CARTESIAN AXIS AND PLANE CONVENTIONS IN C_{nv} SYMMETRY GROUPS

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In this work, we call the attention to the ambiguity found in the literature when labeling vibrations and molecular orbitals as B_1 and B_2 for molecules belonging to the C_{2v} point group as, for example, the water molecule. A survey of several books and some articles shows that this ambiguity comes from a long time ago and persists today, being a source of misunderstanding and a waste of time for students and teachers. It means that, in the case of the point groups C_{nv}, D_n, and D_{nh} (n = 2, 4, 6), it is very important to draw students' attention to this ambiguity that exists in the literature. It is unfortunate that the recommendation made by Mulliken, more than sixty years ago, to always place the water molecule in the *yz* plane, has not been followed.

Keywords: symmetry; vibrational spectroscopy; electronic spectroscopy.

INTRODUCTION

Symmetry and group theory are ubiquitous in chemistry. Their concepts are used to classify molecules in one of the 32-point groups, using the Schoenflies symbols. The irreducible representations of each point group are used to label molecular orbitals and molecular vibrations, following the Mulliken symbols, and help to determine the allowed and forbidden electronic and vibrational transitions, between many other applications.[1,2] To be useful and to serve as a way of communication between researchers, teachers and students, a set of rules and conventions must be followed. In this way, it is very surprisingly that there is not an agreement related to the one of the most studied molecules, the water molecule.

The point we want to call attention is the orientation of the cartesian axes which determine how to label the plane of the water molecule. If different orientations are used (see Figure 1), the Mulliken symbols used to label some irreducible representations (see Table 1) and, consequently, the labels of some molecular orbitals and molecular vibrations, will be exchanged. The lack of an agreement
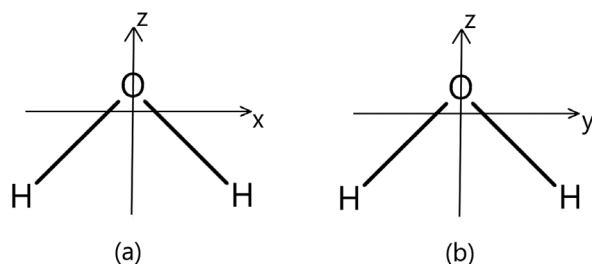

Figure 1. *The two possibilities to label the water plane: (a) the molecule is in the xz plane; (b) the x axis is perpendicular to the plane of the molecule*

Table 1. Character Table for the C_{2v} Point Group

C_{2v}	E	C_2	$\sigma_v^{(xz)}$	$\sigma'_v^{(yz)}$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

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related with this convention has been pointed out by some authors since long time ago.[2-5]

DISCUSSION

These conventions are important, for example, to determine which electronic, vibrational, or rotational transitions can be observed experimentally. For a dipole allowed light absorption process, it is necessary to know the wave functions for the fundamental and the excited states to calculate the probability of a transition to occur. This can be determined, or guessed qualitatively, by considering the integral in Equation 1, where ψ_i is the initial state and ψ_f the final state time-independent wave functions, **μ** is the transition moment, and *e***r** is the dipole moment operator.[6,7]

$$|\mathbf{\mu}| = \langle \psi_f | e\mathbf{r} | \psi_i \rangle \quad (1)$$

This equation describes the transition moment from the state ψ_i to ψ_f by an electromagnetic radiation perturbation. The Einstein transition-probability coefficient between the initial and final states, $B_{i \to f}$, is a function of the square of the transition moment, as shown in Equation 2.

$$B_{i \to f} = \left(\frac{2\pi}{3\hbar^2} \right) |\mathbf{\mu}|^2 \quad (2)$$

The central point is that using symmetry we can determine if the integral in the right side of Equation 1 is equal to zero or not. To be different from zero the direct product of the representations of the initial, ψ_i, the final state, ψ_f, and the dipole, **r**, must contain the totally symmetric representation. In other words, we can determine if a transition is allowed or not, just looking for the irreducible representations of the components of the transition moment.[1,8]

Depending on the choice made for *x* and *y* axes, the plane of the water molecule will be in the $\sigma(xz)$ or in the $\sigma(yz)$ plane, as shown in Figure 1. Because of this choice, the vibrational analysis for this molecule may give two different answers: $\Gamma = 2A_1 + B_1$ or, $\Gamma^* = 2A_1 + B_2$, where Γ and Γ^* are reducible representations and A_1, B_1, and B_2 are irreducible representations.[1,9] Each irreducible representation corresponds to one nondegenerate vibrational mode and, consequently, to a band in the vibrational spectrum. Both results indicate equally that water has three vibrational bands. As *x*, *y*,

and z axes belong to the irreducible representations B_1, B_2, and A_1, respectively, these bands are dipole moment allowed and are observed in the infrared spectrum. By similar arguments, as the products xz, yz, and (x^2, y^2, z^2) belong to these same irreducible representations, respectively, these bands are allowed by the polarizability selection rule and are also observed in the Raman spectrum of water. It means that does not matter the choice we have made for x and y axes (Figure 1). The total number of bands which will appear in the infrared or Raman spectra, will be three in each case.

Of course, everyone will agree that this situation is confusing and time consuming in many circumstances. In class, it always takes a while to explain the students that different authors use different conventions, and after the instructor makes a choice of one of the possibilities shown in Figure 1, the students still may get confused, depending on the textbook they are following to study. Similarly, researchers expend some additional time to understand why different authors assign the water asymmetric stretching vibration as B_1 and others B_2. This difficulty, observed in the case of the water molecule, occurs for all molecules that have two or three planes of symmetry, as pointed out by Shimanouchi.[5] In line with this author, Kettle[2] indicates that this difficulty occurs for all molecules which belong to the C_{nv} point groups, and Mulliken[4] indicates that this problem occurs for

molecules in the point groups C_{nv}, D_n, and D_{nh} (n = 2, 4, 6). For these point groups, which include the water molecule point group C_{2v}, the symmetry label assignment for atomic and molecular orbitals and molecular vibrations has a certain degree of arbitrariness.

Tables 2 and 3 show the results of a limited search in the literature, which illustrates the problem to which we are drawing attention. They indicate the choice of Cartesian coordinates (Figures 1a or 1b), the reducible representations for the three water vibrations, and the irreducible representation for the nonbonding highest occupied molecular orbital (HOMO) in water, made by several authors. As can be seen in Table 2, there are some authors that used both orientations.

Regarding the symmetry reflection planes σ_v and σ_v' (see Table 1), these symbols are not always correlated with the cartesian coordinates xz and yz, respectively, as indicated in the footnote of Table 2. In addition, a prime is not always used to distinguish one plane σ_v from the other reflection plane, and the columns for $\sigma(xz)$ and $\sigma(yz)$ may appear in exchanged order in the character table presented by some authors. It means that it is necessary pay attention for the irreducible representation B_1 and B_2 indicated by each author to verify the correspondence to the cartesian axis x or y, respectively, as shown in Table 1.

Table 2. Designation of the plane of the water molecule in textbooks

Author	$\sigma(xz)$ Figure 1a $\Gamma = 2A_1 + B_1$ HOMO nonbonding (b_2)	$\sigma(yz)$ Figure 1b $\Gamma^* = 2A_1 + B_2$ HOMO nonbonding (b_1)	Reference	Comments
Albright and Burdett		x	10	pg. 119
Barrow		x	7	pg. 163
Bernath		x	8	pg. 174, 177, 238
Bishop		x	11	pg. 182
Carter		x	12	pg. 13
Cotton	x		1	pg. 310
Castellan		x	13	pg. 560
Eyring, Walter, and Kimball	x		14	pg. 276
Harris and Bertolucci	x	x	15	pgs. 17, 139, 140, 370
Herzberg vol II	x		16	pg. 133
Herzberg vol III		x	17	pg. 385
Huheey, J. E.; Keiter, E. A.; Keiter		x	18	pg. 53, 60
Jaffé, H.H.; Orchin, M.		x	19	pg. 14
Kettle		x[1]	2	pg. 21
Lever	x		20	pg. 36
Levine		x	21	pg. 456
McQuarrie		x	22	pg. 456
McWeeny	x		23	pgs. 189, 190
Miessler, Fischer and Tarr	x		24	pg. 97
Murrell, Kettle, and Tedder		x	25	pg. 190
Nakamoto		x	9	pg. 30
Pfennig		x	26	pg. 194
Orchin and Jaffé		x	27	pg. 108
Pilar		x	6	pg. 543
Tsukerblat		x	28	pg. 358
Weller, Overton, Rourke, and Armstrong		x	29	pg. 192
Wilson, Decius, and Cross	x		30	pg. 79

[1]In the character table used by this author, σ_v and σ_v' are reversed when compared with Table 1. Because of this, vibrational assignment is $\Gamma = 2A_1 + B_1$ and the HOMO nonbonding is b_2.

Table 3. Designation of water molecule plane in articles

Author	$\sigma(xz)$ Figure 1a $\Gamma = 2A_1 + B_1$ HOMO nonbonding (b_2)	$\sigma(yz)$ Figure 1b $\Gamma^* = 2A_1 + B_2$ HOMO nonbonding (b_1)	Reference	Comments
Brundle and Turner		x	31	pg. 28
Orchin and Jaffé		x	32	pg. 374
Greinacher	x		33	v_3 (antisymmetric stretching vibrational mode) = B_1
Jayachander Rao and Varandas		x	34	pg. 12372
Luo *et al.*		x	35	HOMO = b_1
Mulliken		x	4	pg. 2002
Shimanouchi	x		5	pg. 1001
Walrafen	x		36	v_3 (antisymmetric stretching vibrational mode) = B_1
Walsh		x	3	pg. 2262

All of this together means that the character table used and the axis choice, (a) or (b) in Figure 1, will determine if the water vibrations will be assigned as $\Gamma = 2A_1 + B_1$ or $\Gamma^* = 2A_1 + B_2$, and also if the nonbonding HOMO will be assigned as b_2 or b_1. Obviously, other C_{2v} molecules, for example, ozone, formaldehyde, nitrogen dioxide, sulfur dioxide, (Z)-1,2-dichloroethylene, and ethylene oxide, will suffer from the same problem caused by different choices for the molecular plane and character table.

THE CONVENTION AND THE IMPACT ON TEACHING

After we have considered the two possible conventions for the plane of water molecule which appears in articles and textbooks, it seems natural that we should be in a good condition to recommend one of these. However, as indicated by several authors, the best recommendation is that every author define very clearly the convention used, presenting, or indicating a figure like Figure 1a or Figure 1b.

The history facts about this convention shows that the choice indicated by Figure 1a was used by the first authors Eyring, Walter and Kimball (1944),[14] Herzberg (vol. II, vibrational spectroscopy, 1945),[16] Wilson, Decius, and Cross (1955),[30] and Greinacher, Lüttke, and Mecke (1955).[33] After the recommendation by Mulliken,[4] in 1955, indicated by Figure 1b, several authors, including Herzberg (vol. III, electronic spectroscopy, 1966),[17] start to follow it. However, it appears that many other authors keep relying on the convention used by Herzberg in his book on vibrational spectroscopy from 1945,[16] and this should be the reason both conventions have propagated until nowadays. It is worth to say that Mulliken[4] stated clearly that he consulted Herzberg during the preparation of his 1955 article, which reinforces the supposition that this last author was convinced by Mulliken to change the designation of the plane of the water molecule to that shown in Figure 1b, which was then used in his book[16] on electronic spectroscopy from 1966.

From the point of view of teaching symmetry, vibrational and electronic spectroscopy, and molecular orbitals, even though most recent textbooks use the convention recommended by Mulliken[4] and by Orchin and Jaffé[32] it will be very helpful if these articles are indicated for the students as the main reference source for conventions. In this way, the orientation shown in Figure 1b for the water molecule will be reinforced and used more frequently, reducing the ambiguity in symmetry labels of vibrations and molecular orbitals, and avoiding unnecessary confusion, and waste of time. In this way, students will be able to compare their assignments of vibration modes and molecular orbitals with literature and understand that different labels may have the meaning that an author is not using the recommended convention.

In the case of original research articles, the authors and reviewers must be aware about this ambiguity when labeling vibrations and molecular orbitals for molecules belonging the point groups C_{nv}, D_n, and D_{nh} and should make the choice to follow the recommendations made by Mulliken[4] and by Orchin and Jaffé[32] to stop propagating the convention used by Herzberg in his book from 1945. Also, textbook authors that did not adhere yet to the recommended convention should consider to revise their texts when writing new issues of their books.

ACKNOWLEDGMENTS

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