Chemistry II: Introduction to Molecular Spectroscopy

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Lecture – 26
Review of Microwave Spectroscopy

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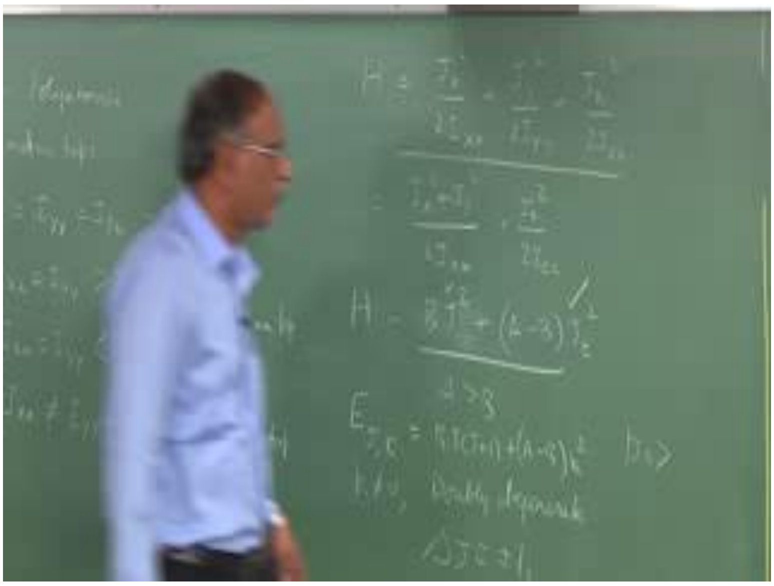

So, we continue with the rotational spectra microwave of polyatomic molecules and I recall that in the case of polyatomic systems, we were only looking at the spectra of symmetric tops and you remember that the symmetric top is one of the special types of molecules in which the movements of inertia have certain relationships. For a general polyatomic molecule the three movements of inertia about the mutually; three mutually perpendicular orthogonal axis all passing through the centre of mass of the molecule or in general different; however, the special case when the principle the so called principle movements of inertia when they are equal in all directions I x x, I y y, I z z this was called the spherical top and some examples are given cubic molecules and perfectly tetrahedron molecules are the best examples for spherical top.

Then we had the special case namely I x x equal to I y y greater than I z z that is not equal to I z z and the other case I x x is equal to I y y less than I z z then this was called prolate and at the I z z is greater than the other 2 equal movements of inertia it was called the oblate symmetric top, both are symmetric tops. The spectrum of symmetric top and the energy levels of the symmetric top are easy to calculate because of the special fact that the Hamiltonian for the symmetric top has a specific; has a special form. Please remember for a molecule which had all the three movements of inertia being different, the Hamiltonian is written as j x square by 2 I x x plus j y square by 2 I y y and j z square by 2 I z z and this I did not solve in this course because it is a; it is called an a symmetric top.

The three cases I x x not equal to I y y, not equal to I z z is called a symmetric form and some examples were given in the lecture and you are supposed to look at the structure of the molecule and any molecule which has a threefold axis of symmetric will most likely be a symmetric top and molecules which do not have a threefold axis of symmetric which have only twofold axis of symmetric or by nature they are a symmetric top. So, there are some special rules I think, I mentioned that in the class in the course.

This was not solved, but what was solved was the special case j x square plus j y square by 2 I x x then I x x is equal to I y y and j z square by 2 I z z. You recall that I wrote this Hamiltonian as; a j; I believe it is b j into j; j square, j z square, let me write b j square plus a minus b, j z square. This was the Hamiltonian form and for a prolate this is a b's are the inverse movements of inertia, 1 by 2; 1 by I x x was related to b and one by I z z was related to a, inverse movements and this when a is greater than b which means I z z is less than I x x it was called the prolate symmetric top and a is less than b it was called oblate symmetric top and you had the energy level diagrams written for j square and j z square operator.

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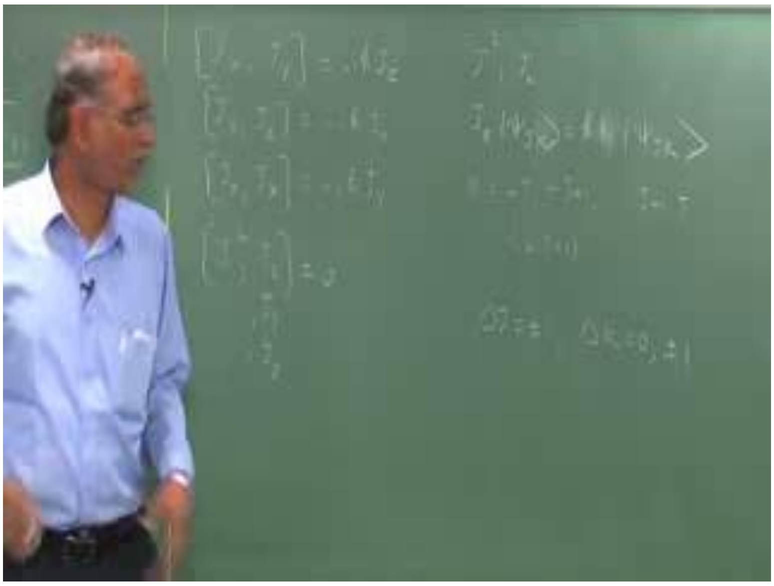

You may recall that angular momentum quantum mechanics particularly for the molecular system does not, the components do not commute with each other and for molecules spectroscopy we use the commutation relation minus I h bar j z because the axis x y z are fixed in the molecule and this essentially means the other components as well j y, j z where minus I h bar j x and j z j x were minus I h bar j y. What it means is that simultaneously you cannot measure the x component of the angular momentum and the y component of the angular momentum for the same system, but you can always measure the absolute square of the angular momentum and one of the three components because in the lecture I remember telling you that j square comma j x is equal to 0 or j y is equal to 0 or j z, that is j square commutes with all the three components, but these do not commute with each other therefore, you have this and one of these and the one of these components was chosen always as j z and j z on the ideal functions I j was shown in hydrogen atom the earlier and in many other cases to be your h bar m or k; I believe I used the index k (Refer Time: 06:27) j k and we used k as the quantum number and the k is the index which is essentially, it is a quantum number which is the projection of the angular momentum on to a chosen molecular axis; the z axis and k has possible values from minus j, minus j plus 1 to j minus 1, 2 j namely 2 j plus 1 values.

The eigen values for the symmetric top where or j z square acting on the ray function therefore, this will give you k square instead of k. Therefore, the energy for the symmetric top is given by two quantum numbers j and k and that is b j into j plus 1 plus a minus b into k square and you can see immediately that k is equal to 0 is a unique energy eigen values it is non-degenerate; one energy state and that state is called j 0. When all the other states plus minus 1, plus minus 2, plus minus 3 all the way up to plus minus k, each one of them they have a slightly different energy because of k square, but both of them will be the same plus k and the minus k will be the same.

Therefore, for all case not equal to 0, the energy levels are doubly degenerate and we also looked at to the prolate and the oblate symmetric top and here also it is important to note that the microwaves spectrum is possible only if the molecule has a permanent dipole moment, but it is possible that the molecule has a dipole moment in an arbitrary axis not along the z axis or along the x axis or y axis that you choose. Therefore, the angular momentum; the dipole moment we have more than one component in the respective directions leading to the fact that there are different selection rules.

But all of them will involve delta j recall to plus minus 1 and depending on the special molecular cases you may have the selection rules, delta j is equal to plus minus 1 and delta k is equal to 0 or plus minus 1, that depends on the molecular nature. We did not elaborate this, but I recalled that this was the stated selection rule for the polyatomic molecular case. We looked at some of the polyatomic systems namely what are symmetric tops and what are a symmetric tops, some examples are given and some of the energy levels were given and basic calculations regarding the dipole moment metrics element that also given. With that I think we sort of completed the basic structure on microwave spectroscopy, we did not move onto the non reject molecular system and also the, a symmetric top molecular system because they are slightly more complex and usually one studies such system in the next level of the introductory course to spectroscopy therefore, I stopped there.

Now, in the next part of this review, overview there is only one more part on this, I will talk a little bit about the review of the vibrational spectroscopy that we looked at with the more important formulas that you need to remember and you also have to keep in mind in taking this course further. So, we will move onto the vibrational spectroscopy of what is called the harmonic oscillator model spectroscopy for the diatomic molecule and then we will also look at the summary of the normal modes that we study along with this one extension model for the non anharmonic model namely the Morse oscillator, that will be the summary of the remaining part of this overview of the whole course.

Thank you.