

9.6: Herzberg Diagrams

One of the important reasons for describing the electronic structures and angular momentum coupling in diatomic molecules is to apply these descriptions to the prediction of the rotational branch structure in molecular spectra. As always, the first concern when predicting patterns in molecular spectra is the determination of selection rules. The selection rules for which the transition moment does not vanish are summarized below.

$$\Delta S = 0$$

$$\Delta \Lambda = 0, \pm 1$$

$$+ \leftrightarrow -, - \leftrightarrow +$$

Based on these selection rules, Herzberg diagrams can be used to predict the rotational branch structure and “first lines” in each branch based on the symmetries of upper and lower states in a given transition.

In order to discuss this very useful tool, we shall begin by discussing the description of a single state, starting with simple symmetry ($^1\Sigma^+$). In order to proceed, it is important to note the +/- symmetry of rotational wavefunctions. Basically, the rotational wavefunction is symmetric with respect to reflection through a plane containing the internuclear axis if R is even, and antisymmetric if R is odd. Thus the symmetry of the total wavefunction, given by

$$\Psi_{tot} = \psi_{elec} \psi_{vib} \psi_{rot}$$

is given by the product of the symmetries of ψ_{elec} , ψ_{vib} and ψ_{rot} . In the case of a $^1\Sigma^+$ state, ψ_{elec} is +. ψ_{vib} is always + for vibration of a diatomic molecule. The rotational contribution (ψ_{rot}) will alternate for increasing R or J . (In the case of a $^1\Sigma^+$ state, R and J have the same value, since $\Lambda = 0$ and $S = 0$.)

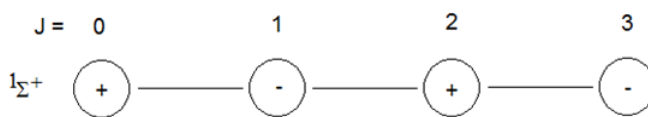


Figure 9.6.1

The above Herzberg diagram summarizes the +/- symmetry for the first few rotational levels.

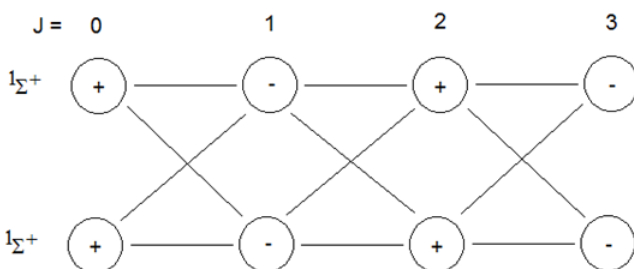


Figure 9.6.2

Based on this diagram, and the selection rule that $+\leftrightarrow -$ and $-\leftrightarrow +$, the branch structure for a $^1\Sigma^+ \leftrightarrow ^1\Sigma^+$ transition can be predicted. Clearly, R- and P-branches are predicted in the rotational structure. This is the proper Herzberg diagram for the description of the 1-0 rotation-vibration spectrum of HCl (or other closed shell heteronuclear diatomic molecules.) Notice that $\Delta J = 0$ (Q-branch) transitions are impossible since the parity (+/- symmetry) does not change in such transitions, and hence they are forbidden.

The Herzberg diagram description of a $^1\Sigma^-$ state is not too different than that for a $^1\Sigma^+$ state. The only difference is that the +/- symmetry changes such that levels with odd J are now + and those with even J are now -.

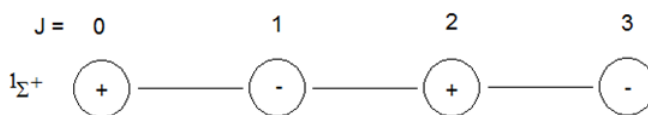


Figure 9.6.3

The description of a ${}^1\Pi$ state can be based on modifications to the descriptions of ${}^1\Sigma^+$ and ${}^1\Sigma^-$ states. Two important differences must be taken into account. First, since J is given by the sum of Λ and R (or Ω and R in Hund's case (a), but this will only be important if $S \neq 0$, which is not the case for a singlet state.) Second, since Π states (like Δ , Φ , etc.) have two components, both must be included in the diagram.

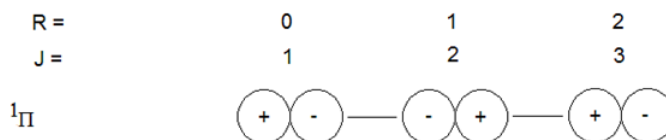


Figure 9.6.4

The description of a ${}^1\Pi \rightarrow {}^1\Sigma^+$ transition can now be constructed. Note that P- Q- and R-branches are predicted. Also notice the "first line" in each branch. If the Π state is the upper state, the first lines in each branch are $P(2)$, $Q(1)$ and $R(0)$. (There can be no $P(1)$ line as the $J = 0$ level is missing in the upper state.) This is a pattern is a one way to recognize a ${}^1\Pi \rightarrow {}^1\Sigma^+$ transition.

A reversal of state, such that the ${}^1\Sigma^+$ state is the upper state, causes the pattern to change. In the case of a ${}^1\Sigma^+ \rightarrow {}^1\Pi$ transition, the first lines in each branch are predicted to be $P(1)$, $Q(1)$ and $R(1)$.

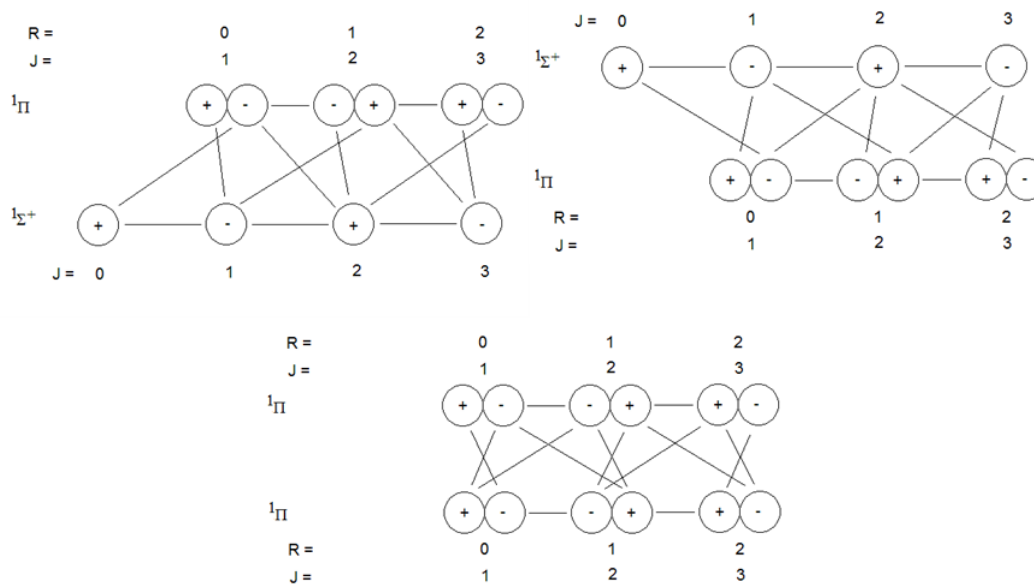


Figure 9.6.5

A ${}^1\Pi \rightarrow {}^1\Pi$ transition becomes a little more complex as well. In this case, it can be seen that there are two Q-branches predicted! These will be resolved only if the two Λ components of at least one of the Π state are significantly different in energy. The first lines are predicted to be $P(2)$, $Q_1(1)$, $Q_2(1)$ and $R(1)$.

While the description here has been limited to singlet states of Σ and Π symmetry, these tools can be extended to describe and predict a great deal of rotational fine structure patterns in spectroscopic transitions (Herzberg, 1950). The patterns can get extremely complex for systems with high spin or orbital angular momenta. The picture can become even more complex when nuclear spin exists in the molecule which can couple to orbital, spin and/or rotational angular momenta. Entire books are dedicated to sorting out these patterns and interpreting the spectra of molecules which require these considerations (Brink, 1994) (Bunker, 2009).

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