Contents

Chapter 1

Introduction

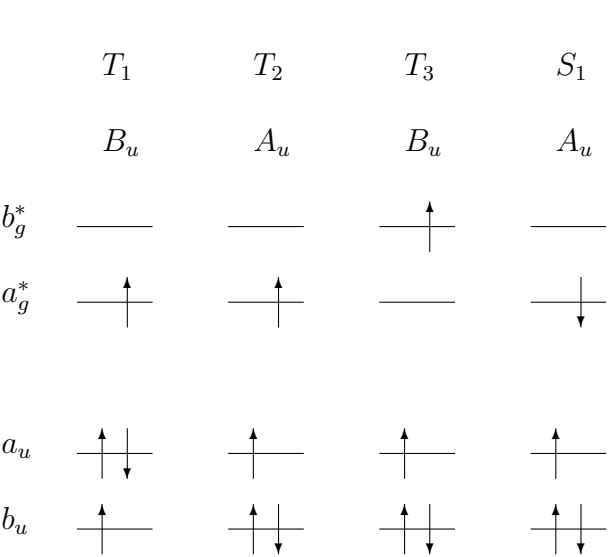
1.1 The importance of studying triplet states and intersystem crossing

$$\gamma = \langle H_{sd} \rangle / \rho_d$$

1.2 The low-lying triplet electronic states of acetylene: molecular orbital theory and *ab initio* calculations

$$\tilde{A}^1 A_u \leftarrow \tilde{X}^1 \Sigma_g$$

Figure 1-1: Principal molecular orbital configurations for the valence excited states of *trans*-bent acetylene. The four lowest-lying electronic states are listed in energy order above the diagram. An electronic transition from S_1 to T_3 involves a change in one antibonding spin orbital, from $a_g^*(\downarrow)$ to $b_g^*(\uparrow)$.



T_3

1.3 A heirichy of electronic coupling in acetylene: evidence from Zeeman anticrossing experiments

$E = 0$

$$E = g\, M_s\, \mu_B\, (B - B_0), \tag{1.1}$$

g

g

M_s

g

2.0023

$$\Delta B = \frac{4\,V}{g\,\mu_B} \tag{1.2}$$

1.3.1 Paper 1: Anomalous behavior of the anticrossing density

$\nu_3 = 1 - 3$

$0 - 8T$

S_0

$T_{1,2} \sim S_0$

S_0

$S_1 \sim T$

T

$T_{1,2} \sim S_0$

$S_1 \sim T$

$S_1 \sim T$

S_0

S_0


$S_1 \sim T_3$

$S_1 \sim T$

T_3

T_2

T_2

1.3.2 Paper 2: Characterization of a large singlet-triplet coupling

T_3

$$\Delta E = \pm 6.67$$

-1

$$J = K = 0$$

S_0


$S_1 \sim T_3$


$S_1 \sim T_3$

0.29

-1

$$K_{T_3} = 0$$

$K_{T_3} = 1$

1.3.3 Paper 3: Quantum beat spectroscopic studies

~ 60

$\nu_3 = 0 - 2$

g

$$\Delta M_S = \pm 1$$

g

2

$S_0 \sim T_{1,2}$

g

S_0

$M_S = 0$

$$T_1 \sim T_2 \gg S_1 \sim T_{1,2} \gg S_0 \sim T_{1,2} \gg S_1 \sim S_0$$

g

S_0

S_0

1.3.4 Paper 4: Study by Fourier transform

$$\rho_{vib} \cdot \langle V \rangle$$

$\nu_3 = 0 - 4$

$$\rho_{vib} \cdot \langle V \rangle$$

1.4 Doorway-mediated intersystem crossing in acetylene: evidence from laser-induced fluorescence and quantum beats

$0.3 - 2.0$

$T_1 \sim T_2$

$0\nu_3' - 2\nu_3'$

S_0


$S_1 \sim T_3$

$0\nu_3' - 2\nu_3'$

$$T_1 \sim T_2 \gg S_1 \sim T \gg S_0 \sim T \gg S_1 \sim S_0 \tag{1.3}$$

1.5 Detection of laser-excited metastables by surface electron ejection

1.6 Summary

T_3