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Molecular Spectroscopy – A Physical Chemist's perspective

Lecture-30

Symmetry in Chemistry: An Introduction

With

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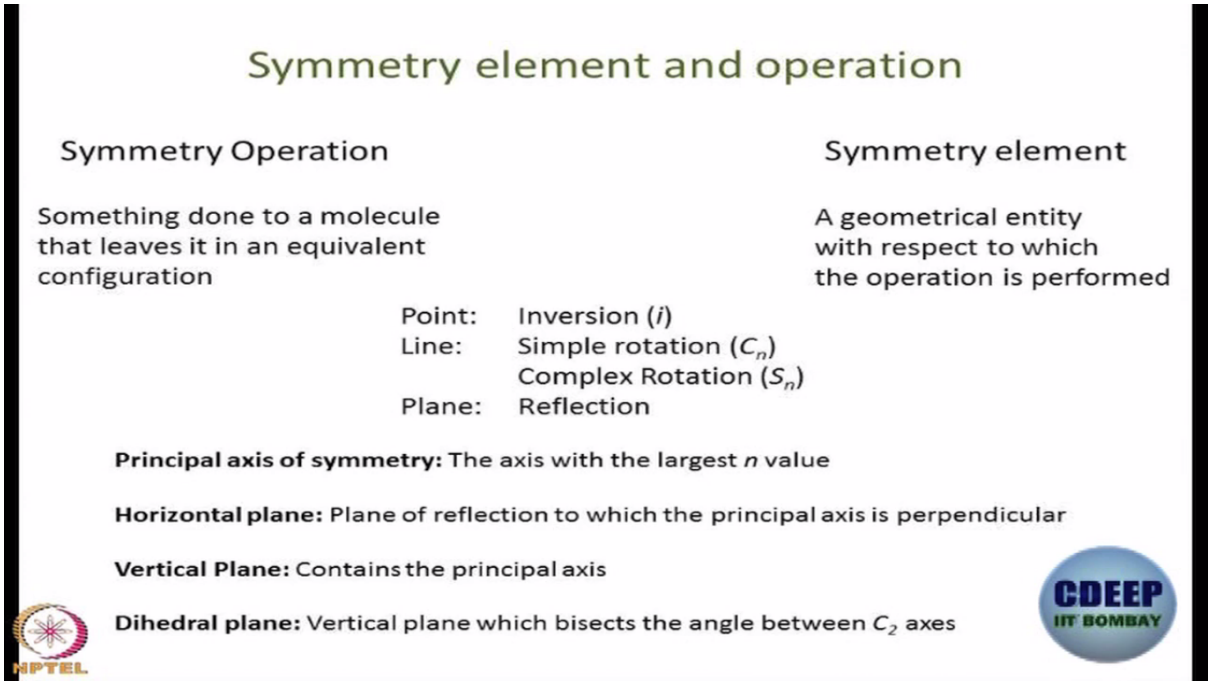


So very quick recap of symmetry classification of molecules. Now what I see is that even in schools, nowadays, they talk about symmetry elements. So I believe all of us know what a symmetry element is, what a symmetry operation is. What is a symmetry operation? What is the formal definition? What's a symmetry operation? We'll come to symmetry element afterwards. Well, symmetry operation is something that we do to a molecule which leaves it in an equivalent configuration. So it looks the same if I put it in the very, very simple words. And symmetry element is a geometric entity with respect to which the operation is performed. I find it easier to define the operation first then go to the element.

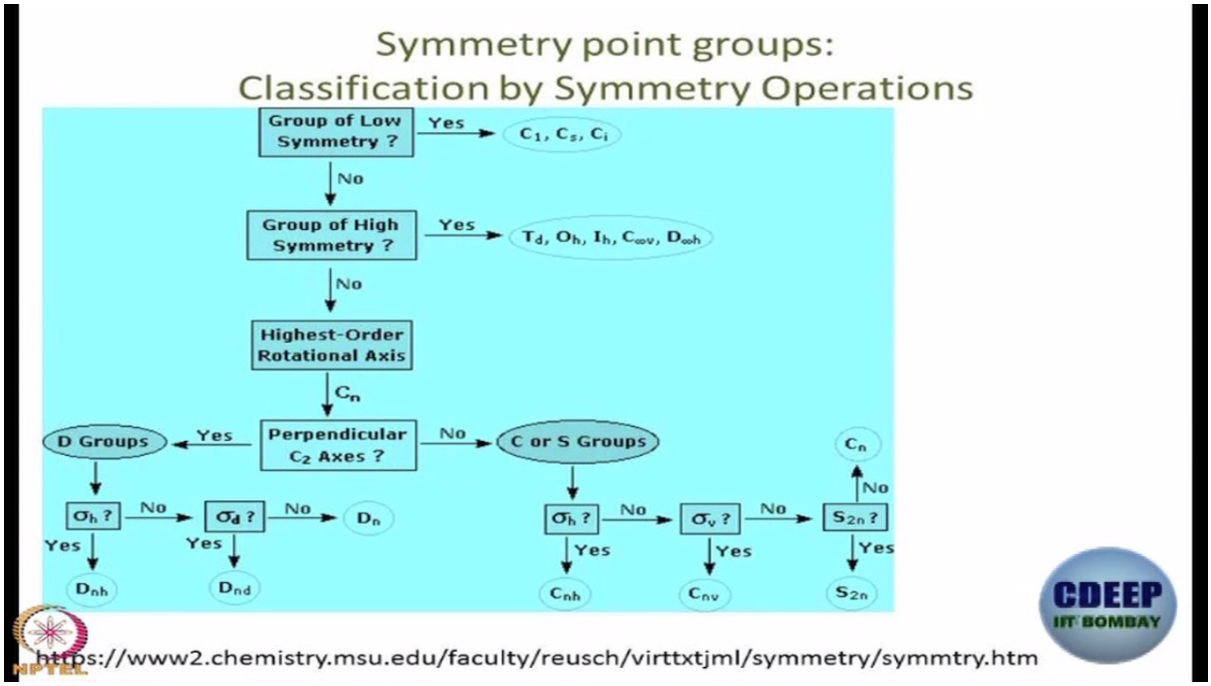
When I say geometric entity, what I mean is point, line or plane. So this is a symmetry operation, this is symmetry element. Now, with the point what do you do? You do an inversion. What is the meaning of inversion? You start from some point of the molecule, go to the point of symmetry, extend the line to an equal distance on the opposite side. If you reach the same entity from where you started then that is a symmetry operation, otherwise not.

Line, what do you do? You can turn simply that is called simple rotation or you can turn and then do a reflection that is the called the axis of alternating rotation and it is written as C_n. What does this n stands for? By which angle you'll rotate, $180^o/n$ or $360^o/n$? $360^o/n$, very good. Complex rotation means you rotate by $360^o/n$ and then you do a reflection along a plane to which this axis is perpendicular.

In plane, plane is perhaps the easiest to understand because that is what we do everyday when we comb our hair hopefully, we do a reflection. Principal axis of symmetry we know is the axis with the largest value of n that mean the axis about which we turn by the biggest angle. Do not say yes without thinking. It is the axis about which we turn by the smallest angle to get the equivalent configuration.

So you see, even though you actually know everything about symmetry, you can go wrong if you are not very careful. n is large, n means is in the denominator, don't forget. Horizontal plane means if this is the principal axis of symmetry then this would be the horizontal plane,

a plane to which the principal axis of symmetry is perpendicular. Naturally vertical plane would be a plane that contains the principal axis of symmetry and sometimes you have things like dihedral planes. Dihedral planes arise when in addition to the principal axis of symmetry your C_2 axis perpendicular to it and there is a vertical plane that bisects the angle between the C_2 axis. By definition they are called dihedral planes.



Knowing this we can do a symmetry classification of molecules. This is a table that nobody has to remember. Very nicely worked-out table which nobody has to remember except for one point. So basically you work out the point group of many molecules, it will come to you automatically. The only confusing part for me even now is this. But we'll come to that. So essentially what you do is first of all, you ask, is it a group of low symmetry. That means you can have molecules that have no symmetry element at all, then it is called C_1. What is C_1? Rotation-wise 360^o. You take anything and rotate it by 360^o you get identical configuration.

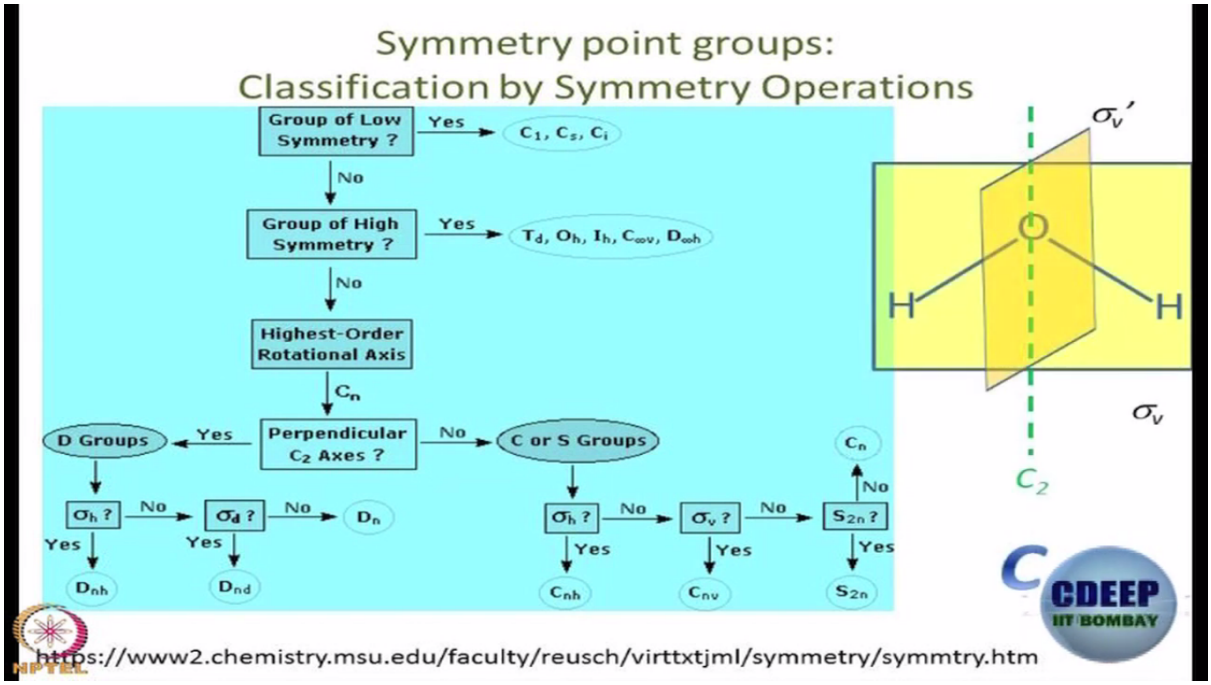
So C_1 is present in any object that you can think of. So there the name is C_1, these names are called point groups. Next question you ask is suppose there is only one plane of symmetry then it is called C_s, s for sigma, sigma means plane. Or maybe there is only an inversion point, then it is called C_i. Point to note is that I did -- well, the question I ask is, is there any -- we did not ask whether there is a point of -- whether there is an axis of symmetry yet.

Next thing you ask is, this is one end of the spectrum where there is hardly any symmetry. Other end of the spectrum is molecules with very high symmetry, more than one principal axis, then the tetrahedron, octahedron, icosahedron, so on and so forth. If you don't know this, come over, we'll discuss. Then we ask, if there is only one principal axis of symmetry, what is the n value. Once you know it, you ask this question, do you have perpendicular C_2 axis. If there is no perpendicular C_2 axis, you call it either c or s. If you have perpendicular C_2 axis, you call it D.

We'll take this side first. If there is D, do you have σ_h, σ_h has highest priority, then you call it D_{nh}. If h is not there then you'll look for dihedral angles. If that is also not there, then you call it D_n. On the other hand, if you don't have C_2 axis then it's going to be either c or s. The same way you look for σ_h. If it is there you call it C_{nh}. Otherwise look for σv, if σ_v is there call it C_{nv}.

If nothing is there, this is where I get confused. So I hope that at least one or two of you also get confused to keep me company. If it is not there then you look for S_{2n} axis.

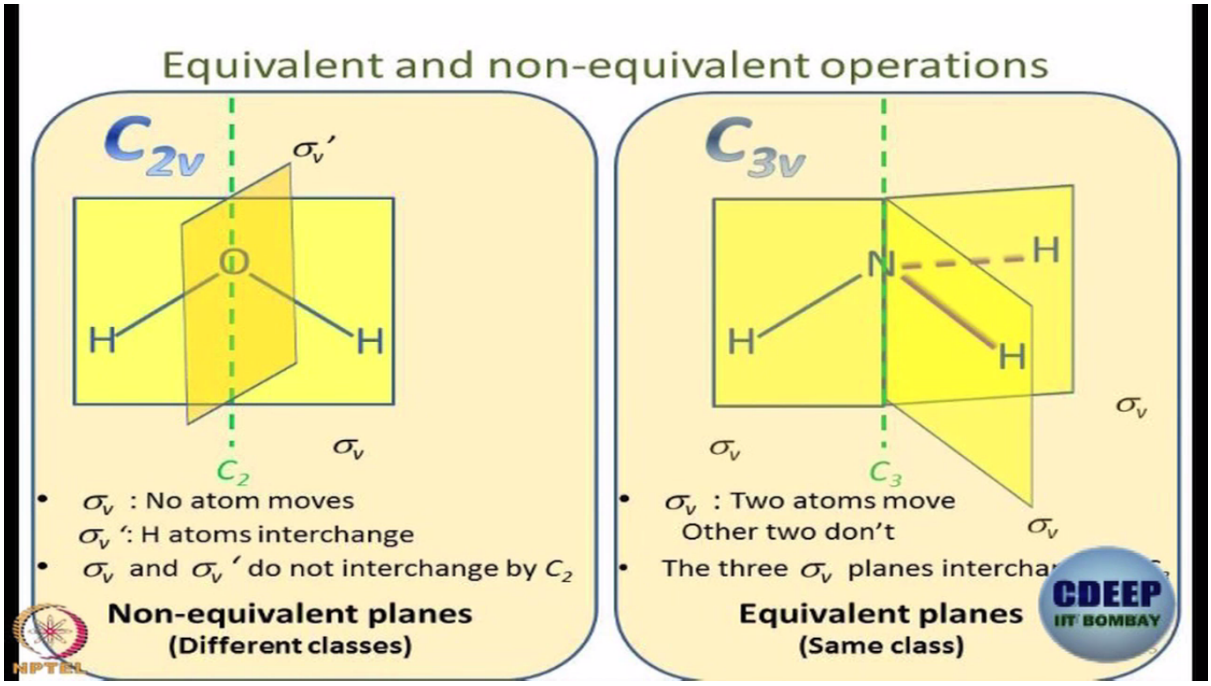
Sometimes even where there is no C_n axis, S_{2n} can be there. If it is there, then you actually call it S_{2n}. only if S_{2n} is also not there, then only you call it C_n. This is the only place where I get confused. Now you can forget everything except for that last part.



First we start with the simplest possible molecule. Well, we can think off even simpler molecules, H_2, but H_2 is actually complicated. So we'll start with water. What is the principal axis of symmetry? Very simple, C_2. This is water. Turn by 180°, you get the same thing. So this is your C_2 axis of symmetry. Do I have planes of symmetry?

If this is water, this is one plane, molecular plane, this is another plane. So two planes of symmetry; this is one molecular plane and this is perpendicular. It's important to understand that these are not equivalent planes, we'll come to that later.

So what will the name be? Since you are doing it the first time, what will the name be? Remember this, what do I look for. I look for principal axis. What is principal axis? C_2. Do you have perpendicular C_2 axis? No. So it cannot be D_2, it has to be C_2. Do I have σ_h? σ_h is horizontal plane. So if this is the axis, if there is a plane like this, then it is σ_h. But the planes that I have here, one is like this, one is like this, no σ_h but these are called vertical planes. So σ_v is there. So this is a C_{2v} molecule. So was that easy or was that easy? Either way, it was easy. So this is a called a C_{2v} molecule, simple.



We'll conclude today's discussion with this thing, NH_3. What is the principal axis of symmetry? Ammonia looks like this, C_3. Do we have horizontal plane? No. What about vertical plane? You see the vertical plane. This is C_3, this is one plane. How do you define that plane? A plane that contains one NH bond and bisects kind of -- so how many such planes are there? Three. So you draw the three planes, it looks like blades of a fan. Nothing else, so this is your C_{3v}.

So one important difference between C_{2v} and C_{3v} is the action of the planes. Think of water. Molecular plane, what happens, no atom changes position. If we use the plane that is perpendicular to the molecular plane then what happens? This hydrogen atom goes here, this hydrogen atom comes here.

If you use the perpendicular plane, just like this, this hydrogen atom will go here, this hydrogen atom will come here. So the action of these two planes are not the same. However, if you look at this, action of any plane is that this nitrogen doesn't change planes, hydrogen atom contained in that plane itself doesn't change place, the other two hydrogen atoms change the place.

So all three planes here are equivalent or what we are going to say later, they belong to the same class, the two planes here are non-equivalent; they belong to different classes.

We'll stop here today and what I'll do is I'll upload the slides. Next day what we'll do is we'll discuss how we can convert all these geometrical operation to try to write an algebraic equation.