Transition dipole moment for HF

We consider the transition dipole moment of HF. The model is based on the idea that there is an electronegativity difference between the H and F atoms that introduces an asymmetry into the molecule. If we consider the ground and excited state molecular orbitals:

$$\Psi_\sigma = \sin\theta_g \ 1s_H + \cos\theta_g \ 2p_{z,F}$$
$$\Psi_{\sigma*} = \sin\theta_e \ 1s_H - \cos\theta_e \ 2p_{z,F}$$

Where the mixing angle $\theta_g = 30^o$ and $\theta_e = 60^o$. You may assume that all resonance or overlap integrals are zero. The Coulomb integrals have the value

$$\int 1s_H z 1s_H dz = z_H = 0.95R_0 \ and \int 2p_{z,F} z 2p_{z,F} dz = z_F = -0.05R_0$$

as defined in the calculation of the ground state dipole moment. Finally, the bond length is $R_0 = |z_H - z_F| = 0.95$ Å.

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Solution: The definition of the transition dipole moment for this case involves one electron since we are considering a single electron excitation.

$$M_{\sigma\sigma*} = e\int \Psi_\sigma z \Psi_{\sigma*} dz$$

We substitute the linear combinations for each orbital.

$$e\int \Psi_\sigma z \Psi_{\sigma*} dz = e\int \left(\sin\theta_g \;\; 1s_H + \cos\theta_g \;\; 2p_{z,F}\right) z \left(\sin\theta_e \;\; 1s_H - \cos\theta_e \;\; 2p_{z,F}\right) dz$$

Here again we assume that

$$\int 1s_H z 2p_{z,F} dz = \int 2p_{z,F} z 1s_H dz = 0$$

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The transition dipole is represented by the two integrals F and H.

$$M_{\sigma\sigma*} = e\left[\sin\theta_g \sin\theta_e \int 1s_H z 1s_H dz - \cos\theta_g \cos\theta_e \int 2p_{z,F} z 2p_{z,F} dz\right]$$

And we use the same identification that was made for the ground state dipole moment:

$$\int 1s_H z 1s_H dz = z_H = 0.95R_0$$

$$\int 2p_{z,F} z 2p_{z,F} dz = z_F = -0.05R_0$$

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We end up with the following values for the transition dipole moment:

$$M_{\sigma\sigma*} = e\left[\sin\theta_g \sin\theta_e \ z_H - \cos\theta_g \cos\theta_e \ z_F\right]$$

$$M_{\sigma\sigma*} = e\left[\sin\theta_g \sin\theta_e \ 0.95R_0 + \cos\theta_g \cos\theta_e \ 0.05R_0\right]$$

$$M_{\sigma\sigma*} = e|(0.433)0.95R_0 + (0.433)0.05R_0| = 0.433\text{e}(0.95\ \text{Å}) = 1.97\ D$$