Determination of the Actual Form of Each Vibrational Mode of H_2S Molecule Using Projection Operator Method

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Abstract— this paper we have set up the combinations of bond stretching vibrations which form the bond streching vibrational modes of H_2S molecule using projection operator method.

Keywords— Symmetry, Reducible and Irreducible representation

I.   INTRODUCTION

The stretching of the bond vectors of a molecule along different directions are most commonly used for the construction of the basis set for a reducible representation of a particular point group (1). In the present case of projection operator method I have extended the mathematic a bit with the knowledge of symmetry theory. We know that H_2S molecule is sp^3 hybridized where four of the sp^3 hybridized orbitals are directed towards the four corner of a regular tetrahedron. In H_2S, two sp^3 hybrid orbitals of S each one having a single electron involve in the bonds formation with two H-atoms containing a unpaired electron in each and the remaining two sp^3 hybrid orbitals contain a lone pair of electrons. The molecular shape of the H_2S molecule is 'V'-shaped and it is under C_{2v} point group. The stretching of the S-H bonds of H_2S can be taken as the basis for a reducible representation of the C_{2v} point group and it is possible to find the symmetry properties of various molecular vibrations with a test on their Infrared and Raman activities (2). In the present paper I have set up the combinations of bond stretching vibrations which form the bond streching vibrational modes of H_2S molecule by projection operator method.

II.   MATERIALS AND METHODS

The different ways the S-H bonds of H_2S molecule can vibrate are as follows

Mode-1

Mode-2

(a) both the hydrogens to move out together and both to move in together as in Mode-1, called symmetric streching and (b) one H-atom moves out while the other moves in as in Mode-2, called anti-symmetric stretching. In symmetric stretching mode the distorted molecule looks the same after applying any of the group operations of the point group (totally symmetric, A1). But in anti-symmetric stretching mode the phase of the vibrations are going to change in a reverse way by the operations C_2 (simple rotation) and by the σ'_v (yz) (vertical plane). The reversal of the phase of the vibrations is represented by the number (-1) in the character table (2).

Figure-1

From Figure-1 it is clear that in symmetric stretching mode of vibration of the two S-H bonds in the H_2S molecule, the resultant bond moment vector is going to oscillate along z-axis (totally symmetric, A_1) and in anti-symmetric stretching mode of vibrations the resultant bond moment vector is going to oscillate along x-axis (B_1). As the resultant bond moment vector along Z-axis not going to get any change of the phase of vibrations by any of the group operations of the C_{2v} point group it is called the totally symmetric and designated as A_1 representation of the C_{2v} point group (3). Whereas, in anti-symmetric stretching the resultant bond moment vector along X-axis going to observe a reverse change of the phase of the vibrations by the operations C_2 (simple rotation) and by the σ'_v (yz) (vertical plane) as the molecule supposed to be in the xz-plane Figure-1. The x belongs to B_1 representation of C_{2v} because this set of numbers represents the effect of the group operations on a p_x orbital, or indeed anything with the same symmetry properties as the x-axis. Therefore we have assigned the anti-symmetric mode of stretching vibrations by the B_1 representation (4). We have drawn a set of vectors (and   ) which formed the basis of the reducible representation of the C_{2v} point group. In projection operator method we have selected one (   ) vector as a generating vector and found the result of operating on it by each of the group operations.

III. RESULTS AND DISCUSSION

The application of the identity operation (E) leaves   unchanged but the simple rotation operation (C_2) moves the   over to   .
Vector   becomes: -

Application of σ_v (xz) leaves   unchanged but application of σ'_v (yz) moves the   over to   . The complete set of the row are as follow

For each irreducible representation we have multiplied each of the above results by the character of the irreducible representation in the character table and made the sum

The character table of the C_{2v} point group

Here x^2-y^2, z^2, xy, xz, yz are the transformation properties of the d-orbitals and x, y and z are the transformation properties of the directions. R_x, R_y and R_z are the transformation properties of the three rotations.
For, A_1 vibration: - $\times 1$+ $\times 1$+ $\times 1$+ $\times 1$= 2 + 2
Similarly

A$_2$ vibration: - $\times 1+$ $\times 1+$ $\times -1+$ $\times -1= 0$
B$_1$ vibration: - $\times 1+$ $\times -1+$ $\times 1+$ $\times -1= 2$ $-$
2
B$_2$ vibration: - $\times 1+$ $\times -1+$ $\times -1+$ $\times 1= 0$

IV. CONCLUSION

For A$_1$ and B$_1$ we have finite values but for A$_2$ and B$_2$ we have zero. Therefore we can conclude that in H$_2$S molecule there is no A$_2$ or B$_2$ bond stretching modes and there are only A$_1$ and B$_1$ modes of stretching vibrations. We have found that the projection operator method has produced modes of vibration described as (2   + 2   ) and (2 $-$ 2   ) instead of (+   ) and ($-$). This is

because all such combinations of bond stretches should be normalized. We have achieved this by making each coefficient   .

The vibrational modes for the H$_2$S molecule

A$_1$:-   (+   ) and B$_1$:-   ($-$)

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