a certain conformer should be guided by the investigation of isotopomers, quantum chemical calculations or other arguments.

Introduction

If two molecules aggregate to form a complex, the question arises how many conformers are compatible with one set of rotational constants or moments of inertia, which determine the rotational spectrum of the complex. Many studies of the rotational spectrum of dimers present this stage of investigation. This publication is an extension of a paper published recently for complexes formed by an asymmetric top molecule and a rare gas atom [1]. The arguments are here by symmetry considerations and are different to those given in [1]. It should be stated that a rotational spectrum contains in general at most three informations, the principal moments of inertia, if finer effects like p.e. hyperfine structure are neglected.

General Considerations

By Steiner's law [2], it is possible to calculate the inertia tensor of the complex with the knowledge of both the inertia tensors of the ligand molecules. The principal inertia axes originating from the center of mass M of the complex and its moments of inertia are the reference. Each molecular inertia tensor or inertia ellipsoid with three different axes x, y, z may be associated to eight different positions of an asymmetric top molecule. This ellipsoid is invariant under the point group $\mathscr{D}_{2h} = \mathscr{V}_h$ [3] of order $h(\mathscr{D}_{2h}) = 8$ with the elements E, C_{2x}, C_{2y}, C_{2z}, σ_{xy}, σ_{yz}, σ_{zx}, i, with C_{2g}, $g = x, y, z$ twofold rotations about the principal inertia axes, $\sigma_{gg'}$, $g \neq g'$, reflection on the planes gg' and i the inversion through the center of symmetry.

The asymmetric top molecules will be classified by point groups. Only subgroups of $\mathscr{D}_{2h}$ can be selected. They are compiled in Table 1. For molecular groups with elements reflection σ and inversion i, it is assumed that "left" and "right" handed forms exist in equal number in the ensemble of molecules which are under spectroscopic investigation. Both lead to the same molecular rotation spectrum and form complexes with equal probability. If the molecule has no symmetry, eight molecular arrangements, connected by the operations of the group $\mathscr{D}_{2h}$, can be associated to the same inertia ellipsoid. On the other hand, when it has a symmetry, the number N_{MON} of discernible arrangements reduces to

$$N_{\mathrm{MON}} = \frac{h(\mathscr{D}_{2h})}{h} = \frac{8}{h}, \tag{1}$$

where $h(\mathscr{D}_{2h})$ is the order of the group $\mathscr{D}_{2h}$ and h is the order of the point group of the molecule.

Heterodimers

For heterodimers composed of two different asymmetric top molecules there exist

$$N_{\mathrm{HED}} = \frac{h^2(\mathscr{D}_{2h})}{h_1 h_2} = \frac{64}{h_1 h_2}, \tag{2}$$

discernible structural arrangements which result in the same inertia tensor of the complex. h_1 and h_2 are the or-

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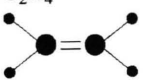
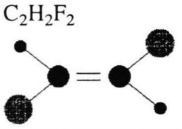
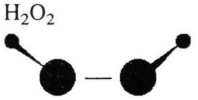
Table 1. Subgroups of $\mathscr{D}_{2h}$ used for consideration of asymmetric top molecules. Compare Tab X-14 of [3]. The arrangement of the axes x, y, z is free in principle. In many cases z is the axis of highest symmetry.

Group	Group Elements	Order h	Example
$\mathscr{D}_{2h}$	E, C_{2x}, C_{2y}, C_{2z}, σ_{xy}, σ_{yz}, σ_{zx}, i	8	C_2H_4 
$\mathscr{D}_2$	E, C_{2x}, C_{2y}, C_{2z}	4	$(C_6H_5)_2$ twisted 
$\mathscr{C}_{2v}$	E, C_{2z}, σ_{yz}, σ_{zx}	4	H_2O 
$\mathscr{C}_{2h}$	E, C_{2z}, σ_{xy}, i	4	$C_2H_2F_2$ 
$\mathscr{C}_2$	E, C_{2z}	2	H_2O_2 
$\mathscr{C}_s$	E, σ	2	HDO 
$\mathscr{C}_i$	E, i	2	trans CHFI-CHFI
$\mathscr{C}_1$	E	1	CHFCLI

ders of the subgroups assigned to the selected molecules forming the heterodimer. We suppose that the dimer is an asymmetric top.

If a heterodimer is composed of an asymmetric top and a symmetric top molecule, (1) is still valid for the asymmetric top. For the symmetric top the three axis ellipsoid degenerates to an ellipsoid with rotational symmetry with its symmetry axis coinciding with the symmetry axis of the symmetric top molecule. This ellipsoid is invariant under the point group $\mathscr{D}_{\infty h}$ with the elements E, $(2C_\infty^\Phi)$, ..., $(\infty\sigma_v)$, (i), $(2S_\infty^\Phi)$, ..., (∞C_2). C_∞^Φ is a rotation about the symmetry axis, σ_v a reflection on a plane containing the symmetry axis, i the inversion, S_∞^Φ a rotation-reflection about the symmetry axis and C_2 a twofold rotation about an axis perpendicular to the symmetry axis. The brackets enclose classes of the infinite group. The numbers in front of the group operation symbols indicate the number of elements in the class. Symmetric top molecules belong to the point group $\mathscr{D}_{nh}$, $\mathscr{C}_{nv}$ with $n \geq 3$ or $\mathscr{D}_{nd}$ with $n \geq 2$. In many cases $n=3$. As a C_∞^Φ about the symmetry axis or S_∞^Φ about the rotation-reflection axis of the symmetric top or σ_v do not change the inertia ellipsoid or, in other words, the ellipsoid does not give any information on the rotational position with respect to the symmetry axis of the molecule, subgroups are sufficient for the consideration, as given in Table 2.

The number of discernible structural positions of a symmetric top molecule "within" the ellipsoid is

$$N_{\mathrm{MON}} = \frac{h(\mathscr{C}_i)}{h} = \frac{2}{h} \quad \text{with} \quad h = 1, 2\,. \tag{3}$$

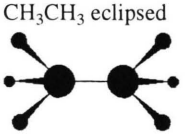
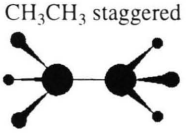
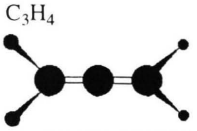
It results $N_{\mathrm{MON}}=1$ for ethane in the staggered conformation ($\mathscr{D}_{3d}$) or in the eclipsed conformation ($\mathscr{D}_{3h}$) and for allene ($\mathscr{D}_{2d}$). For ammonia ($\mathscr{C}_{3v}$), $N_{\mathrm{MON}}=2$.

For a heterodimer of an asymmetric and a symmetric top (2) modifies to

$$N_{\mathrm{HED}} = \frac{h(\mathscr{D}_{2h})}{h_1}\,\frac{h(\mathscr{C}_i)}{h_2} = \frac{16}{h_1\,h_2} \tag{4}$$

with h_1 the order of the point group of the asymmetric top from Table 1 and h_2 the order of the subgroup assigned to the symmetric top according Table 2.

Table 2. Subgroups $\mathscr{D}_{\infty h}$ used for the consideration of symmetric top molecules.

Group	Subgroup	Subgroup Elements	Order h	Example
$\mathscr{D}_{\infty h}$	$\mathscr{C}_i$	E, i	2	
$\mathscr{D}_{nh}$	$\mathscr{C}_s$	E, σ_h	2	CH_3CH_3 eclipsed 
$\mathscr{D}_{nd}$ n odd	$\mathscr{C}_i$	E, i	2	CH_3CH_3 staggered 
$\mathscr{D}_{nd}$ n even	$\mathscr{C}_2$	E, C_2	2	C_3H_4 
$\mathscr{C}_{nv}$	$\mathscr{C}_1$	E	1	CF_3H

There are N_{HED} discernible arrangements with the same inertia tensor of such a complex. For a heterodimer of two symmetric top molecules, (4) changes to

$$N_{\mathrm{HED}} = \frac{h^2(\mathscr{C}_i)}{h_1 h_2} = \frac{4}{h_1 h_2}. \tag{5}$$

h_1 and h_2 are the orders of the subgroups assigned to the two different symmetric tops.

Linear molecules may be treated as a special case of a prolate symmetric top with an inertia ellipsoid degenerated to a circular cylinder. The conclusions of (4) and (5) are still applicable.

If in a heterodimer one asymmetric top degenerates to a mass point, a rare gas atom, (1) gives the number of heterodimers, which is $N_{\mathrm{HED}}=8$ in maximum and reduces according (1), if the asymmetric top has a certain point group symmetry. This is in agreement with the results of [1]. It is essentially the same, if a mass point is arranged in eight positions "around" a three axis inertia ellipsoid resulting in the same inertia tensor of the complex, or if the molecule is put into eight positions within the three axis ellipsoid with a fixed position of the rare gas outside the molecular ellipsoid.

The complex benzonitrile-water, $C_6H_5CN\text{---}H_2O$, may be taken as an example. As both ligands have a $\mathscr{C}_{2v}$ symmetry, (2) results in $N_{\mathrm{HED}}=4$ structural arrangements. This number could be reduced to one by the investigation of isotopomers [4, 5] and the existence of hydrogen bonds O...H and N...H favoring a ring like structure.

Another example is provided by the complex morpholine-water, $C_4H_9NO\text{---}H_2O$, [6], which is composed of molecules with $\mathscr{C}_s$ and $\mathscr{C}_{2v}$ point group symmetry, respectively. According (2), $N_{\mathrm{HET}}=8$ structural forms are compatible with the set of three rotational constants or principal moments of inertia. Four of them were excluded by the authors by the assumption of linear hydrogen bonds, three by a consideration of the dipole moment components.

Homodimers

As in general the inertia tensor of the homodimer is associated with a three axis ellipsoid, only a limited number of point group operations, that of a group $\mathscr{D}_{2h}^{(C)}$ have to be considered to account for the symmetry of the mutual arrangement of the identical molecules. The superscript (C) indicates application on the homodimer complex. All symmetry elements of $\mathscr{D}_{2h}^{(C)}$ have the center of mass of the homodimer in common. The group operations of $\mathscr{D}_{2h}^{(C)}$: $E^{(C)}$, $C_{2x}^{(C)}$, $C_{2y}^{(C)}$, $C_{2z}^{(C)}$, $\sigma_{xy}^{(C)}$, $\sigma_{yz}^{(C)}$, $\sigma_{zx}^{(C)}$, $i^{(C)}$ have to be checked, if they are covering operations of the two molecular ellipsoids. If this is not fullfilled, the operation has to be eliminated. In continuing this procedure, one will end up with a subgroup $\mathscr{U}^{(C)}$ of $\mathscr{D}_{2h}^{(C)}$ isomorphic to one of Table 1.

The next step is to translate the covering operations of $\mathscr{U}^{(C)}$ into point group operations applicable to the molecules. The centers of mass of the molecules are now the reference.

It should be stated that the mutual arrangement of the two molecular inertia ellipsoids may be described by the following coordinates, which are displayed in Figure 1. An angle α_j, $j=1, 2$ between $\overline{m_jM}$ and the semiaxis z_j of the ellipsoid j and an angle β_j between $\overline{m_jM}$ and the semiaxis y_j. The semiaxes should be selected in correspondance. In addition a dihedral angle γ has to be specified as $\gamma = \angle\, y_1\overline{m_1M}/y_2\overline{m_2M}$. In total, five coordinates have to be given. The principal axis system of the complex originates in its center of mass M. With the knowledge

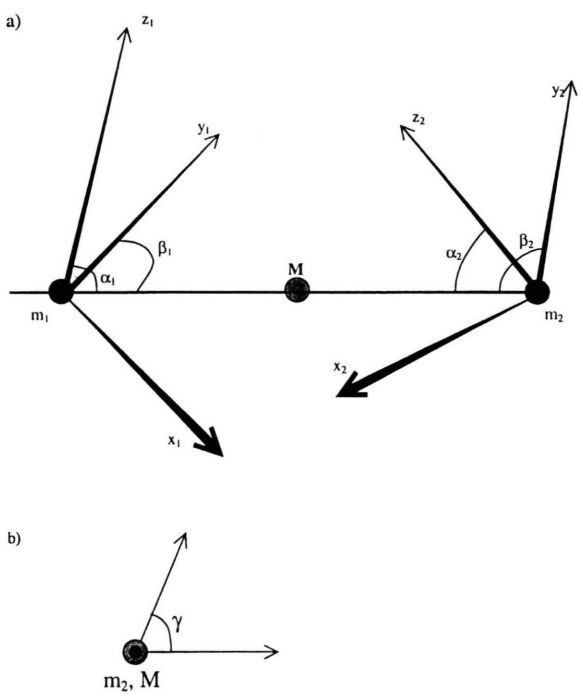


Fig. 1. Coordinates for the description of the mutual position of two identical molecules in a dimer. m_j center of mass of molecule j ($j=1, 2$), M center of mass of the dimer. $\alpha_j = \angle\, z_j\overline{m_jM}$, $\beta_j = \angle\, y_j\overline{m_jM}$, $\gamma = \angle\, y_1\overline{m_1M}/y_2\overline{m_2M}$. a) Perspective view, b) view along m_2Mm_1.

of the inertia tensor of the molecules it is always possible to calculate the inertia tensor of the complex and its principal axis system X, Y, Z. In special cases it may be found by symmetry arguments. Such a case will be considered as an example for the procedure for other cases. It may be much more complicated generally.

As displayed in Fig. 2, we choose $\alpha_1=\alpha_2=90°$, $\beta_1=\beta_2<90°$ and $\gamma=180°$.

Here the complex reference axes are X_r: $\overline{m_1Mm_2}$, $Z_r \| z_1 \| z_2$ ($z_1 \| z_2$), Y_r: $\perp X_r$, Z_r. Z_r is a principal inertia axis, X_r, Y_r, are generally not. But the plane $X_r Y_r$ is an inertia plane. M is the center of the complex inertia ellipsoid. From the operations of $\mathscr{D}_{2h}^{(C)}$ only the operations $E^{(C)}$, $C_{2z}^{(C)}$, $\sigma_{xy}^{(C)}$, $i^{(C)}$, defining a group $\mathscr{D}_{2h}^{(C)}$, lead to a covering of the ellipsoids of both molecules. These operations may be translated to point group operations to be applied to the molecules:

$$\begin{aligned} E^{(C)} &= E^{(1)}E^{(2)}, \\ C_{2Z}^{(C)} &= C_{2z}^{(1)}C_{2z}^{(2)}P, \\ \sigma_{XY}^{(C)} &= \sigma_{xy}^{(1)}\sigma_{xy}^{(2)}, \\ i^{(C)} &= i^{(1)}i^{(2)}P, \end{aligned} \tag{6}$$

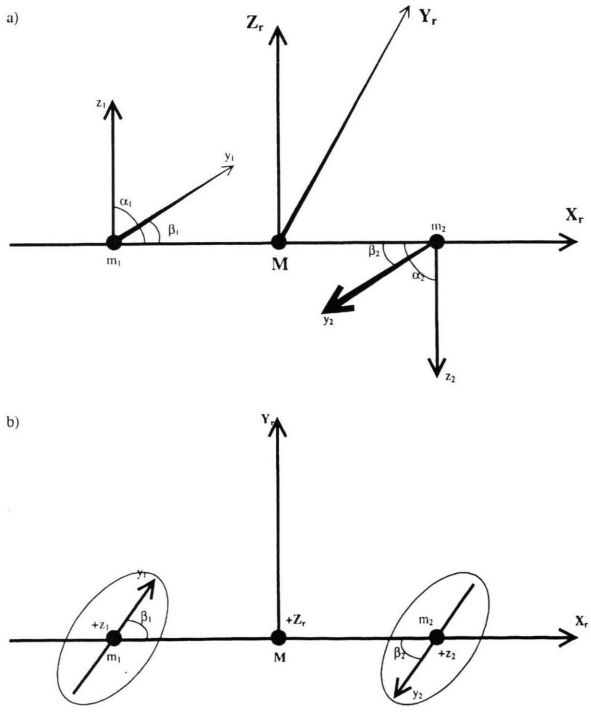


Fig. 2. Special choice of the mutual position of the dimer molecules: a) Perspective view. b) Projection on $X_r Y_r$ plane, $\alpha_1=\alpha_2=90°$, $\beta_1=\beta_2<90°$, $\gamma=180°$. In b) the ellipsoids have been indicated by their projection.

where an operation like $C_{2z}^{(j)}$ applies only to molecule j or its ellipsoid and P means a permutation (exchange) of the molecular ellipsoids 1 and 2 without changing their orientation. We choose as example a molecule of $\mathscr{C}_s$ symmetry like HDO. According to (1), four discernible positions of the molecule within its inertia ellipsoid exist, as indicated in Figure 3. We assigned to each position a letter from a to d.

In Table 3 we give the result of the application of the operations of (6): $E^{(j)}$, $C_{2z}^{(j)}$, $\sigma_{xy}^{(j)}$, $i^{(j)}$ to the molecule j. The planes $x_j y_j$ of the molecular ellipsoids ($j=1, 2$) are coplanar to the plane $X_r Y_r$ of the homodimer ellipsoid in this case. It can be seen that the subgroup $E^{(j)}$, $C_{2z}^{(j)}$ would have been sufficient. $\sigma_{xy}^{(j)}$ produces the same positions as the molecule is planar.

The position of the molecules in the homodimer may be discerned by the following 16 binary expressions (combinations of second order of four multiply selectable elements with defined order [7]):

aa, ab, ac, ad,
ba, bb, bc, bd,
ca, cb, cc, cd,
da, db, dc, dd. (7)

From these 10 binary expressions remain, which we name basic expressions.

The set is:

aa, ab, ac, ad,
ba, bb, bc,
ca, cb,
da. (8)

But this set is not unique. Other sets of basic expressions may be found with the same number of expressions. With these 10 basic expressions, the 16 expressions (7) may be generated by application of the operations $E^{(1)}E^{(2)}$ and $C_{2z}^{(1)}C_{2z}^{(2)}P$.

This set of the 10 basic expressions describes the number of discernible positions of the molecule of $\mathscr{C}_s$ symmetry in this specially selected homodimer. All are compatible with the principal moments of inertia of the homodimer.

It seems to us that many cases of homodimers can be treated in this way. But a general and complete consideration affords much more efforts, which is beyond the scope of this paper.

The principal aim of this paper is to show that ambiguities exist and conclusions concerning the structure should be made with great care.

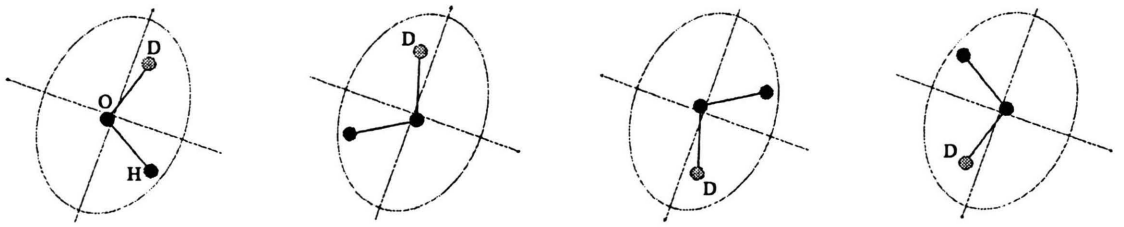


Fig. 3. Four possible positions a, b, c, d of a $\mathscr{C}_s$ symmetric molecule within its inertia ellipsoid according (1) resulting in the same inertia tensor.

Table 3. Result of the operations (6) applied to the positions a, b, c, d of Figure 3.

$E^{(j)}$	$C_{2z}^{(j)}$	$\sigma_{xy}^{(j)}$	$i^{(j)}$
a	d	a	d
b	c	b	c
c	b	c	b
d	a	d	a

Conclusion

It was shown that generally many structures are compatible with *one* set of the moments of inertia of a binary complex. If one structure is selected, this should be done by the investigation of a sufficient number of isotopomers or convincing other arguments like the existence of hydrogen bonding.

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