CARTESIAN AXIS AND PLANE CONVENTIONS IN Cnv SYMMETRY GROUPS

Lucas A. L. Dias* and Roberto B. Faria*†,‡
*Instituto de Química, Universidade Federal do Rio de Janeiro, 21941-909, Rio de Janeiro – RJ, Brasil
†E-mail: faria@iq.ufrj.br

Recebido em 11/05/2021; aceito em 26/05/2021; publicado na web em 29/06/2021

In this work, we call the attention to the ambiguity found in the literature when labeling vibrations and molecular orbitals as B1 and B2 for molecules belonging to the Cnv 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 Cnv, Dnv, and Dnh (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 related with this convention has been pointed out by some authors since long time ago.3,4

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 \( \psi_i \) is the initial state and \( \psi_f \) the final state time-independent wave functions, \( \mu \) is the transition moment, and \( e \mathbf{r} \) is the dipole moment operator.6,7

\[
|\mu| = \langle \psi_f | e \mathbf{r} | \psi_i \rangle
\]

(1)

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

\[
B_{ Transition } = \frac{2\pi}{3\hbar} |\mu|^2
\]

(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, \( \psi_i \), the final state, \( \psi_f \), and the dipole, \( e \mathbf{r} \), 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.1,5

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 \( \Gamma \) and \( \Gamma^* \) are reducible representations and \( A_1, B_1, \) and \( B_2 \) are irreducible representations.1,6 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, z...
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. In line with this author, Kettle indicates that this difficulty occurs for all molecules which belong to the \( C_{nv} \) point groups, and Mulliken indicates that this problem occurs for molecules in the point groups \( C_{nv}, D_{nv}, \) 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 \( \sigma_v \) and \( \sigma_v' \) (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 \( \sigma_v \) 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                        | \( \sigma(xz) \) | \( \sigma(yz) \) | 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                | 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    |          |

1In the character table used by this author, \( \sigma_v \) and \( \sigma_v' \) are reversed when compared with Table 1. Because of this, vibrational assignment is \( \Gamma = 2A_1 + B_1. \)
Cartesian axis and plane conventions in $C_{nv}$ symmetry groups

Table 3. Designation of water molecule plane in articles

| Author                          | $\sigma(xz)$ Figure 1a | $\sigma(yz)$ Figure 1b | Reference | Comments |
|---------------------------------|------------------------|------------------------|-----------|----------|
| Brundle and Turner             | $\Gamma = 2A_1 + B_1$ | HOMO nonbonding ($b_2$) | 31        | pg. 28   |
| Orchin and Jaffé                | $\Gamma = 2A_1 + B_1$ | HOMO nonbonding ($b_1$) | 32        | pg. 374  |
| Greinacher                      | x                      | 33                     | $v_1$ (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                     | $v_1$ (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 $C_{nv}$ 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),15 Wilson, Decius, and Cross (1955),16 and Greinacher, Lüttke, and Mecke (1955).17 After the recommendation by Mulliken,7 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 Mulliken7 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 book8 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 Mulliken7 and by Orchin and Jaffe12 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 $C_{nv}$, $D_{nv}$, and $D_{nh}$ and should make the choice to follow the recommendations made by Mulliken7 and by Orchin and Jaffe12 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

The authors thank the financial support from Ministério da Ciência, Tecnologia e Inovações – MCTI and Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq (Grant 303.260/2019-0). This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

REFERENCES

1. Cotton, F. A.; Chemical Applications of Group Theory, 2nd ed., John Wiley & Sons: New York, 1971.
2. Kettle, S. F. A.; Symmetry Structure - Readable Group Theory for Chemists, 3rd ed., John Wiley & Sons: New York, 2007.
3. Walsh, A. D.; J. Chem. Soc. 1953, 2260.
4. Mulliken, R. S.; J. Chem. Phys. 1955, 23, 1977.
5. Shimanouchi, T.; J. Phys. Chem. Ref. Data 1977, 6, 993.
6. Pilar, F. L.; Elementary Quantum Chemistry, McGraw-Hill Book Company: New York, 1968.
7. Barrow, G. M.; Introduction to Molecular Spectroscopy, McGraw-Hill Book Company: Singapore, 1962.
8. Bernath, P. F.; Spectra of Atoms and Molecules, 3rd ed., Oxford University Press: Oxford, 2016.
9. Nakamoto, K.; Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A. Theory and Applications in Inorganic Chemistry, 6th ed., Wiley: New York, 2009.
10. Albright, T. A.; Burdett, J. K.; Problems in Molecular Orbital Theory, Oxford University Press: Oxford, 1992.
11. Bishop, D. M.; Group Theory and Chemistry, Dover: New York, 1993.
12. Carter, R. L.; Molecular Symmetry and Group Theory, John Wiley & Sons: New York, 1998.
13. Castellan, G. W.; Physical Chemistry, 3rd ed., Addison-Wesley Publishing Company: Reading, MA, 1983.
14. Eyring, H.; Walter, J.; Kimball, G. E.; *Quantum Chemistry*, John Wiley & Sons: New York, 1944.
15. Harris, D. C.; Bertolucci, M. D.; *Symmetry and Spectroscopy*, Dover: New York, 1989.
16. Herzberg, G.; *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*, Krieger Publishing Company: Malabar, FL, 1945.
17. Herzberg, G.; *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*, Krieger Publishing Company: Malabar, FL, 1966.
18. Huheey, J. E.; Keiter, E. A.; Keiter, R. L.; *Inorganic Chemistry. Principles of Structure and Reactivity, 4th ed.*, HarperCollins College Publishers: New York, 1993.
19. Jaffé, M.; Orchin, H. H.; *Symmetry in Chemistry*, John Wiley & Sons: New York, 1966.
20. Lever, A. B. P.; *Inorganic Electronic Spectroscopy*, Elsevier Publishing Company: Amsterdam, 1968.
21. Levine, I. N.; *Quantum Chemistry*, 4th ed., Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1991.
22. McQuarrie, D. A.; Simon, J. D.; *Physical Chemistry: a Molecular Approach*, University Science Books: Sausalito, California, 1997.
23. McWeeny, R.; *Symmetry. An Introduction to Group Theory and Its Applications*, Dover Publications, Inc.: Mineola, NY, 2002.
24. Miessler, G. L.; Fischer, P. J.; Tarr, D. A.; *Inorganic Chemistry*, 5th ed., Pearson Education Limited: Harlow, United Kingdom, 2013.
25. Murrell, J. N.; Kettle, S. F. A.; Tedder, J. M.; *Valence Theory, 2nd ed.*, John Wiley & Sons Ltd.: London, 1970.
26. Pfennig, B. W.; *Principles of Inorganic Chemistry*, John Wiley & Sons, Inc.: Hoboken, NJ, 2015.
27. Orchin, M.; Jaffé, H. H.; *Symmetry, Orbitals, and Spectra (S.O.S.*), John Wiley & Sons, Inc.: New York, 1971.
28. Tsukerblat, B. S.; *Group Theory in Chemistry and Spectroscopy*, Academic Press: London, 1994.
29. Weller, M.; Overton, T.; Rourke, J.; Armstrong, F.; *Inorganic Chemistry*, 6th ed., Oxford University Press: Oxford, 2014.
30. Wilson, E. B.; Decius, J. C.; Cross, P. C.; *Molecular Vibrations*, Dover: New York, 1980.
31. Brundle, C. R.; Turner, D. W.; *Proc. R. Soc. London, Ser. A* 1968, 307, 27.
32. Orchin, M.; Jaffé, H. H.; *J. Chem. Educ. 1970, 47, 372.*
33. Greinacher, Von E.; Lüttke, W.; Mecke, R.; *Z. Elektrochem. 1955, 59, 23.*
34. Jayachander Rao, B.; Varandas, A. J. C.; *J. Phys. Chem. A* 2015, 119, 12367.
35. Luo, Z.; Chang, Y.; Zhao, Y.; Yang, J.; Chen, Z.; Cheng, Y.; Che, L.; Wu, G.; Yang, X.; Yuan, K.; *J. Phys. Chem. A* 2021, 125, 3622.
36. Walrafen, G. E.; *J. Chem. Phys.* 1964, 40, 3249.

This is an open-access article distributed under the terms of the Creative Commons Attribution License.