

# Why Equivalent Bonds Appear as Distinct Peaks in Photoelectron Spectra

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Students of chemistry are often bothered by the observation that molecules with sets of equivalent bonds display vibrational frequencies that are distinct rather than identical. For example,  $\text{H}_2\text{O}$  has two equivalent bonds yet produces both symmetric and asymmetric stretching frequencies in its infrared spectrum. However,  $\text{CH}_4$  has four equivalent bonds and produces only two distinct vibrational frequencies in the C-H bond stretching region.

Students often ask

If there are four equivalent bonds in  $\text{CH}_4$ , why are there not four equal vibrational energies?

Analogous questions arise when equivalent-bond or lone-pair orbitals are discussed.  $\text{H}_2\text{O}$  has two equivalent O-H bonds and two equivalent nonbonding lone-pair orbitals. So why does its photoelectron spectrum display two distinct peaks in the region of ionization of the lone-pair orbitals and two more peaks in the O-H bond ionization region? This paper addresses these issues by emphasizing the difference between bonds or orbitals being equivalent and being independent.

## The Fundamental Question

The following fundamental question is addressed in this paper.

In molecules that have  $N$  symmetry-equivalent bonds (e.g.,  $\text{H}_2\text{O}$  with two identical OH bonds,  $\text{NH}_3$  with three identical bonds, and  $\text{CH}_4$  with four identical bonds), why do photoelectron spectroscopy experiments not yield  $N$  identical ionization energies corresponding to  $N$  equal orbital energies?

The key to this question is to understand the difference between bonds being *equivalent* (e.g., by symmetry) and bonds being *independent*—and thus *noninteracting*.

Different orbital energies should be expected to arise even when equivalent bonds are present. To show this I give a parallel analysis of the vibrational frequencies that occur for equivalent bonds. I begin by treating bond vibrational motions using tools of classical mechanics because these are more familiar to students of science. Then I use the quantum mechanical Schrödinger equation to study bond-orbital energies, with familiarity in the former area (1) helping introduce the latter.

I begin by carrying out a Lagrange equation classical dynamics (2) treatment of the stretching vibrations of two equivalent bonds in  $\text{H}_2\text{O}$ . Then I give the analogous Schrödinger equation treatment of the orbital energies of two equivalent bonds or lone pairs. Then connections to infrared and photoelectron spectroscopy are made, and extensions to more than two equivalent orbitals are discussed.

## The Two Different Vibrational Frequencies of the Two Identical Bonds in $\text{H}_2\text{O}$

Before examining the electronic orbital issue head on, let us consider a similar situation that is quite familiar to students of chemistry (1)—the stretching vibrations of the  $\text{H}_2\text{O}$  molecule. The question at hand is

How can a molecule with two identical OH bonds have two different vibrational frequencies for movement of these OH bonds?

In the analysis that follows, we use the coordinate system shown below in Figure 1.

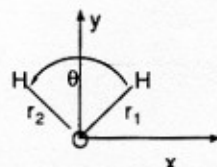


Figure 1. Coordinate system in which the two OH bond lengths of  $\text{H}_2\text{O}$  are defined.

## Classical Mechanical Kinetic and Potential Energies

The classical kinetic energy ( $T$ ) for movement of the two H atoms can be written in terms of time derivatives  $\dot{x}$  and  $\dot{y}$  of the  $x$  and  $y$  coordinates of these atoms, as shown below.

$$T = \frac{1}{2}m_H(\dot{x}_1^2 + \dot{y}_1^2 + \dot{x}_2^2 + \dot{y}_2^2)$$

Then the Cartesian coordinates are transformed to polar coordinates, that are appropriate to the above coordinate system.

$$x_1 = r_1 \sin\left(\frac{\theta}{2}\right)$$

$$x_2 = -r_2 \sin\left(\frac{\theta}{2}\right)$$

$$y_1 = r_1 \cos\left(\frac{\theta}{2}\right)$$

$$y_2 = r_2 \cos\left(\frac{\theta}{2}\right)$$

Thus, the kinetic energy can be rewritten in terms of time rates of change of  $r_1$ ,  $r_2$ , and  $\theta$ .

$$T = \frac{1}{2}m_H\left(\dot{r}_1^2 + \dot{r}_2^2 + \frac{r_1^2}{4}\dot{\theta}^2 + \frac{r_2^2}{4}\dot{\theta}^2\right)$$

The potential energy  $V$  of the  $\text{H}_2\text{O}$  molecule (i.e., the energy of the molecule as a function of its internal geometrical coordinates) can be expanded as follows in a Taylor series around the equilibrium-geometry point ( $r_{1,e}$ ,  $r_{2,e}$ ,  $\theta_e$ ) at which  $V$  is a minimum.

$$V = \left(\frac{\partial V}{\partial r_1}\right)_e (r_1 - r_{1,e}) + \left(\frac{\partial V}{\partial r_2}\right)_e (r_2 - r_{2,e}) + \left(\frac{\partial V}{\partial \theta}\right)_e (\theta - \theta_e)$$

$$+ \frac{1}{2} \begin{bmatrix} (r_1 - r_{1,e}) & (r_2 - r_{2,e}) & (\theta - \theta_e) \end{bmatrix} \begin{bmatrix} \frac{\partial^2 V}{\partial r_1^2} & \frac{\partial^2 V}{\partial r_1 \partial r_2} & \frac{\partial^2 V}{\partial r_1 \partial \theta} \\ \frac{\partial^2 V}{\partial r_2 \partial r_1} & \frac{\partial^2 V}{\partial r_2^2} & \frac{\partial^2 V}{\partial r_2 \partial \theta} \\ \frac{\partial^2 V}{\partial \theta \partial r_1} & \frac{\partial^2 V}{\partial \theta \partial r_2} & \frac{\partial^2 V}{\partial \theta^2} \end{bmatrix} \begin{bmatrix} (r_1 - r_{1,e}) \\ (r_2 - r_{2,e}) \\ (\theta - \theta_e) \end{bmatrix} + \dots$$

$V$  has a minimum at  $(r_{1,e}, r_{2,e}, \theta_e)$ . Thus,

$$\left( \frac{\partial V}{\partial r_1} \right)_e = \left( \frac{\partial V}{\partial r_2} \right)_e = \left( \frac{\partial V}{\partial \theta} \right)_e = 0$$

Thus, the first nonvanishing terms in the Taylor expansion, which presumably dominate for small vibrational displacements, are the so-called harmonic terms. Such quadratic approximations form the basis of much of the interpretation of vibrational spectroscopy in terms of force constants (i.e., second-derivative matrix elements as seen above) and atomic masses, which arise as shown below.

### Bond Lengths

We do not deal here with why  $H_2O$  has two bonds of equal length. There is a fundamental physical framework (3) in which one can examine such questions. For example, one would need to determine whether, at the  $C_{2v}$  geometry whose stability is in question, the electronic ground-state energy  $E$  of  $H_2O$  has positive or negative curvature along the asymmetric stretching mode  $Q_A$ . The evaluation of

$$\frac{\partial^2 E}{\partial (Q_A)^2}$$

can be expressed in terms of changes in the ground-state's electronic wavefunction

$$\frac{\partial \psi}{\partial Q_A}$$

induced by asymmetric-mode distortion and second derivatives of the electronic Hamiltonian.

$$\frac{\partial^2 H}{\partial (Q_A)^2}$$

It turns out that contributions to

$$\frac{\partial^2 E}{\partial (Q_A)^2}$$

from

$$\frac{\partial^2 H}{\partial (Q_A)^2}$$

are always positive, but contributions from

$$\frac{\partial \psi}{\partial Q_A}$$

may be positive or negative. If the molecule has an excited state whose symmetry is coupled to that of the ground state by asymmetric-mode distortions, the contributions from

$$\frac{\partial \psi}{\partial Q_A}$$

can be negative. For  $H_2O$ , the ground state has  $^1A_1$  symmetry in the  $C_{2v}$  point group, and the asymmetric mode is of  $b_2$  symmetry. Hence, a low-lying excited state of  $A_1 \times b_2 = B_2$

symmetry would be needed to (possibly) cause the molecule to be unstable along the asymmetric mode. For  $H_2O$ , there is no such low-lying  $B_2$  electronic state. Thus,  $H_2O$  is stable at its symmetric geometry.

### Classical Mechanical Hamiltonian and Lagrangian

We ignore the bending motion for now. Two different vibrational frequencies are still produced, so it will not qualitatively alter the conclusions drawn here.

Retaining only the harmonic parts of the potential, we can write the following in matrix notation: the classical Hamiltonian (2), which is defined as the sum of the kinetic and potential energy,  $H = T + V$ ; and the Lagrangian (2), which is defined as the difference between the kinetic and potential energies,  $L = T - V$ .

$$H \text{ (or } L) = \begin{bmatrix} \dot{r}_1 & \dot{r}_2 \end{bmatrix} \begin{bmatrix} \frac{1}{2}m_H & 0 \\ 0 & \frac{1}{2}m_H \end{bmatrix} \begin{bmatrix} \dot{r}_1 \\ \dot{r}_2 \end{bmatrix} + \frac{1}{2} \begin{bmatrix} (r_1 - r_{1,e}) & (r_2 - r_{2,e}) \end{bmatrix} \begin{bmatrix} \frac{\partial^2 V}{\partial r_1^2} & \frac{\partial^2 V}{\partial r_1 \partial r_2} \\ \frac{\partial^2 V}{\partial r_2 \partial r_1} & \frac{\partial^2 V}{\partial r_2^2} \end{bmatrix} \begin{bmatrix} (r_1 - r_{1,e}) \\ (r_2 - r_{2,e}) \end{bmatrix}$$

As discussed above, the equilibrium values of both OH bond lengths are identical ( $r_{1,e} = r_{2,e} = r_e$ ), giving the molecule  $C_{2v}$  symmetry. Thus, the diagonal elements of the second-derivative matrix are equal. (They will be denoted as  $f$ .)

$$\left( \frac{\partial^2 V}{\partial r_1^2} \right)_e = \left( \frac{\partial^2 V}{\partial r_2^2} \right)_e = f$$

Because  $V$  is an analytical function of  $r_1$ ,  $r_2$ , and  $\theta$ , the off-diagonal elements are also equal. (The off-diagonal element is called  $g$ .)

$$\left( \frac{\partial^2 V}{\partial r_1 \partial r_2} \right)_e = \left( \frac{\partial^2 V}{\partial r_2 \partial r_1} \right)_e = g$$

### Lagrange's Equations of Motion for Vibrations

Clearly the motion of the two bonds are coupled by the  $g$  elements of the potential. Thus, we say that these two bonds are equivalent but not independent because the potential energy's dependence on each bond length varies as a function of the other bond length. If this were not the case,  $g$  would vanish and the two bonds' motions would not be coupled. They are determined by the Lagrange equations of classical mechanics.

$$0 = \frac{d}{dt} \frac{\partial L}{\partial \dot{r}_k} - \frac{\partial L}{\partial r_k} = m_H \ddot{r}_k + \left( \frac{\partial^2 V}{\partial r_k^2} \right)_e (r_k - r_{k,e})$$

where  $k = 1$  and  $k = 2$  label the two bonds.

Simple harmonic motion would result.

$$\Delta r_k(t) = r_k(t) - r_{k,e} = (r_k(0) - r_{k,e}) \cos \left( \left( \frac{f}{m_H} \right)^{1/2} t \right)$$

The frequency

$$\omega = \left( \frac{f}{m_H} \right)^{1/2}$$

would be identical for both bonds.

However, the "potential coupling"  $g$  does not vanish in general. Thus, the motions of the two bonds,  $\Delta r_1$  and  $\Delta r_2$ , are coupled.

#### Uncoupling the Equations by Forming Symmetry-Adapted Coordinates

To solve the coupled-bond problem, one needs to find two combinations of  $\Delta r_1$  and  $\Delta r_2$  in terms of which the Hamiltonian and Lagrangian expressions will be "diagonal" (i.e., will contain no factors in which both coordinates appear). The particular combinations

$$S = \frac{1}{\sqrt{2}} (\Delta r_1 + \Delta r_2)$$

and

$$A = \frac{1}{\sqrt{2}} (\Delta r_1 - \Delta r_2)$$

which describe the symmetric ( $S$ ) and asymmetric ( $A$ ) movements of the two bonds, are the appropriate combinations as we now demonstrate.

If we use the Lagrange equations

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{r}_k} \right) - \left( \frac{\partial L}{\partial r_k} \right) = 0$$

that are obeyed by  $\Delta r_1$  and  $\Delta r_2$

$$m_H \ddot{\Delta r}_1 + f \Delta r_1 + g \Delta r_2 = 0$$

$$m_H \ddot{\Delta r}_2 + f \Delta r_2 + g \Delta r_1 = 0$$

and if we use the above expressions for  $S$  and  $A$  in terms of  $\Delta r_1$  and  $\Delta r_2$ , we can show that

$$m_H \ddot{S} = -(f+g)S$$

and

$$m_H \ddot{A} = -(f-g)A$$

#### The Symmetric and Asymmetric Mode Solutions

These equations for  $S$  and  $A$  are clearly uncoupled; the equation for  $A$  does not contain  $S$ , and the equation for  $S$  does not contain  $A$ . Moreover, the form of these two differential equations is of the simple sinusoidal type. Hence, the symmetric-stretch and antisymmetric-stretch variables,  $S$  and  $A$ , undergo simple harmonic motion.

$$S(t) = S(0) \cos \left( \left( \frac{f+g}{m_H} \right)^{1/2} t \right) \quad \dots$$

$$A(t) = A(0) \cos \left( \left( \frac{f-g}{m_H} \right)^{1/2} t \right)$$

They do so at different frequencies

$$\omega_S = \left( \frac{f+g}{m_H} \right)^{1/2}$$

$$\omega_A = \left( \frac{f-g}{m_H} \right)^{1/2}$$

If the bond-coupling term is  $g > 0$ , the symmetric stretch frequency  $\omega_S$  will exceed  $\omega_A$ . When  $g < 0$ , the reverse is true. For  $H_2O$  the experimentally determined values are  $\omega_S = 3652 \text{ cm}^{-1}$  and  $\omega_A = 3756 \text{ cm}^{-1}$ , so  $g < 0$ .

#### Summary

The two identical OH bonds in  $H_2O$  are not independent; They have coupling in their potential force fields. This

causes the two resonant stretching-vibrational frequencies of this system to be different. One frequency  $\omega_S$  describes in-phase movement of the two bonds; the other  $\omega_A$  describes out-of-phase motion<sup>1</sup> (see Fig. 2 below).

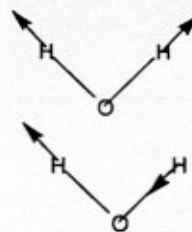


Figure 2. Representation of the symmetric (top) and asymmetric (bottom) vibrational modes of  $H_2O$ .

Stated another way, the two vibrations of the two OH bonds of the  $H_2O$  can be viewed as independent only by considering a symmetric motion and an independent asymmetric motion; it is impossible to think of each OH bond moving independently with a well-defined frequency. As students of physical chemistry are aware (1), the infrared absorption spectrum of  $H_2O$  clearly supports this picture; distinct symmetric and asymmetric stretching-vibrational frequencies are observed.

#### The Two Different Bonding Orbital Energies

The following question also requires an understanding that the two O-H bonds are identical but not independent.

How can the OH bonding orbitals of  $H_2O$  have different energies even though the bonds are equivalent?

Consider an electron moving in the region of space covered by one of the O-H bonding orbitals. (We denote these orbitals by  $\sigma_1$  and  $\sigma_2$ , as shown in Figure 3. The corresponding nonbonding lone-pair orbitals are labeled  $n_1$  and  $n_2$ .)

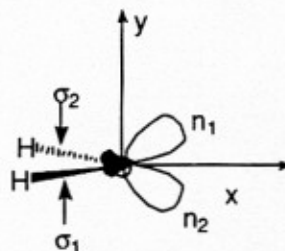


Figure 3. Representation of the two OH bonding orbitals of  $H_2O$ , labeled  $\sigma_1$  and  $\sigma_2$ . The two equivalent nonbonding lone-pair orbitals are denoted by  $n_1$  and  $n_2$ .

This electron experiences a potential that is due to its Coulombic interactions with the nuclei and electrons of the other OH bond. This potential involves the other OH bond's electrons. As we now demonstrate, even within the most elementary formulation of such electronic structure issues, such couplings arise.

#### The Schrödinger Equation for the Orbitals

For example, within one-electron pictures of electronic motion, the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t}(r, t) = H(r)\psi(r, t)$$

describes an electron's wave function  $\psi$  as a function of position  $r$  and time  $t$ . This equation can be solved approxi-

<sup>1</sup>If the molecule were not stable at the symmetric  $C_{2v}$  geometry, the frequency corresponding to asymmetric stretching motion would be imaginary.

mately by expressing  $\psi$  as a combination of the two O-H bond orbitals

$$\psi(r, t) = C_1(t)\sigma_1(r) + C_2(t)\sigma_2(r)$$

where  $C_1$  and  $C_2$  are time-dependent amplitudes.

This expansion is inserted into the above Schrödinger equation, and the resulting equation is multiplied on the left by  $\sigma_1^*$  (or  $\sigma_2^*$ ). Then integration over the spatial coordinate

$$r^2 (\sin \theta) dr d\theta d\phi$$

is performed, yielding a set of equations for the unknown amplitudes.

$$i\hbar \begin{bmatrix} \dot{C}_1 \\ \dot{C}_2 \end{bmatrix} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \end{bmatrix}$$

Here the elements

$$H_{ij} = \int \sigma_i^*(r) H(r) \sigma_j(r) r^2 (\sin \theta) dr d\theta d\phi$$

are the matrix elements of the Hamiltonian between the two O-H bond orbitals. The Hamiltonian operator  $H(r)$  contains the kinetic energy  $T$  of the electron. It also contains the electron's Coulombic potential energies of attraction—to the oxygen and two hydrogen nuclei—and repulsion—from the other electrons of the  $H_2O$  molecule.

Notice that the structure of the above Schrödinger-based matrix equation is similar to that of classical Lagrangian-based equations encountered in the previous section that dealt with vibrational frequencies. Because the two O-H bond orbitals are equivalent,  $H_{11}$  is identical to  $H_{22}$ . (In analogy with the vibration case, we denote these elements as  $f$ .) Thus,

$$H_{11} = H_{22} = f$$

because the orbitals  $\sigma_1$  and  $\sigma_2$  are identical in every manner except for their orientation in the  $x, y, z$  coordinate system of the  $H_2O$  molecule.

However, these two orbitals are not independent because, in general, the coupling element

$$H_{12} = H_{21} = g$$

does not vanish.

#### Symmetric and Asymmetric Orbital Combinations Are Used To Find the Energies of the Orbitals

As in the bond-vibration case, the symmetry of the Hamiltonian matrix

$$\mathbf{H} = \begin{bmatrix} f & g \\ g & f \end{bmatrix}$$

suggests that symmetric and asymmetric combinations of the  $C_1$  and  $C_2$  amplitudes may be useful in reducing the two coupled equations to two separate, uncoupled equations. Hence, we define

$$S = \frac{1}{\sqrt{2}}(C_1 + C_2)$$

and

$$A = \frac{1}{\sqrt{2}}(C_1 - C_2)$$

We can substitute these definitions into the matrix equation to generate the following equations for  $S$  and  $A$ .

$$i\hbar \dot{S} = (f + g)S$$

$$i\hbar \dot{A} = (f - g)A$$

As in the bond-vibration case, the symmetry-based combination of orbitals obey uncoupled time-dependent equa-

tions. The solutions of these equations show how  $S$  and  $A$  undergo simple sinusoidal motion.

$$S(t) = S(0) \exp\left(-\frac{i}{\hbar}(f + g)t\right)$$

$$A(t) = A(0) \exp\left(-\frac{i}{\hbar}(f - g)t\right)$$

However, the frequencies are different.

$$\omega_S = \frac{f + g}{\hbar}$$

$$\omega_A = \frac{f - g}{\hbar}$$

#### Summary

Clearly, the two equivalent OH bonds of  $H_2O$  produce two different energy levels

$$\epsilon_S = f + g$$

$$\epsilon_A = f - g$$

If  $g < 0$ ,  $\epsilon_S$  belongs to the lower energy molecular orbital (MO).

$$\sigma_S = \frac{1}{\sqrt{2}}(\sigma_1 + \sigma_2)$$

Then  $\epsilon_A$  belongs to the higher energy MO.

$$\sigma_A = \frac{1}{\sqrt{2}}(C_1 - C_2)$$

If  $g > 0$ , the energy of  $\sigma_A$  ( $\epsilon_A$ ) lies below that of  $\sigma_S$ .

The physical nature of the  $\sigma_S$  and  $\sigma_A$  MO's is described in Figures 4a and 4b for the  $H_2O$  molecule. The analogous symmetric and asymmetric combinations of the two equivalent nonbonding lone-pair orbitals  $n_1$  and  $n_2$  of  $H_2O$  are shown in Figure 4c.

#### Implications for Vibrational and Photoelectron Spectroscopy

That equivalent bonds can produce different vibrational frequencies and different orbital energies has direct experimental ramifications. In particular, the infrared spectra of molecules containing sets of  $N$  equivalent bonds display up to  $N$  distinct peaks (for fundamental, overtone, and combi-

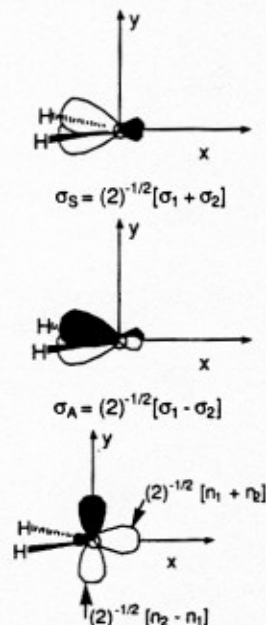


Figure 4. Depiction of the symmetric (top) and asymmetric (middle) combinations of the two equivalent OH bonding orbitals  $\sigma_1$  and  $\sigma_2$  of  $H_2O$  and of the symmetric and asymmetric combinations of the nonbonding lone-pair orbitals (bottom).

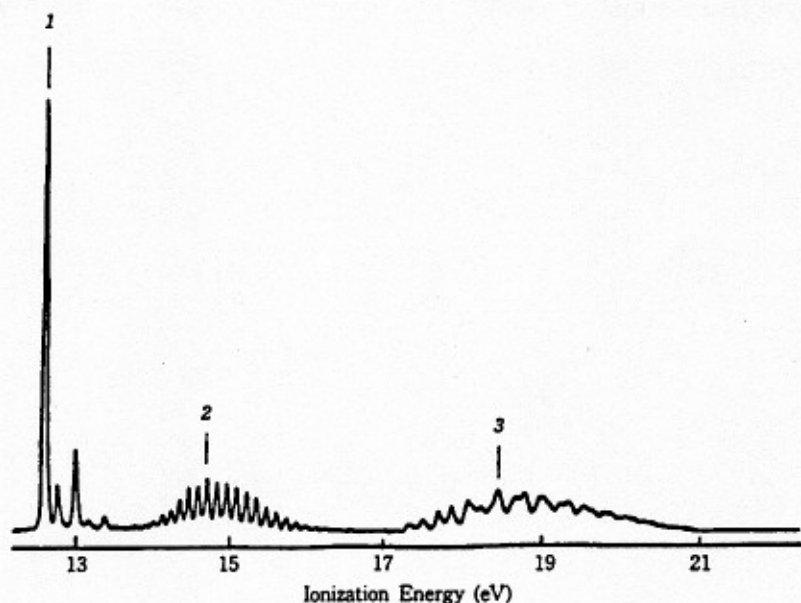


Figure 5. Photoelectron spectrum of  $\text{H}_2\text{O}(\text{g})$ . Interpretation of the three primary groups of peaks is provided in the text.

nation transitions) due to motion of these bonds at up to  $N$  distinct frequencies. Likewise, the photoelectron spectra of these same molecules contain up to  $N$  peaks due to the unique orbital binding energies.

#### Interpretation of Photoelectron Spectroscopy

In photoelectron spectroscopy (4), molecules are exposed to the electromagnetic energy of a fixed-frequency ( $\nu$ ) laser. Usually the laser that is used will have a photon energy  $h\nu$  that exceeds many of the molecule's orbital-ionization potentials. The electrons ejected from the molecule are subjected to kinetic energy (KE) analysis. Photoelectrons will be detected that have kinetic energies in the range described below that includes ionization events that convert a neutral molecule in vibrational state  $v_i$  (with energy  $E_{v_i}$ ) in the ground electronic state ( $E_0$ ) to a cation in vibrational state  $v_f$  (with energy  $E_{v_f}$ ) in electronic state ( $E_f$ ).

$$KE = h\nu - (E_f - E_0 + E_{v_f} - E_{v_i})$$

Thus, for each electronic state of the cation, a series of peaks, one for each  $v_i \rightarrow v_f$  vibrational transition, should be observed.

Within a given neutral-to-cation electronic transition, and for a given vibrational state  $v_i$  of the neutral species, the spacings between peaks are energy spacings in the vibrational levels of that particular electronic state of the cation. The relative intensities of such progressions of vibrational peaks depends on the population of the neutral-molecule vibrational level  $v_i$  and the so-called Franck-Condon factors between  $v_f$  and  $v_i$ . The latter involves squares of overlap integrals

$$\int \Psi_{v_f}^* \Psi_{v_i} dq$$

between the neutral-molecule's vibrational wavefunction and the cation's vibrational wavefunction, that is between  $\Psi_{v_i}$  and  $\Psi_{v_f}$ .

#### The Equivalent OH Bonds and Lone Pairs of $\text{H}_2\text{O}$

Such results are observed when the ionization energies of  $N$  equivalent lone-pair orbitals are examined. For example, the two equivalent nonbonding lone-pair orbitals of

$\text{H}_2\text{O}$  ( $n_1$  and  $n_2$ ) do not produce a single peak in the photoelectron spectrum of  $\text{H}_2\text{O}$ . Instead, two peaks are observed. One corresponds to the energy of the symmetric combination of the two orbitals.

$$\frac{1}{\sqrt{2}}(n_1 + n_2)$$

The other corresponds to the energy of the odd combination.

$$\frac{1}{\sqrt{2}}(n_2 - n_1)$$

A portion of the photoelectron spectrum of  $\text{H}_2\text{O}(\text{g})$  is shown below in Figure 5. The series of peaks near 13 eV corresponds to the removal of an electron that has the electronic binding energy expressed as below.

$$\int n_1^* H n_1 r^2 (\sin \theta) dr d\theta d\phi - \int n_1^* H n_2 r^2 (\sin \theta) dr d\theta d\phi$$

Those peaks near 15 eV arise when an electron with binding energy

$$\int n_1^* H n_1 r^2 (\sin \theta) dr d\theta d\phi + \int n_1^* H n_2 r^2 (\sin \theta) dr d\theta d\phi$$

is removed.

These binding energies are the energies that belong to the following symmetric and odd MO's

$$\frac{1}{\sqrt{2}}(n_1 + n_2)$$

and

$$\frac{1}{\sqrt{2}}(n_2 - n_1)$$

These are shown in Figure 4.

That the two different orbital-ionization processes each produce a set of peaks can be understood in terms of vibrational excitation of the respective cation states. Each peak in the range 12.5–13.2 eV belongs to a different  $v_i \rightarrow v_f$  transition, in which the cation is produced when one electron is removed from the following higher energy MO.

$$n_A = \frac{1}{\sqrt{2}}(n_2 - n_1)$$

(This produces a  ${}^2\text{B}_1$  electronic state of the cation.) The spacings between these peaks provide data about the vibrational energy levels of this  ${}^2\text{B}_1$  state of the cation.

Each peak in the range 14.0–16.0 eV belongs to a different  $v_i \rightarrow v_f$  transition, in which the cation is produced when one electron is removed from the following MO.

$$n_S = \frac{1}{\sqrt{2}}(n_2 + n_1)$$

(This produces a  ${}^2\text{A}_1$  electronic state of the cation.) Again, the spacings between these peaks provide data about the vibrational energies of this  ${}^2\text{A}_1$  state of the cation.

The series of peaks in the 17.0–21.0 eV range arise from various  $v_i \rightarrow v_f$  transitions in which the cation has one electron ejected from the following OH bonding MO.

$$\sigma_A = \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_2)$$

This produces a  ${}^2\text{B}_2$  cation.

The peaks belonging to the process in which an electron is ejected from

$$\sigma_S = \frac{1}{\sqrt{2}}(\sigma_1 + \sigma_2)$$

are not present in Figure 5 because the corresponding ionization energy  $\epsilon_S$  lies beyond the 21-eV limit of this experimental apparatus.

### Symmetry Can Cause Photoelectron Spectra To Contain Fewer Peaks Than Expected

#### Ammonia

There are situations in which  $N$  equivalent lone-pair orbitals or  $N$  equivalent bonds produce fewer than  $N$  unique ionization thresholds in the photoelectron spectrum. In such cases, the molecule's symmetry causes certain MO's—those that result from combining the equivalent but not independent orbitals—to have equal energy, that is, to be degenerate. The  $\text{NH}_3$  molecule's photoelectron spectrum shown in Figure 6 illustrates the point.

The series of peaks in the 10.5–12.0 eV range belong to a vibrational progression ( $v_i \rightarrow v_f$ ) in which the cation has one electron removed from the lone-pair orbital shown in Figure 7a. The large set of peaks in the 14.9–18.5 eV range are due to vibrational progressions of two degenerate cation states. These two-cation states occur when an electron is removed from either of the degenerate N–H bonding orbitals shown in Figures 7b and 7c. The peaks due to the cation state formed when an electron is removed from the totally symmetric N–H bonding orbital shown in Figure 7d lie at higher energies. They are not shown in Figure 6.

Why do the three equivalent N–H bonds of  $\text{NH}_3$  produce two degenerate MO's and one nondegenerate MO? The answer lies in the structure of the  $3 \times 3 \mathbf{H}_{ij}$  matrix that is the  $\text{NH}_3$  analog of that considered for  $\text{H}_2\text{O}$  in the previous section on OH bonding orbitals with different energies. This matrix has three equal diagonal elements because the three N–H bond orbitals  $\sigma_1$ ,  $\sigma_2$ , and  $\sigma_3$  are equivalent.

$$H_{11} = H_{22} = H_{33} = f$$

It has all off-diagonal elements that are also equal because the distances and orientations of the three N–H  $\sigma$  bonds relative to one another are identical.

$$H_{12} = H_{13} = H_{23} = g$$

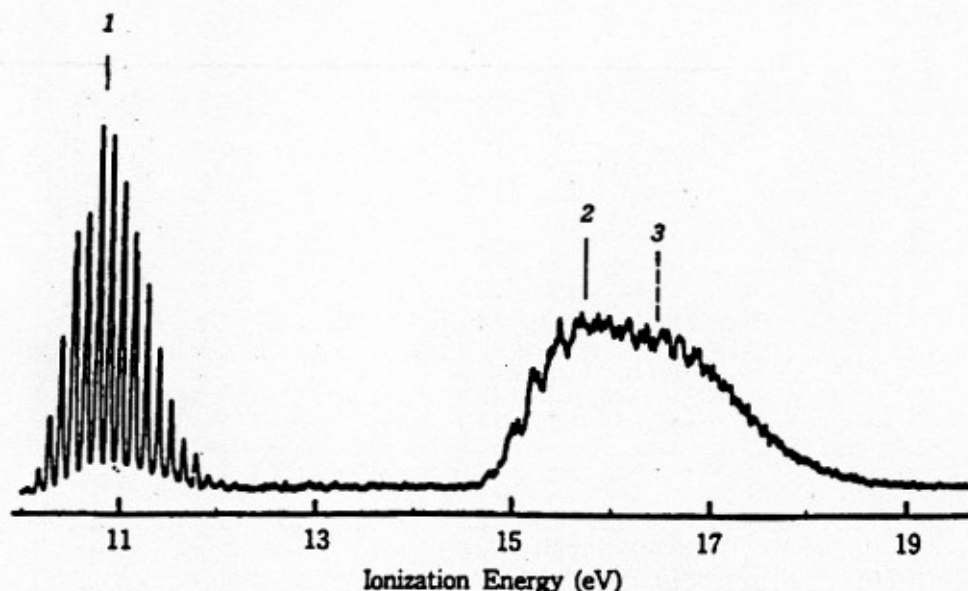
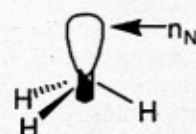


Figure 6. Photoelectron spectrum of  $\text{NH}_3(\text{g})$ . Interpretation of the two primary groups of peaks is provided in the text.



$$(6)^{-1/2}[2\sigma_1 - \sigma_2 - \sigma_3]$$



$$(2)^{-1/2}[\sigma_2 - \sigma_3]$$



$$(3)^{-1/2}[\sigma_1 + \sigma_2 + \sigma_3]$$

Figure 7. Orbitals of  $\text{NH}_3(\text{g})$  whose ionizations appear in the photoelectron spectrum. The nonbonding orbital of  $a_1$  symmetry (a), the degenerate NH bond orbitals of  $e$  symmetry (b and c), and the bond orbital of  $a_1$  symmetry (d).

The three eigenvalues of this  $3 \times 3$  matrix

$$\mathbf{H} = \begin{bmatrix} f & g & g \\ g & f & g \\ g & g & f \end{bmatrix}$$

are

$$\epsilon_{a_1} = f + 2g$$

and

$$\epsilon_e = \epsilon_{e'} = f - g$$

The following equations give the corresponding eigenvectors.

$$\mathbf{C}_{a_1} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \end{pmatrix}$$

$$\mathbf{C}_e = \begin{pmatrix} \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \end{pmatrix}$$

$$\mathbf{C}_{e'} = \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix}$$

These solutions, which are depicted above in Figure 7b–7d, are labeled by their  $C_{3v}$  point group symmetry names (5). The low-energy orbital belongs to the  $a_1$  irreducible representation, and the two degenerate orbitals belong to the  $e$  representation.

This  $\text{NH}_3$  example illustrates how a molecule's symmetry can cause a set of  $N$  equivalent orbitals (bonds or lone pairs) to produce  $N$  MO's whose energies are not

all distinct. If the MO's belong to degenerate representations (5) (i.e.,  $E$ ,  $T$ , etc., representations) of the point group, then the photoelectron spectrum will have fewer than  $N$  separate ionization thresholds.

#### Other Examples

The molecule's symmetry is reflected in the  $N \times N$   $H_{ij}$  matrix that corresponds to the equivalent  $N$  orbitals. In all such cases, the diagonal elements are equal for all  $i$ .

$$H_{ii} = f$$

The relative values of the off-diagonal elements are defined by the spatial symmetry relations among the  $N$  original orbitals.

Further examples include the four CH bonds in  $\text{CH}_4$  for which

$$H_{12} = H_{13} = H_{14} = H_{23} = H_{24} = H_{34} = g$$

due to the tetrahedral disposition of these four orbitals. Another example is the six SF bonds in  $\text{SF}_6$  for which all off-diagonal  $H_{ij}$  are identical ( $\equiv g$ ) except those  $H_{ij}$ 's that correspond to orbitals  $\sigma_i$  and  $\sigma_j$  that are trans (e.g., orbital pairs  $\sigma_1$  and  $\sigma_2$  in Figure 8).

In the former case, the four equivalent CH bond orbitals produce one MO with  $a_1$  symmetry of the tetrahedral ( $T_d$ ) point group (5) and three degenerate MO's of  $t_2$  symmetry. Thus, for  $\text{CH}_4$  only two (not four) ionization thresholds are expected in the CH bond region of the photoelectron spec-

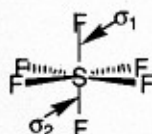


Figure 8. Sketch of the octahedral  $\text{SF}_6$  molecule's six equivalent SF bonds.

trum. In the  $\text{SF}_6$  case, the six equivalent SF  $\sigma$  bond orbitals yield one MO with  $a_{1g}$  symmetry in the octahedral  $O_h$  point group, a pair of degenerate MO's with  $e_g$  symmetry, and a set of three degenerate MO's with  $t_{1u}$  symmetry. Hence, for this molecule, only three distinct ionization thresholds (not six) are expected.

#### Conclusion

This paper provides a framework within which students of chemistry can address the following question.

In molecules that have  $N$  symmetry-equivalent orbitals (e.g.,  $\text{H}_2\text{O}$  with two identical OH bonds,  $\text{NH}_3$  with three equiv-

alent bonds,  $\text{CH}_4$  with four equivalent bonds, and  $\text{H}_2\text{O}$  with two equivalent lone pairs), why do photoelectron spectroscopy experiments not yield  $N$  identical ionization energies corresponding to  $N$  equal orbital energies?

The physical essence of the answer to this question is summarized by the following statement.

Although the bond or lone-pair orbitals may be equivalent (i.e., identical in all aspects but having spatial orientations that differ in a manner dictated by the molecule's symmetry), they are by no means independent of one another.

This same insight allows students to understand why equivalent bonds such as the pair of OH bonds in  $\text{H}_2\text{O}$  are not be viewed as vibrating independently of one another. They are more correctly viewed as undergoing symmetric or asymmetric stretching motions (with different frequencies).

The mathematical analyses of the classical Lagrange equation treatment of vibrational motion and the quantum Schrödinger equation treatment of orbital energies both give rise to matrix eigenvalue problems. The eigenvalues of the matrix provide the molecule's (harmonic) vibrational frequencies in the former case and the molecular orbitals' energies in the latter. The dimension  $N$  of the matrix is equal to the number of equivalent bonds or equivalent orbitals (bonding or lone pair) in the respective cases. The diagonal elements of the matrix are all equal; the off-diagonal elements depend upon the spatial distances and orientations that exist among the  $N$  bonds or orbitals. The  $N$  resultant eigenvalues may or may not be distinct. Molecular point group symmetry, which admits degenerate irreducible representations, can cause two or more of the energies to be equal. As a result, the  $N$  equivalent bonds or orbitals can give rise to up to  $N$  distinct vibrational or orbital energies. Several examples of these general conclusions have been provided throughout this paper.

#### Acknowledgments

This work was supported through National Science Foundation Grants CHE 881475 and 9116286 and by The Office of Naval Research.

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### European Workshop on Electrochemical Technology of Molten Salts

A Workshop on Electrochemical Technology of Molten Salts will be held March 14–17, 1993, in the Hotel Tivoli Sintra, Sintra, Portugal. The workshop will consider the contribution of fundamental studies of molten salt chemistry and electrochemistry to the improvement of industrial processes in two fields: Molten Salt Extractive Metallurgy (chemical processes and electrowinning applied to aluminum, refractory metals, rare earths, and other noncommon metals) and High Temperature Fuel Cells and Batteries, which are in a period of growth and development.

Authors are invited to submit titles of papers covering any of the above or related topics by August 31, 1992. They should be sent to: C. A. C. Sequeira, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal. Program details will be available from the same address after October 1992.