

## Introduction

While the last lecture served to make the connection between molecular symmetry and vibrational spectroscopy, today's lecture turns to the relationship between molecular vibrations and chemical reactions. Important concepts to review are those connected to the potential energy surface (PES) and the reaction coordinate (RC). In the last lecture, we talked about the correspondence between the number of bands observed in the infrared spectrum and the structure of a molecule. Now, we will again consider the relationship between molecular symmetry and the number of bands observed in a particular kind of spectroscopic measurement.

## Sets of Equivalent Fluorine Atoms in $\text{PF}_5$

Consider a molecule such as  $\text{PF}_5$ . In principle, this molecule could adopt any of several structures. For example, the molecule could have  $D_{3h}$  symmetry or alternatively it could have  $C_{4v}$  symmetry or it might even be possible for the molecule to be planar and have  $D_{5h}$  symmetry. On the other hand, the  $\text{PF}_5$  molecule could be pyramidal with a structure belonging to the  $C_{5v}$  point group. Here's a question we can ask concerning these various possible structures for the  $\text{PF}_5$  molecule: for a given structure, how many fluorine environments are present?

In the first case, the  $D_{3h}$  structure provides two different fluorine environments which are present in a 2 to 3 ratio. Actually, we can determine this through application of the operations of the  $D_{3h}$  point group. For example, carrying out a  $C_3$  operation leads to exchange of fluorine positions in the equatorial plane, but does not affect the two axial fluorine atoms. On the other hand, we also see that if we carry out a  $C_2$  operation, this leads to pairwise exchange of equatorial fluorine atoms at the same time as it leads to pairwise exchange of the axial fluorine atoms. What we will find is that none of the group operations leads to exchange between the axial and the equatorial positions. This is why  $D_{3h}$  symmetry for  $\text{PF}_5$  mandates the presence of two distinct fluorine environments in a 2 to 3 ratio. Think about it this way: an axial fluorine atom has three neighbors close by at  $90^\circ$  angles, whereas an equatorial fluorine has four neighbors (two at  $90^\circ$  angles and two at  $120^\circ$  angles).

Carrying out a similar analysis, in the case of the  $C_{4v}$  geometry,  $\text{PF}_5$  again would have two fluorine environments, but now these would be present in a 1 to 4 ratio. This can be seen by carrying out the various operations of the  $C_{4v}$  point group. Carrying out a reflection operation leads to exchange of equatorial fluorine atoms, as does carrying out a fourfold rotation operation. None of the operations of the  $C_{4v}$  point group leads to exchange of the axial fluorine with any of the equatorial fluorine atoms.

The two other possible structures we can conceive of for  $\text{PF}_5$ , namely the  $D_{5h}$  and the  $C_{5v}$  geometries, share a common feature: they both have only a single fluorine environment.

If we had access to some kind of spectroscopy that could tell us how many fluorine environments are actually present, then we could potentially distinguish between the above possibilities with the exception of the  $D_{5h}$ - $C_{5v}$  case. Fortunately, we do have access to a type of spectroscopy that will tell us how many fluorine environments there are! The spectroscopy we generally use for this is called nuclear magnetic resonance, or NMR, spectroscopy. This takes advantage of the fact that when atomic nuclei are in different environments, they will resonate at different frequencies when placed inside a strong magnetic field and. The most common applications of NMR spectroscopy are two problems involving nuclei possessing a magnetic dipole moment. Examples of such nuclei are  $^1\text{H}$  and  $^{13}\text{C}$ . The former conveniently has a high natural abundance, whereas the latter has a low natural abundance. Both fluorine and phosphorus have a high natural abundance isotope that

is very useful for NMR spectroscopy:  $^{31}\text{P}$  and  $^{19}\text{F}$  are the nuclei in question.

Therefore, we ought to be able to just take the  $^{19}\text{F}$  NMR spectrum of  $\text{PF}_5$  to find out the number of fluorine environments. In most cases, this approach works very well to determine the number of environments that are present for a particular type of NMR active nucleus in the molecule. However, it turns out that in the case of  $\text{PF}_5$ , and other molecules in this category termed “fluxional”, this does not work. The reason it does not work is that NMR is a relatively slow type of spectroscopy. Unlike in the case of an infrared spectrum, wherein the atomic nuclei are effectively frozen on the time scale of measurement, with NMR spectroscopy is sometimes possible for the atoms in a molecular structure to rearrange themselves rapidly relative to the time it takes to acquire the measurement; in this case the environments become averaged. So indeed, although we do find only a single  $^{19}\text{F}$  NMR signal for  $\text{PF}_5$  at room temperature, the infrared spectrum is consistent only with the  $D_{3h}$  structure.

Now the question becomes, what is the mechanism by which axial and equatorial fluorine atoms can exchange with one another so rapidly? The accepted explanation is called the Berry pseudo-rotation, or BPR.

## Berry Pseudorotation

We will now examine the basic idea of the BPR, and look at the relationship of this mechanism to the definition of intermediates and transition states along a potential energy surface (PES).

Starting at the structure for  $\text{PF}_5$  that has  $D_{3h}$  symmetry, we will pick one of the equatorial fluorine atoms which along with the phosphorus atom will remain stationary as we proceed along the reaction coordinate (RC, a 2D slice through the PES). The motion described by the molecule is one in which the two axial fluorine atoms will increase their bond angle with reference to the stationary fluorine starting from  $90^\circ$  and progressing to  $120^\circ$ . At the very same time, the two fluorine atoms originally equatorial will decrease their bond angles with reference to the stationary fluorine such that that parameter begins at  $120^\circ$  and ends at  $90^\circ$ . In this way, the molecule executes a continuous change in bond angles leading to pairwise exchange of axial and equatorial fluorine atoms. The structure begins with  $D_{3h}$  symmetry and it ends with  $D_{3h}$  symmetry. The final structure differs from the original structure only in the sense that it appears to have undergone a  $90^\circ$  rotation about the axis that is defined by the phosphorus and the stationary fluorine. Hence the name Berry pseudo-rotation.

We can ask ourselves also the following question: what is the symmetry of the structure of  $\text{PF}_5$  during the BPR process at the point of maximum energy? The structure at this point of maximum energy has  $C_{4v}$  symmetry and is referred to as the transition state (TS) structure. We can strive to describe the BPR process completely in terms of symmetry. The process starts out at a potential energy minimum having  $D_{3h}$  symmetry. As soon as the aforementioned angle changes begin to take effect, the structure takes on  $C_{2v}$  symmetry. At the highest point on the PES the structure instantaneously gains  $C_{4v}$  symmetry and then drops down again to  $C_{2v}$  before proceeding on to an equivalent potential energy minimum possessing  $D_{3h}$  symmetry. Most of the time,  $\text{PF}_5$  is simply vibrating about its equilibrium nuclear configuration having  $D_{3h}$  symmetry, but every once in a while it goes on and hops over that small energy barrier in the process we call BPR. That energy barrier in the case of  $\text{PF}_5$  is very small, only around 3.5 kcal/mol, which is similar to or less than the energy of a typical hydrogen bond. So, the BPR process is rapid and the  $^{19}\text{F}$  nuclei are exchanging their environments rapidly relative to the time it takes to make the NMR measurement such that only a single resonance peak is seen. In principle, we should be able to cool the sample down to a temperature where BPR becomes slow on the NMR timescale, and then we should see

two peaks in the  $^{19}\text{F}$  NMR spectrum in a 3 to 2 ratio, consistent with what infrared spectroscopy tells us about the molecule's symmetry.

Though we cannot generally see a transition state structure, the TS has the property that one of its  $3N - 6$  normal modes becomes negative/imaginary. This is not the case for a structure located in a potential energy minimum. The normal mode for the transition state structure that has a calculated energy that is negative corresponds in fact to the nuclear motions connecting reactants and products. In the case of  $\text{PF}_5$ , the negative normal mode for the  $C_{4v}$  TS can be visualized and behaves like a movie of the BPR reaction coordinate.

Another molecule that is fluxional is  $\text{SF}_4$ . The equilibrium structure of this molecule is very similar to that of  $\text{PF}_5$ , except that one of the equatorial fluorine atoms is missing and conceptually can be replaced by a sulfur lone pair of electrons. So the description of BPR is very similar for  $\text{SF}_4$  in terms of the way that axial and equatorial fluorine atoms can undergo pairwise exchange.