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NOTES

Chapter 1

Evidence for a singlet~triplet dynamical “double doorway” in acetylene $\tilde{A}^1A_u - \tilde{X}^1\Sigma_g^+ V_0^3K_0^1$

1.1 Introduction

The $\tilde{A}^1A_u - \tilde{X}^1\Sigma_g^+ V_0^3K_0^1$ transition of acetylene has been heavily studied, in part because it plays host to several interesting energy resonances. Firstly, a singlet vibrational level involving 4 quanta of the Fermi-resonant bending modes ν_4 and ν_6 is near degenerate with $3\nu_3$ at $J = 0$. This singlet perturber quickly detunes due to a relatively large difference in rotational constant. However, due to strong anharmonic and Coriolis interactions between modes 4 and 6, the singlet level has never been assigned. A series of recent ultra-sensitive LIF studies have resulted in the conclusive assignment of this level as **TODO: Get assignment**.

Secondly, a vibrational level of the T_3 electronic state crosses the S_1 $3\nu_3$ level near $J = 3$. The interaction between this

TODO: Include citations: Ryan + Adya (2004), Drabbels (1994), Abramson (80's), other triplet SEELEM (90's, 00's), Dupre papers (90's)

Review the data from Mattijs and make the trends in ($S1$, $T3$) vs. ($T1$, $T2$)

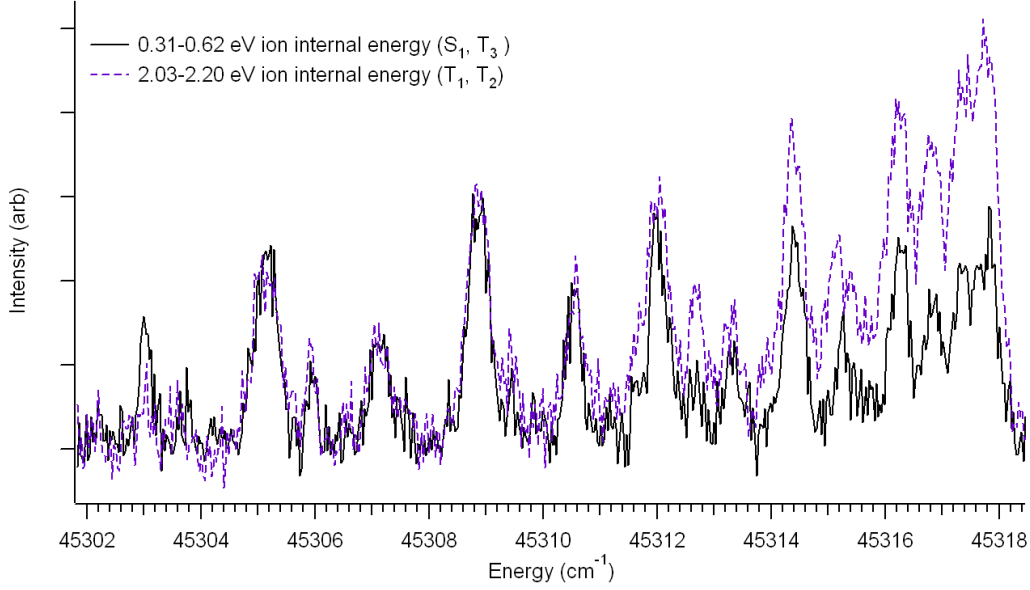


Figure 1-1: Energy-resolved photoelectron intensity from acetylene $S_1 V_0^3 K_0^1$.
TODO: Get permission to use this data.

intensity more apparent. Recently, DeGroot *et al.* have observed in photoelectron kinetic energy experiments that the coupling between $S_1 3\nu_3$ and the manifold of $T_{1,2}$ states *increases* with rotational quantum number.

A magnetic field of approximately 1 T was used in the energy-resolved photoelectron experiments. This has the effect of splitting the triplet level into three components according to the possible values of the laboratory-fixed projection of spin, $M_S = 0, \pm 1$. The change in energy with magnetic field is given by the linear approximation of the Zeeman effect:

$$\Delta E = M_S g \mu_B \Delta B, \quad (1.1)$$

where g is the Landé g factor for the triplet level, and $\mu_B = 0.4669 \text{ cm}^{-1}/\text{T}$ is the Bohr magneton. For a triplet level in the limit of Hund's case (b), the g factor is expected to be close to the "free electron" value of 2.0015. Under the experimental conditions of DeGroot *et al.*, the magnetic field-induced splitting in the local T_3 perturber is about 1 cm^{-1} .

Report the spectroscopic parameters of the local doorway to the best of our understanding. The matrix element between $S_1\ 3\nu_3$ and the local triplet perturber is approximately 0.1 cm^{-1} . We have shown conclusively in the last chapter, by applying a compound spectral deconvolution technique to high-resolution LIF spectra, that the local T_3 doorway level crosses the $S_1\ 3\nu_3$ e -symmetry levels at $J = 3$ and tunes away in energy as J increases. The rotational constant and...

Discuss the assignment of the local T_3 perturber as the F_2 component of a $K_T = 1$ level. An F_1 or F_3 component with a reasonable B -value would only be near-resonant with the singlet level for a single value of J .

Give the resulting dependence of spin-orbit matrix element on J . Stevens and Brand have derived vibronic spin-orbit matrix elements for polyatomic molecules. For the F_2 component of a local doorway with $K_T = 1$, the spin-orbit matrix element is

$$\langle \psi_{S_1} J_S 1 | H^{SO} | \psi_{T_3} J_S 1 \rangle = \frac{1}{\sqrt{J_S(J_S + 1)}} \langle \psi_{S_1} | \psi_{T_3} \rangle \langle H^{SO}(R_z) \rangle, \quad (1.2)$$

that is, the spin-orbit matrix element decreases weakly with rotation. If the local doorway instead has $K_T = 0$, the rotational dependence of the spin-orbit coupling disappears completely:

$$\langle \psi_{S_1} J_S 1 | H^{SO} | \psi_{T_3} J_S 0 \rangle = \frac{1}{2} \langle \psi_{S_1} | \psi_{T_3} \rangle (\langle H^{SO}(R_x) \rangle - \langle H^{SO}(R_y) \rangle). \quad (1.3)$$

Under either circumstance, the spin-orbit interaction is not expected to increase with rotation.

Therefore, if the local T_3 doorway level were the sole mediator for intersystem crossing between $S_1\ 3\nu_3$ and the manifold of $T_{1,2}$ levels, one would expect the $S_1 \sim T_{1,2}$ coupling to decrease with the $S_1 \sim T_3$ energy difference. The authors address this issue by proposing that an unobserved, energetically distant T_3 level interacts more strongly with the $S_1\ 3\nu_3$ level. Interference between the local and distant doorway levels could cause the $S_1 \sim T_{1,2}$ coupling to decrease in the vicinity of the local $S_1 \sim T_3$ crossing.

Discuss Figure 1-1: Early and late photoelectron signals from $2\nu'_3$ and $3\nu'_3$.

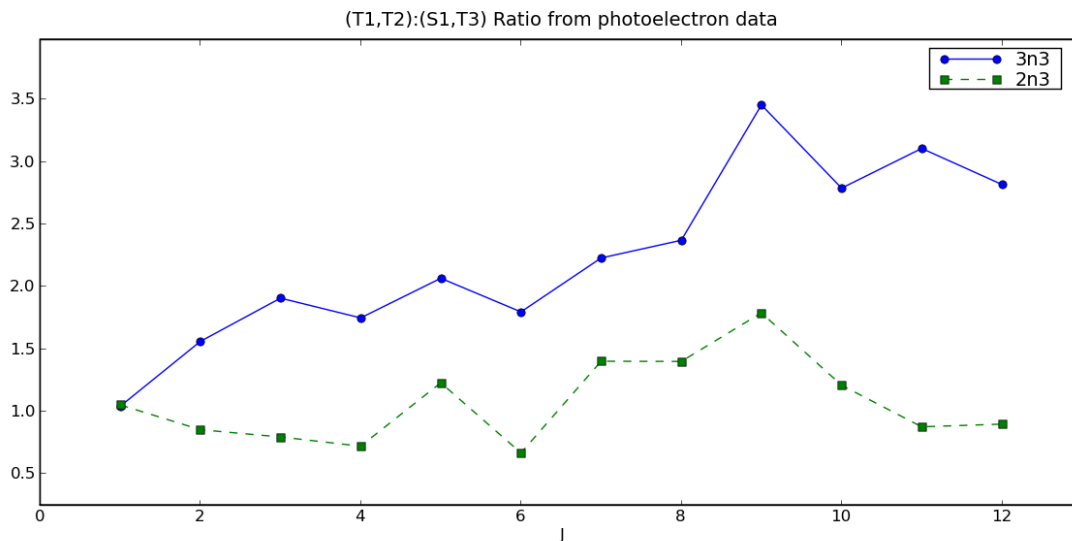


Figure 1-2

Discuss J -dependent effects in spin-orbit coupling and rule out other mechanisms (L -uncoupling) capable of producing the same effect. Terms including $B(L \cdot J)$ are diagonal in spin, increase linearly with J , and is a Coriolis-type interaction. Check Bob's book, Herzberg, and B&J. (see p.55 of 11/2007–1/2008 notebook)

1.2 Experiment

Experimental procedures. Chamber optics measurements on p.13 of 9/2006–1/2007 notebook. The experimental apparatus has been described previously. **TODO: Cite apparatus papers and theses.** Briefly, 355nm light from a 20Hz pulsed Nd:YAG laser (Spectra-Physics) is used to pump a dye laser (Lambda-Physik FL3002) operating with Coumarin 440. The dye laser output is frequency doubled in a BBO crystal to produce up to 1 mJ of radiation in the vicinity of 220nm. Using an intracavity etalon, the (incoherent) frequency resolution of the doubled radiation is approximately 0.006cm^{-1} .

Pure acetylene (Matheson) is expanded without purification from a pulsed valve (Jordan) at 10Hz into a differentially pumped vacuum chamber. During operation, the pressure in the “source” chamber is 10^{-5} torr. At a distance of 2cm from the nozzle,

the laser beam crosses the free jet of acetylene perpendicular to its direction of flow. Laser induced fluorescence is collected in this region by an $f/4$ quartz lens system and filtered (UG-5) before it enters a UV-sensitive photomultiplier (Hamamatsu R375). The time-resolved output from the photomultiplier tube is averaged on a digital oscilloscope (Model#) and transferred to a computer.

At a distance of 5cm from the nozzle, the molecular beam passes through a 3mm skimmer and enters the SEELEM detection chamber. The SEELEM detector is located 34cm from the laser excitation region. The active detection hardware consists of a gold surface, heated to 300C, oriented at a normal angle to the beam, and an electron multiplier (Model#). The entrance aperture of the electron multiplier is positioned immediately adjacent to the gold surface at a perpendicular angle, facing the area of intersection with the molecular beam. The electron signal from the multiplier is sent to a preamplifier/discriminator, and the resulting electron counts are recorded on a separate computer using a PCI counting hardware from WHERE? The LIF and SEELEM detection systems are kept in sync by means of a stepping motor, which is triggered from the LIF computer to periodically hit the space bar on the SEELEM computer.

Relate survival probability and lifetime. Give R value for our SEELEM detector. Show plot of C_{S_1} vs. lifetime/survival probability for eigenstates of acetylene. (See p.97 of 8/2007–10/2007 notebook.)

1.3 Results: new and revised assignments

TODO: Prepare a comparison to the Au:SEELEM data from our own lab, with integrated intensities out to $J' = 7$.

TODO: Figure: integrated LIF + SEELEM intensities from our data.

A more extensive and detailed Au:SEELEM/LIF spectrum has been recorded in the vicinity of the $V_0^3K_0^1$ subband. This data set covers the upper state energy levels $J' = 1 - 8$, from 45273.3 to 45314.7 cm^{-1} .

Present overview of spectrum. Compare with R&A dataset.

TODO: Figure: spectrum overview.

TODO: Figure: SEELEM comparison with R&A. (see p.56 in 11/2007–1/2008 notebook)

Explain gated fluorescence measurements and present theory.

TODO: Figure: example of gated fluorescence spectrum.

Assignment of LIF and SEELEM features by ground state combination differences.

TODO: Figure: Show each line and its combination difference for LIF and SEELEM. Explain what qualities must be preserved between the two energy regions. See p.110,128,138 of 9/2006–1/2007 notebook.

Present the spectrum of 4^16^3 , the complimentary member of the B^4 polyad, and show that it has no appreciable SEELEM intensity + a short lifetime. (Scan on 2/2/07)

1.3.1 Assignments revised from Mishra *et. al.*

Measurement of fluorescence lifetimes has led to many corrections to the assignments in Mishra et. al.

Mis-assignments of triplet transitions

As stated in [Ryan & Bryan], the transitions assigned to the O(3,4,5) of T_3 were later observed to have short lifetimes, therefore this assignment cannot be correct. The S(1) transition assigned in [MTF] at 45310.397 cm^{-1} has been re-assigned as R(4) after careful comparison with ground state combination differences. This re-assignment slightly changes the rotational constant for the triplet perturber inferred from the reduced term value plot.

The singlet perturber line $R_e(3)$ was mis-assigned as T_3 R(4). This transition has a short fluorescence lifetime and a ground state combination difference with a $P_e(5)$ transition at 45289.69 cm^{-1} . (The S_1 Q(9) transition partially overlaps this $P_e(5)$ line.) This new assignment is reflected in the reduced term value plot. Our gated fluorescence method allows us to observe $R_e(4)$, which is partially overlapped with

the blue end of the S_1 R(6) cluster.

TODO: Adapt reduced term value plot, page 132 of 8/2007–10/2007 notebook.

This kills all the $\Delta N = \pm 1$ triplet transitions, so the K assignment of the triplet perturber is called into question. Discuss what this affects.

Combination differences killed to O and S branches, therefore we return to N-only assignments in the lack of other evidence. Lines assigned to triplet perturbers $Q(1)$ $J' = 2$ and $Q(2)$ $J' = 3$ are blended, according to Drabbels. Lines assigned to $Q(2)$ $J' = 1$ and $Q(3)$ $J' = 2$ are mis-assigned, disagree with Drabbels assignments based on relative intensity at different beam temperatures.

We still retain the assignment of the triplet perturber as the F_2 ($N = J$) component, because an F_1 or F_3 component would not be nearly degenerate with the singlet level over several consecutive N . By a process of elimination, this leads to the conclusion that the local triplet perturber must have $K_T = 1$. A triplet level with $K_T = 0$ would interact with only one parity of the S_1 $3\nu'_3$ $K = 1$ level, and such a perturbation would be observed exclusively in *either* the Q or (P, R) branches. The local T_3 perturbation is present in all three branches, thus it must have $K_T \neq 0$. A triplet perturber with $K_T = 2$ would have no rotational level with $J = N = 1$, however such a level perturbs the $J = 1$ levels of S_1 $3\nu'_3$ in both parities. We have thus eliminated all possibilities but $K_T = 1$.

TODO: Re-create figure from page 133 of 8/2007–10/2007 notebook.

Mis-assignments of singlet transitions

The lines at 45298.262 and 45291.818 cm^{-1} , assigned to Q(1) transitions of $S_1(2\nu'_4 + 2\nu'_6) - S_0(K_0^1)$, have also been re-assigned due to long lifetimes. The former line is re-assigned as part of the fractionated S_1 $3\nu'_3 - S_0(K_0^1)$ Q(4) cluster. The energy of the latter line agrees with previous observations of the S_1 $3\nu'_3 - S_0(K_0^1)$ Q(8) transition.

The singlet perturber has basically been definitively assigned as $3\nu'_4 + \nu'_6$. This accounts for the large rotational constant, because torsional motion raises the effective B value. What else does this mean for the analysis in [MTF]?

The lines previously assigned to the S_1 $4\nu'_4 - S_0(K_0^0)$ Q(1,2,3) all have long lifetimes,

which precludes their assignment to a pure bending polyad. For the lines at 45298.262 and 45297.999 cm^{-1} , we return to the Drabbels assignment of the $S_1\ 3\nu'_3 - S_0(K_0^1)$ Q(4) cluster. On the basis of lifetime and temperature dependence, we re-assign the line at 45296.332 to the $S_1\ 3\nu'_3 - S_0(K_0^1)$ Q(5) cluster. The line previously assigned as $S_1\ 4\nu'_4 - S_0(K_0^0)$ Q(4) does have a short lifetime, but cannot be assigned conclusively in light of the current data.

The assignment of the $S_1\ 4\nu'_6 - S_0(K_0^0)$ Q-branch is also called into question by the current data. The lines assigned to Q(1) and Q(4) are overlapped with the $S_1\ 3\nu'_3$ Q(8) and Q(9) clusters in the current data, and so cannot be commented on. One of the two remaining lines, assigned to Q(2), has a long lifetime, and therefore cannot be assigned as a singlet perturber. The line at 45290.401 cm^{-1} , previously assigned to Q(3), has a short lifetime, but cannot be assigned conclusively in light of the current data.

Table 1.1 shows new LIF assignments in the R-branch of $S_1\ 3\nu'_3$

Table 1.2 shows new SEELEM assignments in the R-branch of $S_1\ 3\nu'_3$

1.4 Analysis: Relative LIF-SEELEM intensity distributions

Discuss the integrated intensity results/moments of distributions for the SEELEM and LIF data. Focus on the data, and reference elsewhere the derivations of intensity distributions.

Show the systematic skew of the spectral intensity distribution. Compare predicted skewness for single and double doorway models?

Must show conclusively that the intensity distributions are the same for LIF and SEELEM, therefore a SEELEM intensity cross term cannot account for the skewness. Avoid direct reference to SEELEM de-excitation mechanisms. (If you must discuss them, see p.7 of 8/2007–10/2007 notebook.)

Address the change in various parameters with mixing coefficient under a single

Table 1.1: Revised assignments in the LIF spectrum of $V_0^3K_0^1$.

Assignment	Energy	Intensity	Assignment	Energy	Intensity
$R(0)$	45302.716		$R(3)$	45308.495	
	2.881			8.765	
	3.186			8.975	
$R_e(0)$	3.568			9.222	
	3.657			9.297	
$R(1)$	45304.440		$R_e(3)$	10.866	
	4.651		$R(4)$	45310.335	
	4.750			10.397	
	4.973			10.594	
	5.085		$R_e(4)$	13.573	
	5.246		$R(5)$	45311.620	
	5.333			11.818	
$R_e(1)$	5.991			12.053	
	6.200			12.177	
$R(2)$	45306.977			12.473	
	7.062		$R(6)$	45313.153	
	7.295			13.240	
	7.613			13.499	
$R_e(2)$	8.360		$R(7)$	45314.278	
				14.389	

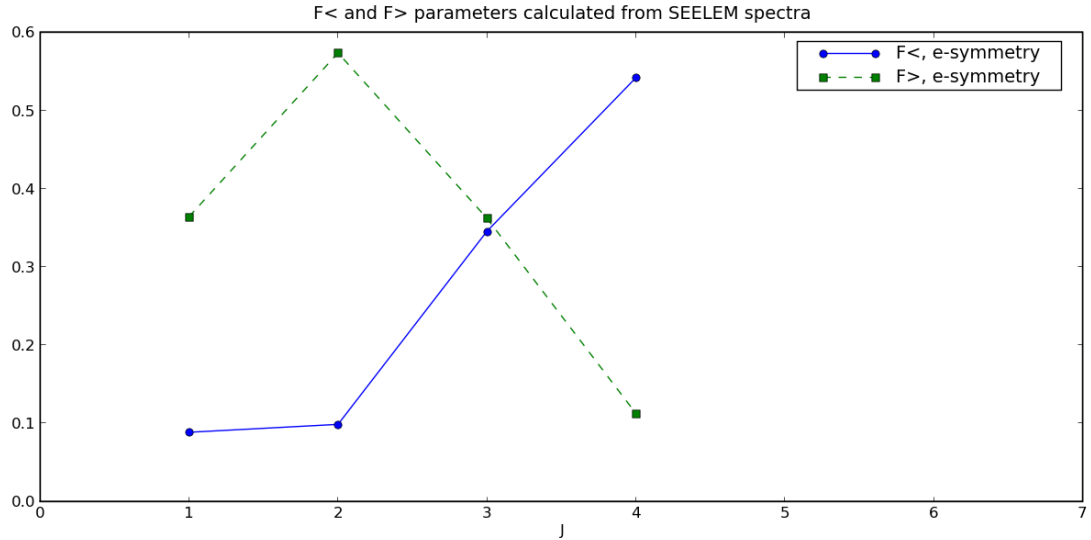
Table 1.2: Revised assignments in the Au:SEELEM spectrum of $V_0^3K_0^1$. Transition energy is given in units of cm^{-1} . The intensity is given in electron counts per 100 laser shots.

Assignment	Energy	Intensity	Assignment	Energy	Intensity
R(0)	45301.584		R(2)	45306.474	
	1.864			6.964	
	2.029			7.062	
	2.271				
	2.449			7.136	
	2.601			7.319	
	2.741			7.613	
	2.894		R(3)	45308.495	
				8.569	
	3.212			8.765	
	3.301				
	3.644			8.839	
R(1)	45303.733			8.926	
	4.471			8.987	
	4.585			9.049	
	4.661			9.173	
	4.763			9.247	
	4.890			9.321	
	4.954			9.445	
	5.005			9.519	
	5.081			9.580	
	5.119			9.852	
	5.221				
	5.348				
	6.225				

Table 1.3

Assignment	Window	Counts _{<}	Counts _{>}	Ratio
R(0)	1.0	263014	202732	1.30
R(1)	1.0	433225	191193	2.27
R(2)	0.7	96684	88121	1.10
R(3)	1.0	114986	185850	0.62
R(4)	0.7	27116	22422	1.21
R(5)	0.5	30252	26668	1.13
R(6)	0.5	12711	11619	1.09
R(7)	0.4	5638	5105	1.10

Figure 1-3



or double doorway model. (See p.41 of 11/2007–1/2008 notebook.)

Table 1.3 presents intensity ratios on either side of the nominal bright state.

Fractionation arguments - F-value should be the same on either side of the nominal bright state. States cannot change order. Support this argument with evidence from simulations. Can the variance of the F-value be derived from the assumption of direct coupling and the average matrix element?

Figure 1-3 shows the fractionation on either side of the nominal bright state.

1.5 Analysis: Deconvolution and deperturbation

Present full deconvolution results.

Perform a continuous deconvolution for $J' = 5 - 8$.

TODO: Figure: matrix elements and dE's from a LK deconvolution.

Use deconvolution results to place $S_1 \sim T_3$ interaction in the spectrum of weak coupling – strong coupling. Is a “nominal doorway state” observed in the spectrum? How close is its intensity to the mixing fraction α^2 ? What total amount of singlet character is borrowed by nominal $T_{1,2}$ states?

1.6 Analysis: Parsimonious trees

Examine the LIF and SEELEM spectra using parsimonious trees. Show that certain matrix elements keep popping up, and speculate on what this means. The results will probably not be conclusive, but the previous sections should lend them some more weight.

1.7 Discussion: A local+distant “double doorway” model

What does the double doorway model mean for the rotational constant of the local perturber? Could this account for the observed reversal of rotational constants for the two asymmetry (e and f) components?

Prepare and discuss a “two slit” figure for the double doorway model. (See p.43–45 of 11/2007–1/2008 notebook.)

1.8 Conclusions

Can there be anything left to say about this band?

We'll talk about where the distant doorway might be, and how it would appear in the spectrum.