The Finger Physics Of Vector Correlations

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Outline

Types of correlations

- μ and v
- μ and J
- v and J
- [μ, v, and J]

μ is the transition dipole moment of a parent compound, v is the relative velocity between fragments, and J is the rotational angular momentum of one fragment

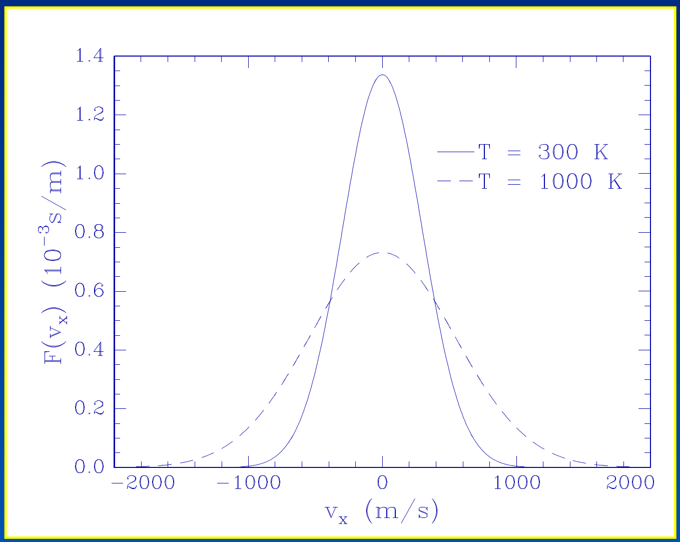
The Legacy Of Johann Christian Doppler

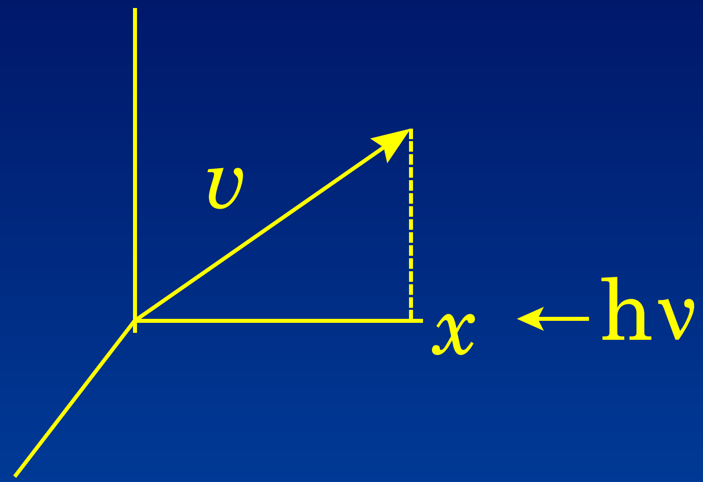
The formulae we need

- $\nu_{obs} = \nu_0[1 + v_x/c]$
  - Johann Christian Doppler (1803-1853)
- $I_{abs} = |\mu \cdot E|^2 \quad \propto \cos^2\theta$
  - James Clerk Maxwell (1831-1879)
- $\oint \cos^2\theta = ½$
  - Rubber Bible (CRC, 1965 ed.)

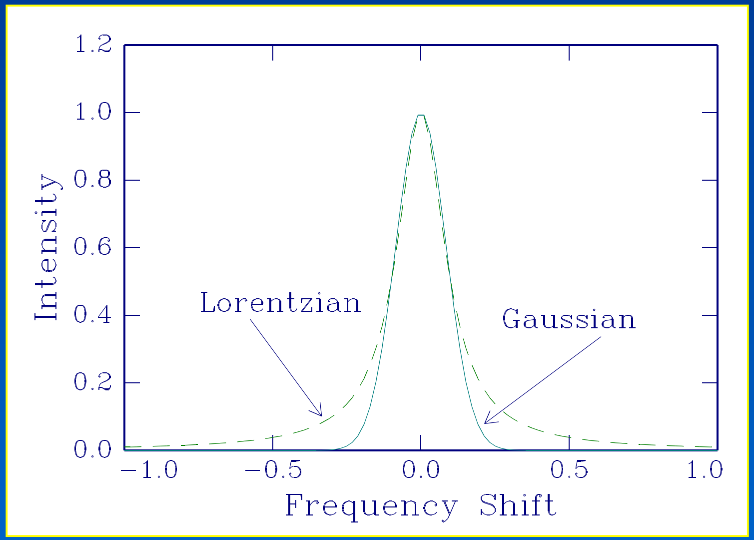
Maxwell-Boltzmann

$$P(v_x) = C\exp(-mv_x^{\,2}/2kT)$$



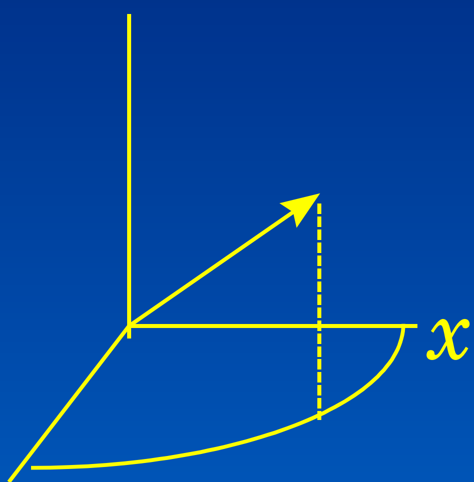


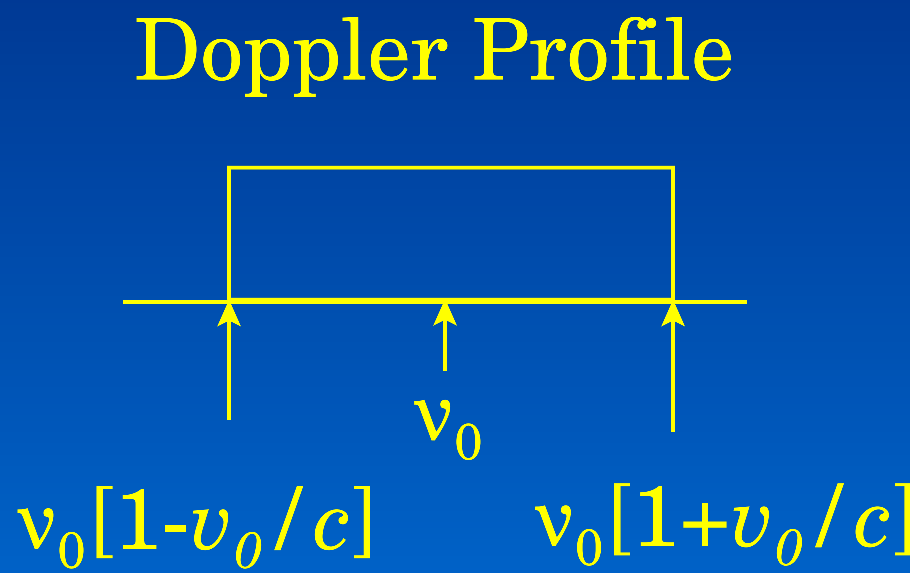
$$v_x = c\left(\frac{\upsilon_{obs} - \upsilon_0}{\upsilon_0}\right)$$



Doppler Profile for Single v

$$P(v) = \delta(v - v_0)$$

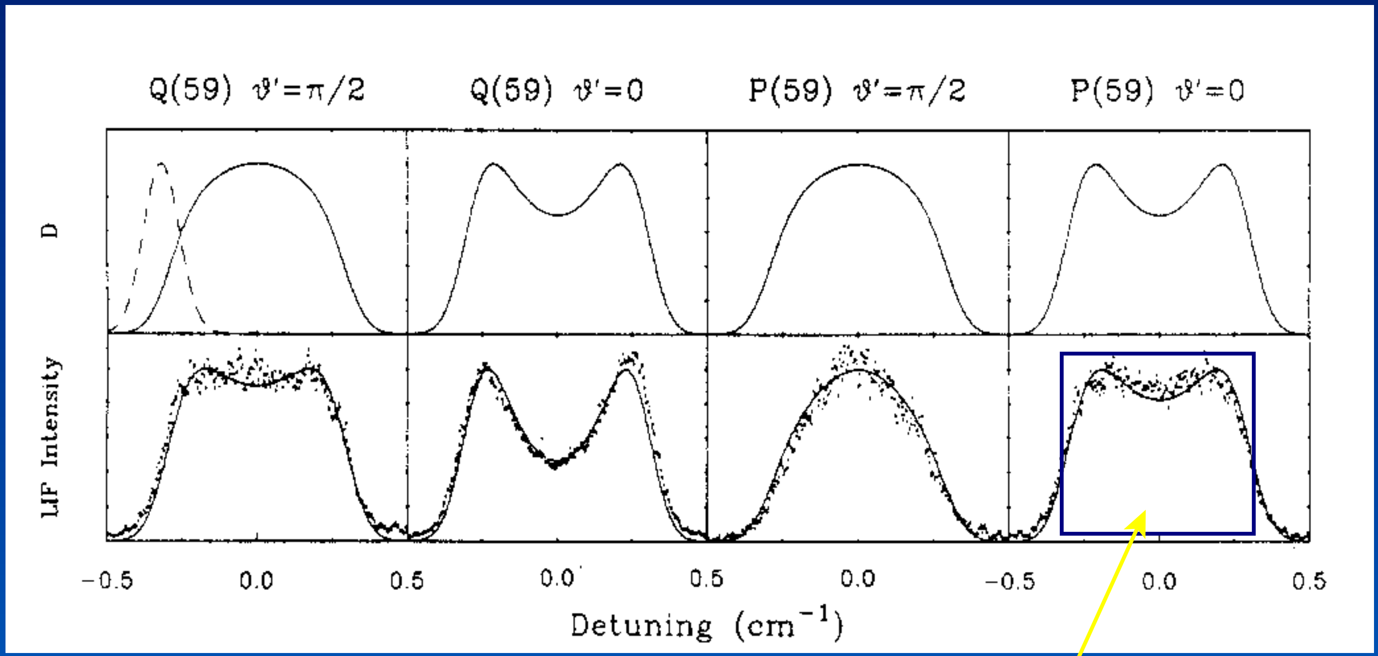




$OCS \rightarrow CO(\upsilon, J) + S(^1D)$

$\rightarrow CO(\upsilon, J) + S(^3P)$

But what causes shape?

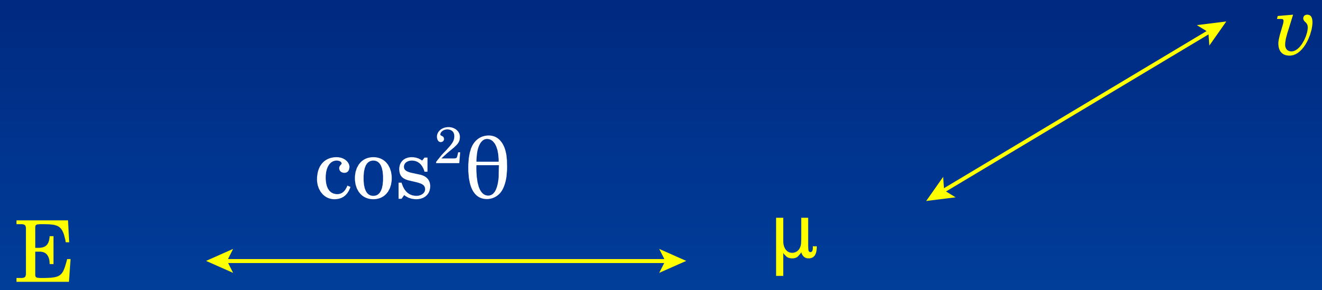


Width correct for ^1D

G. E. Hall, N. Sivakumar, P. L. Houston, and I. Burak, Phys. Rev. Lett. 56, 1671-1674 (1986)

Anisotropy of Fragment Recoil

NB: Alignment of v is diminished if parent rotates before it dissociates



Photon | Parent | Product

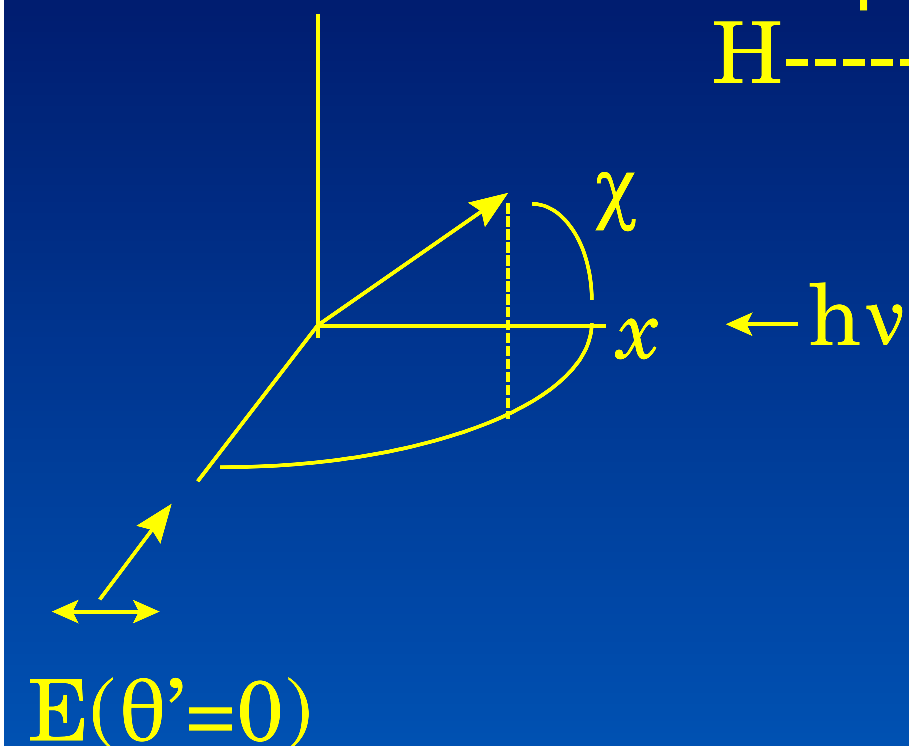
E aligns μ in the lab frame, and since v and μ are related, then v is aligned in lab frame

←μ→

H-----------I Favors $\chi=0$

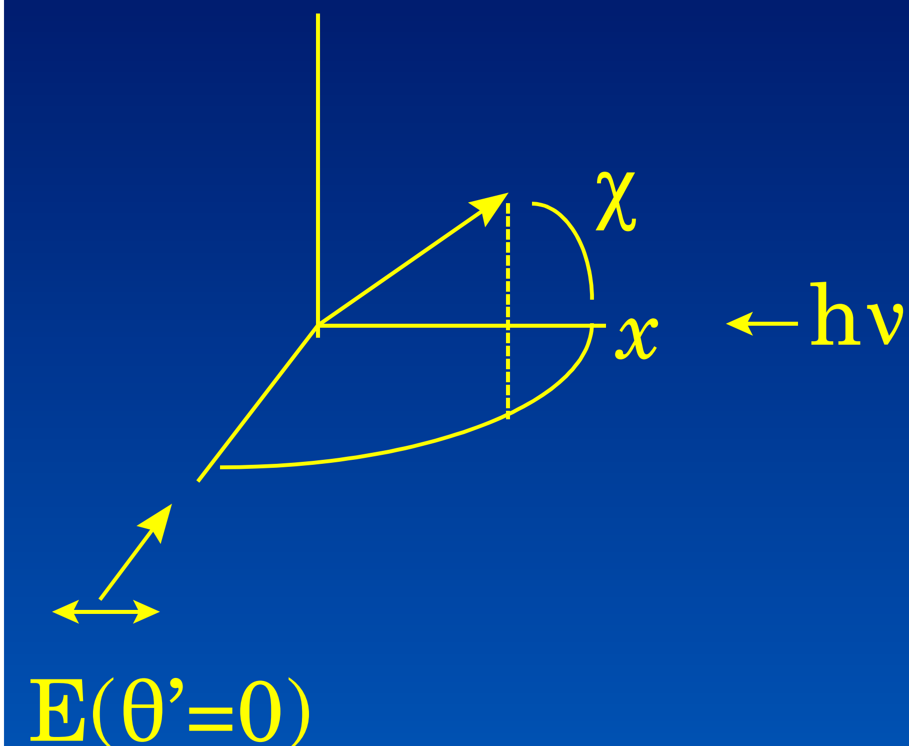
μ↕

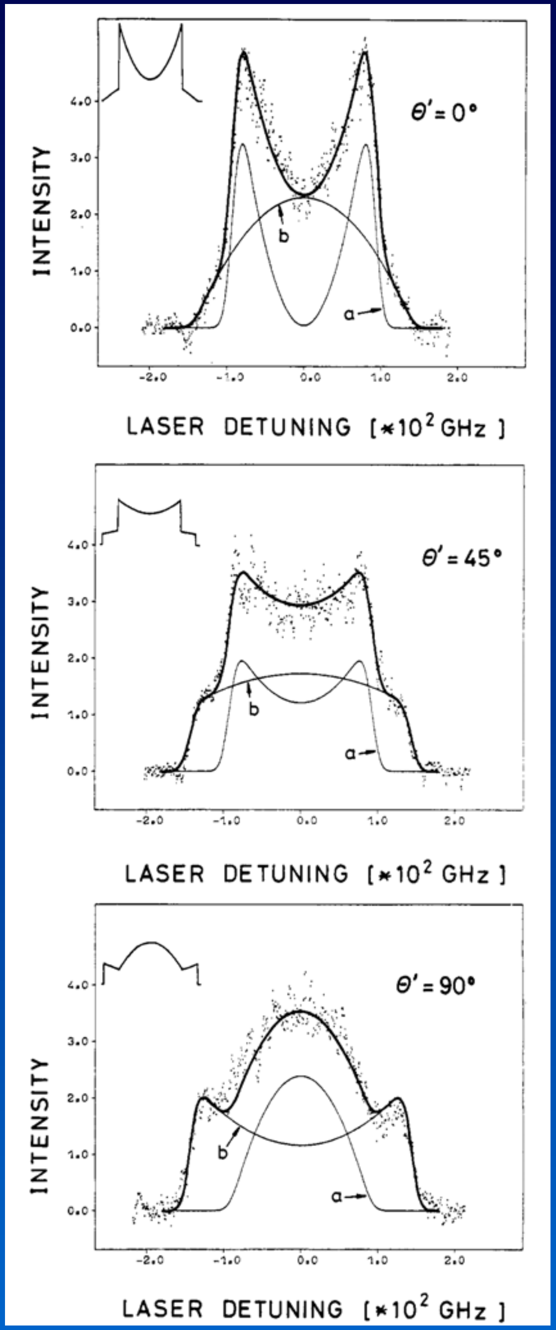
H-----------I Favors $\chi=90$



HI

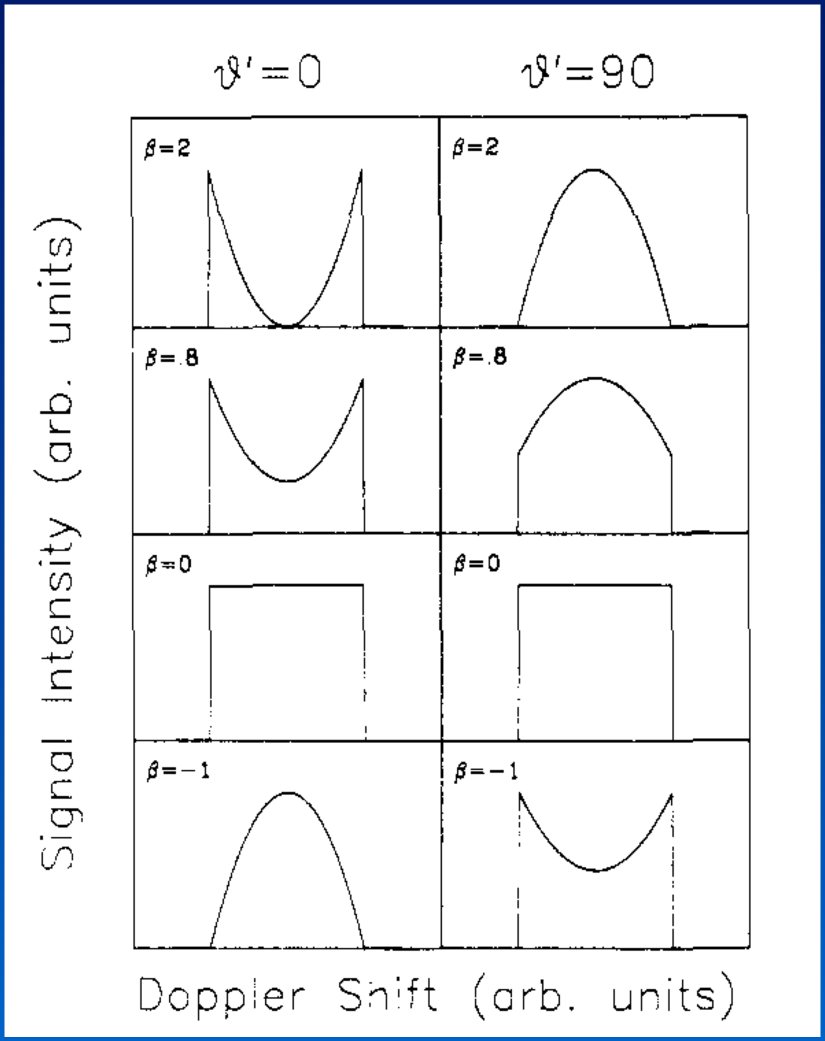
$$I = 1 + \beta P_2(\cos\theta')P_2(\cos\chi)$$





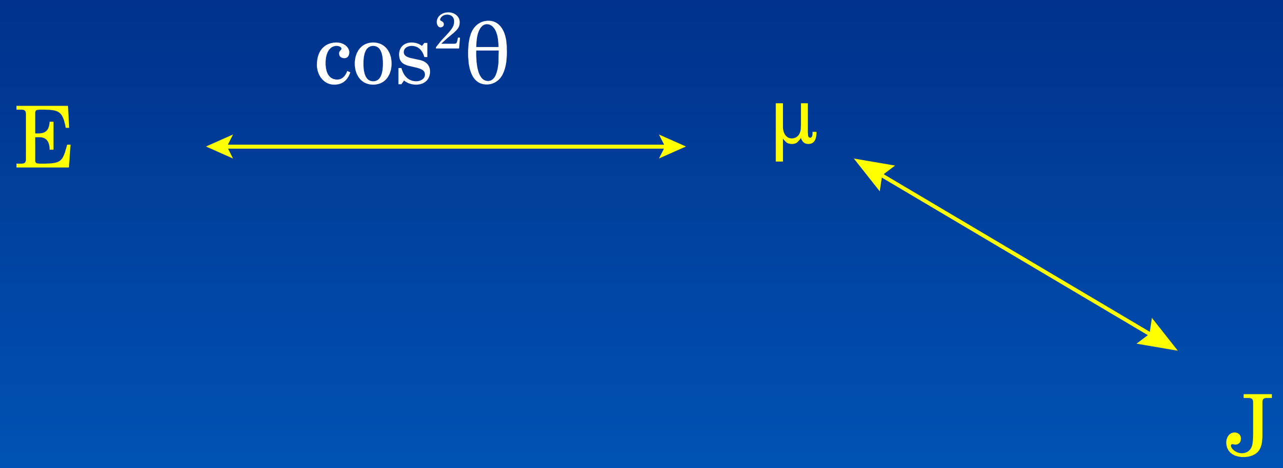
Schmiedl, R.; Dugan, H.; Meier, W.; Welge, K. H.
Z. Phys. A 1982

Doppler Profiles For Different β

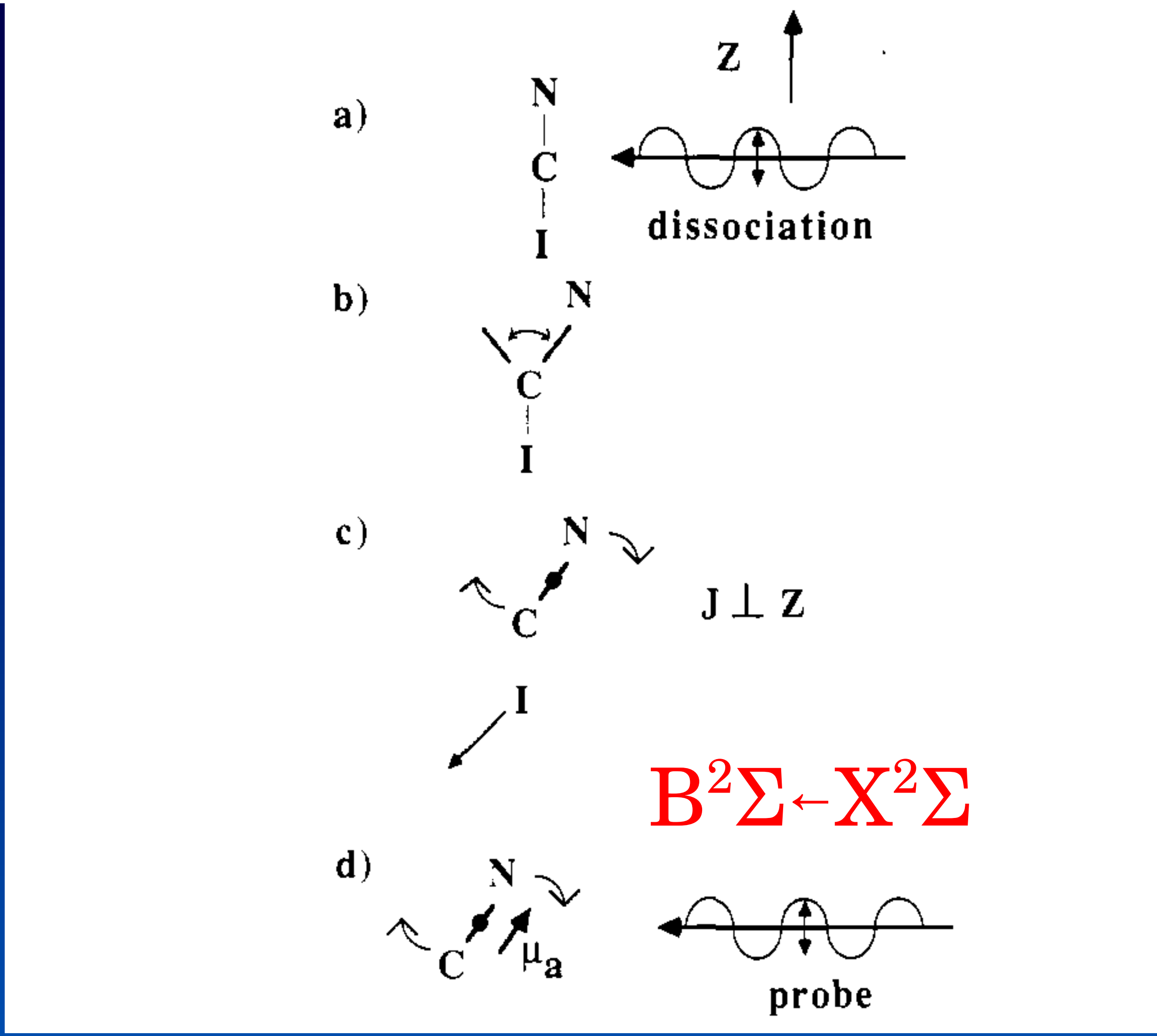


Rotational Alignment

NB: Again, correlation is diminished if parent rotates before dissociation



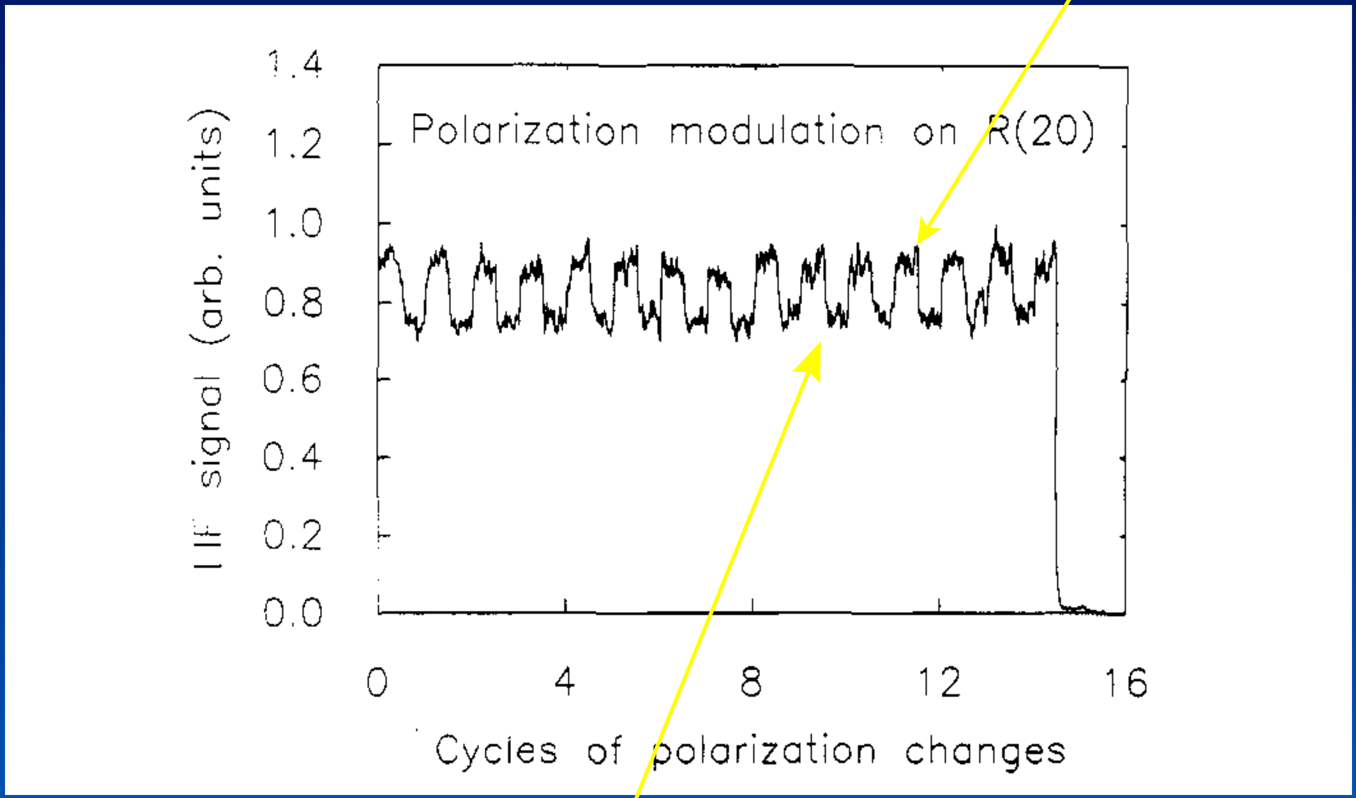
E aligns μ in lab frame, ans since μ and J are correlated, J is aligned in lab frame.



More signal with parallel polarizations

Hall, G. E.; Sivakumar, N.; Houston, P. L. J. Chem. Phys. 1986,84,, 2120.

Parallel



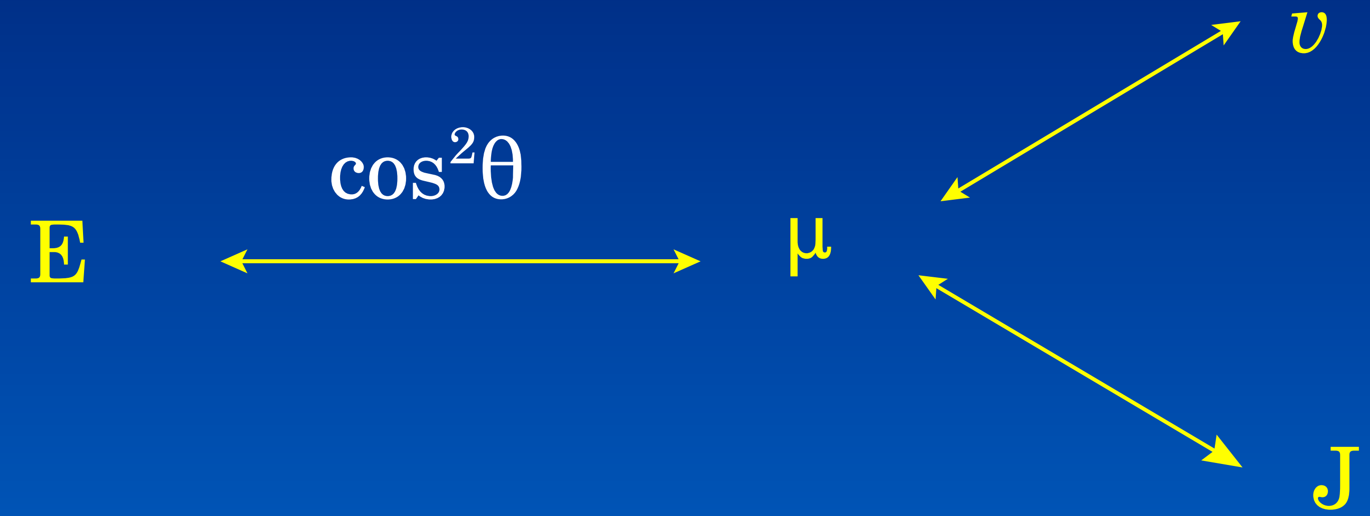
Perpendicular

Hall, G. E.; Sivakumar, N.; Houston, P. L. J. Chem. Phys. 1986,84,, 2120.

The *v*-*J* Correlation

NB: The correlation between v and J made at moment of dissociation persists even if parent rotates before dissociation !

Photon | Parent | Product



Since v is correlated to μ and J is correlated to μ, it shouldn't be surprising that v and J are correlated

Triatomics

A simple reason why v and J might be correlated

$OCS(J=0) \rightarrow CO(v, J \approx 50) + S(^1D_2)$

Conservation of Angular Momentum:

$0 = \boldsymbol{J}_{co} + \boldsymbol{J}_{o} + \mu \boldsymbol{v} \times \boldsymbol{b}$; with $J_{CO} >> J_O$

thus

$\boldsymbol{J}_{CO} \approx - \mu \boldsymbol{v} \times \boldsymbol{b}$; or $\boldsymbol{J}_{CO}$ is perp to $\boldsymbol{v}$

OCS → S ------------ C-O J out of plane

v $J \perp v$

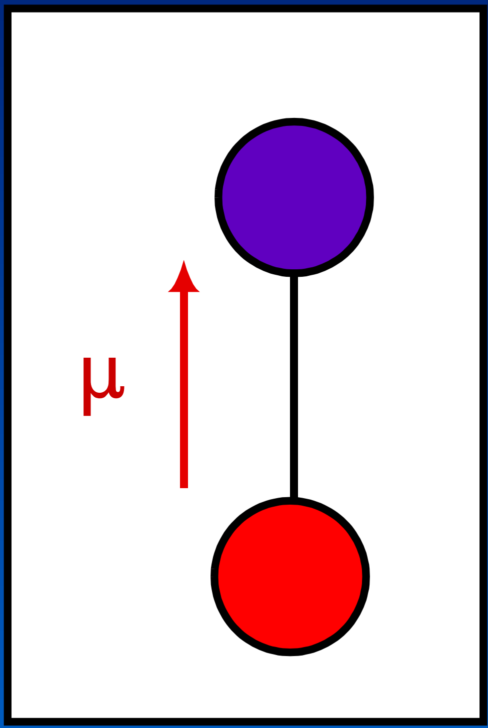
Need to think about how the Diatomic absorbs light

What is the relation between its transition dipole and its rotation vector?

Parallel Transition

μ is parallel to internuclear axis

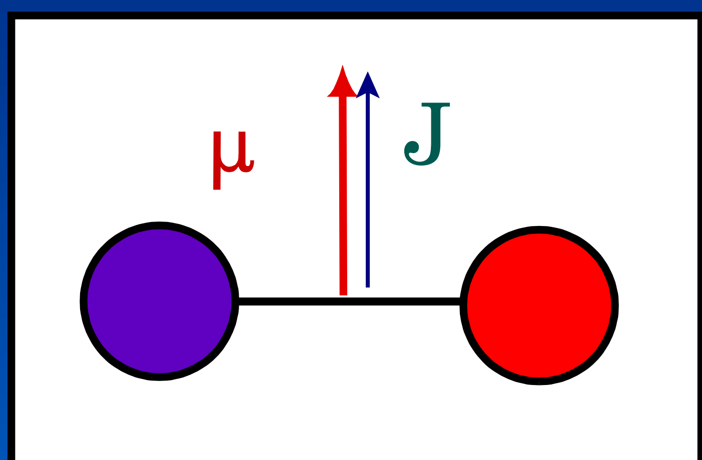
By necessity, J is perpendicular to μ, P and R lines only



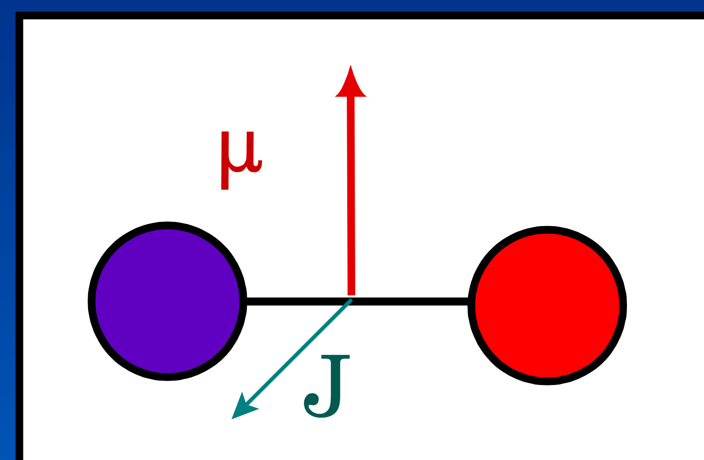
Perpendicular Transition

μ is perpendicular to the internuclear axis

μ is parallel to J for Q branch and perpendicular to J for P and R branch



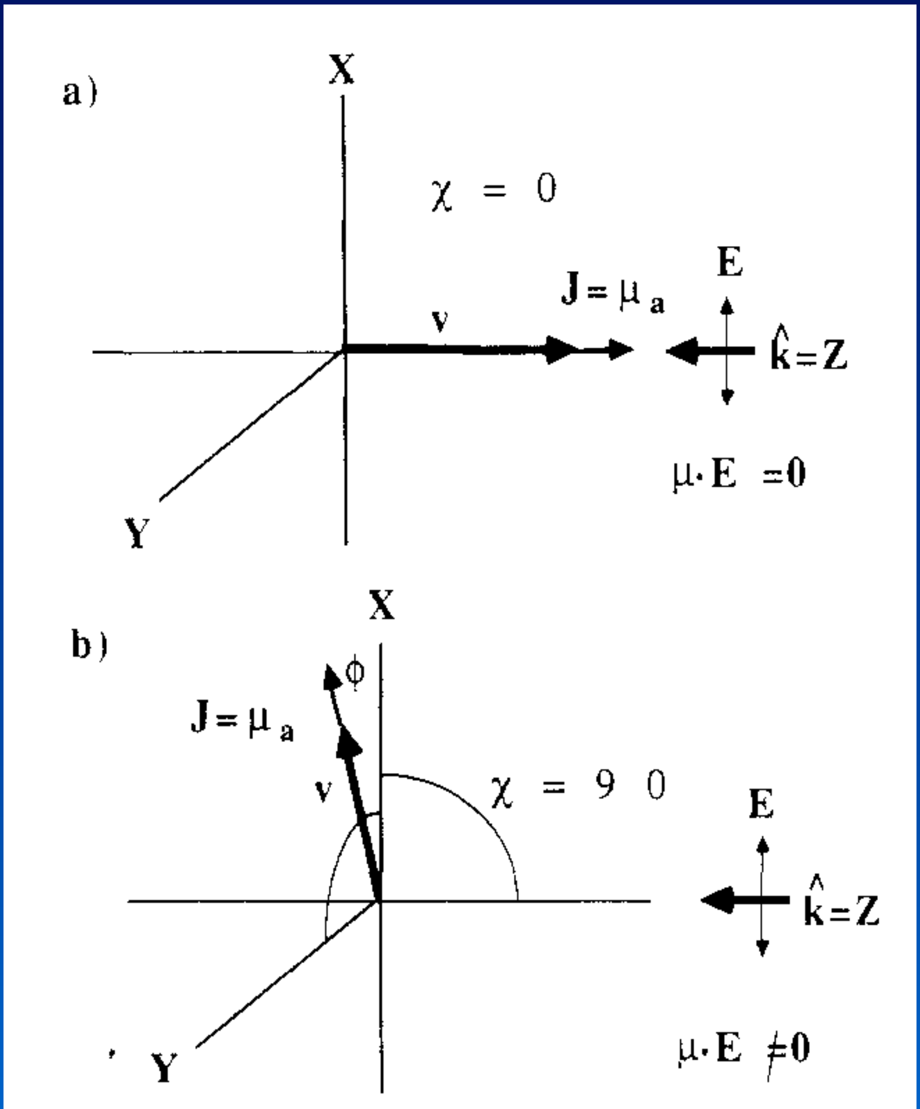
Q



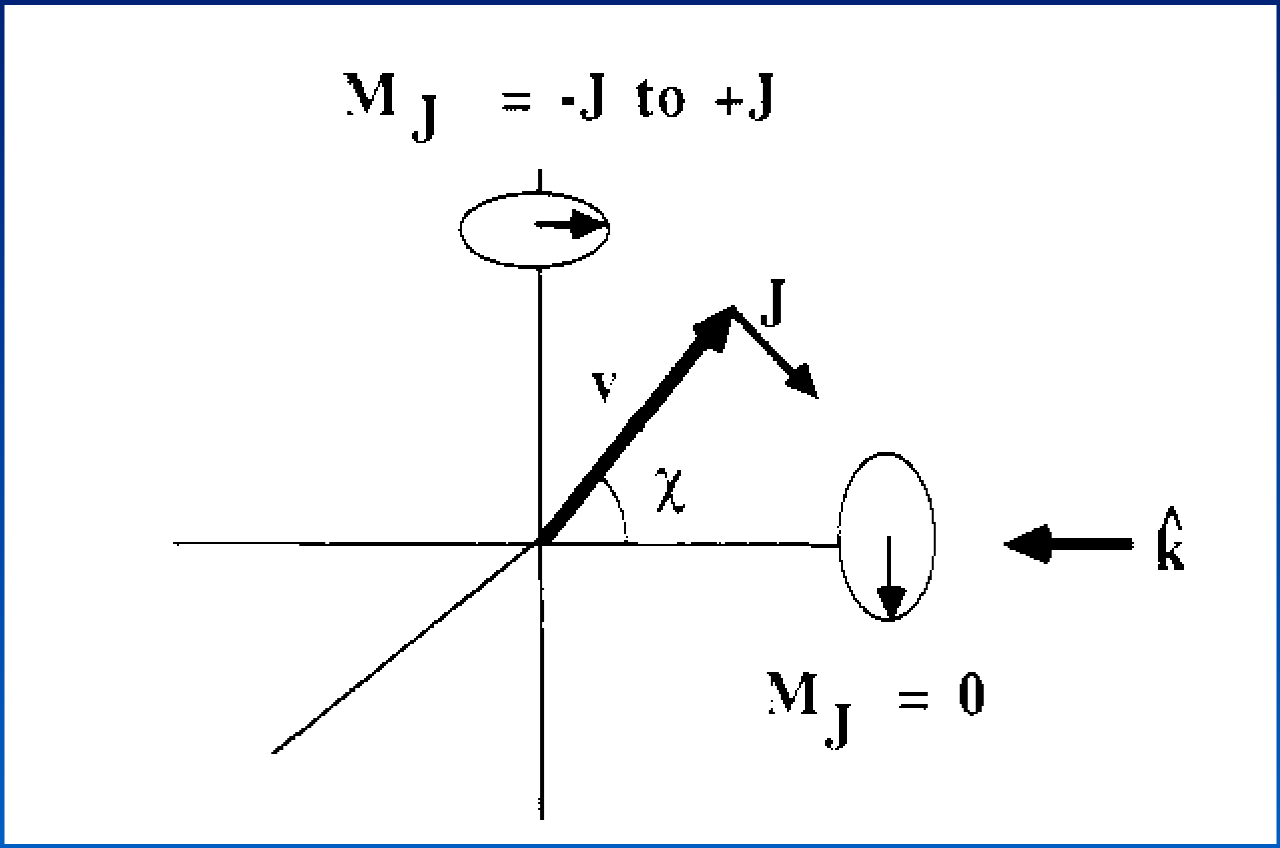
P,R

How does *v-J* affect Doppler Profile?

- Suppose isotropic
- Suppose *J* parallel *v* (rather than perpendicular as required in OCS case)
- Suppose probed on Q-branch of a perpendicular transition, where μ_{abs} is parallel to *J*
- Result: no abs on wings, max absorption in center - Doppler profile won't be rectangular



A more QM way of thinking



Examples

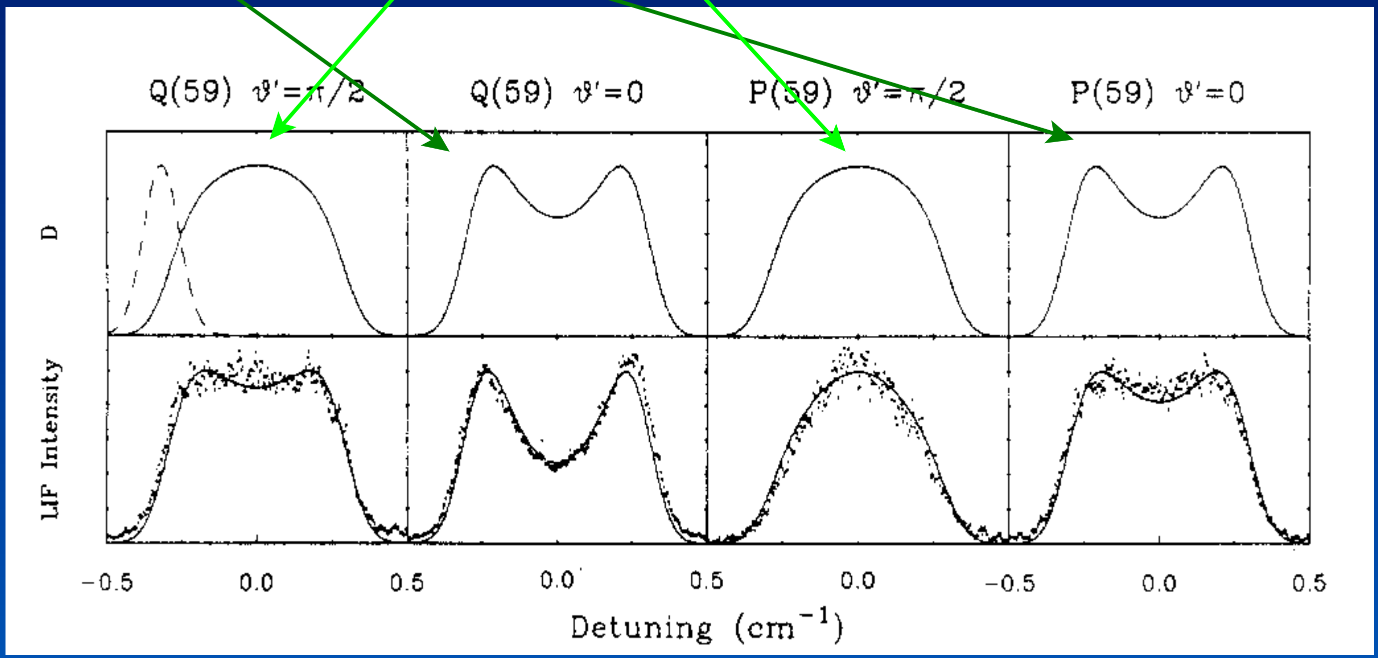
- $OCS \rightarrow CO + S$
- Glyoxal:

  $HCOCOH \rightarrow H_2CO + CO$

OCS: General features of Doppler Profile are similar to parallel dissociation with E parallel or perpendicular to probe direction

Expected with no vJ

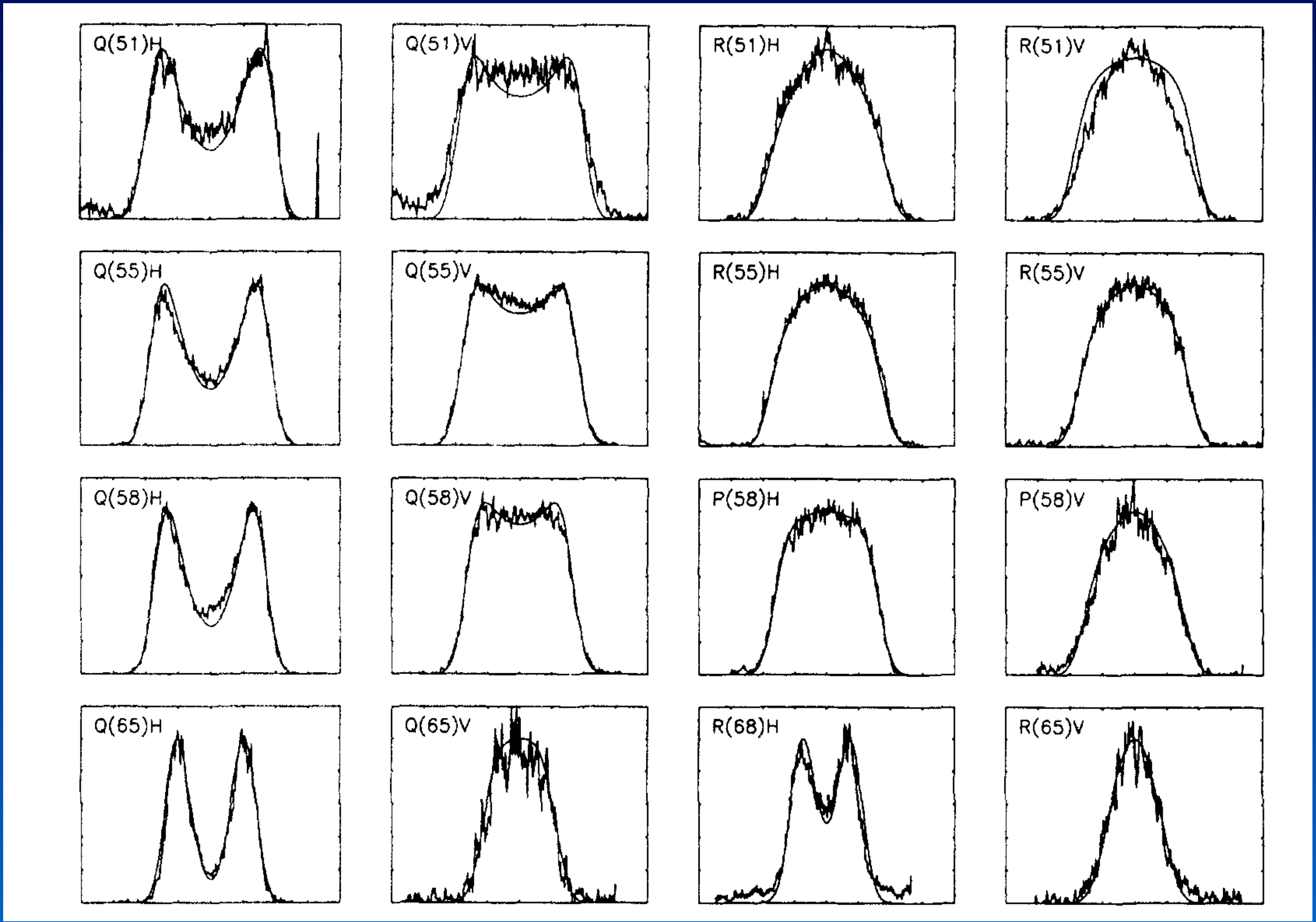
Result of vJ correlation



G. E. Hall, N. Sivakumar, P. L. Houston, and I. Burak, Phys. Rev. Lett. 56, 1671-1674 (1986)

But note that details are different for Q vs P

OCS Doppler Profiles

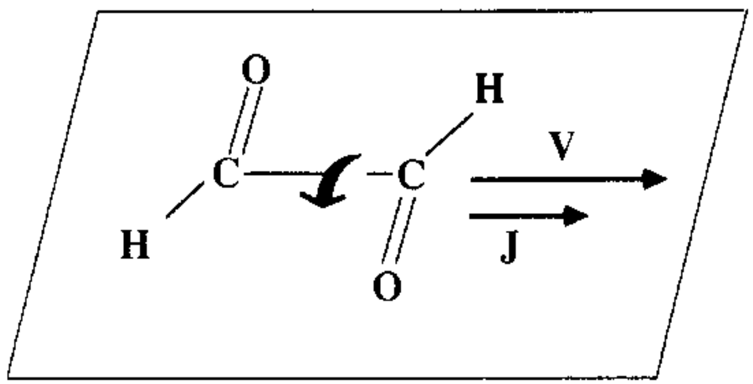


N. Sivakumar, G. E. Hall, P. L. Houston, I. Burak, and J. W. Hepburn, J. Chem. Phys. 88, 3692-3708 (1988).

Glyoxal Dissociation

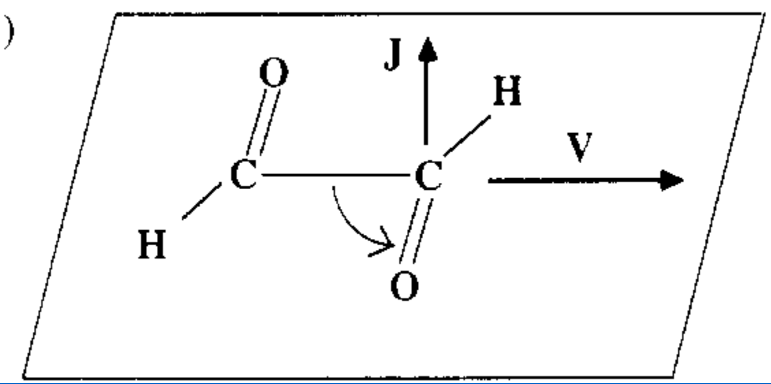
Non-Planar vs Planar

a)



Twisting out of plane
vs
Bending in plane

b)

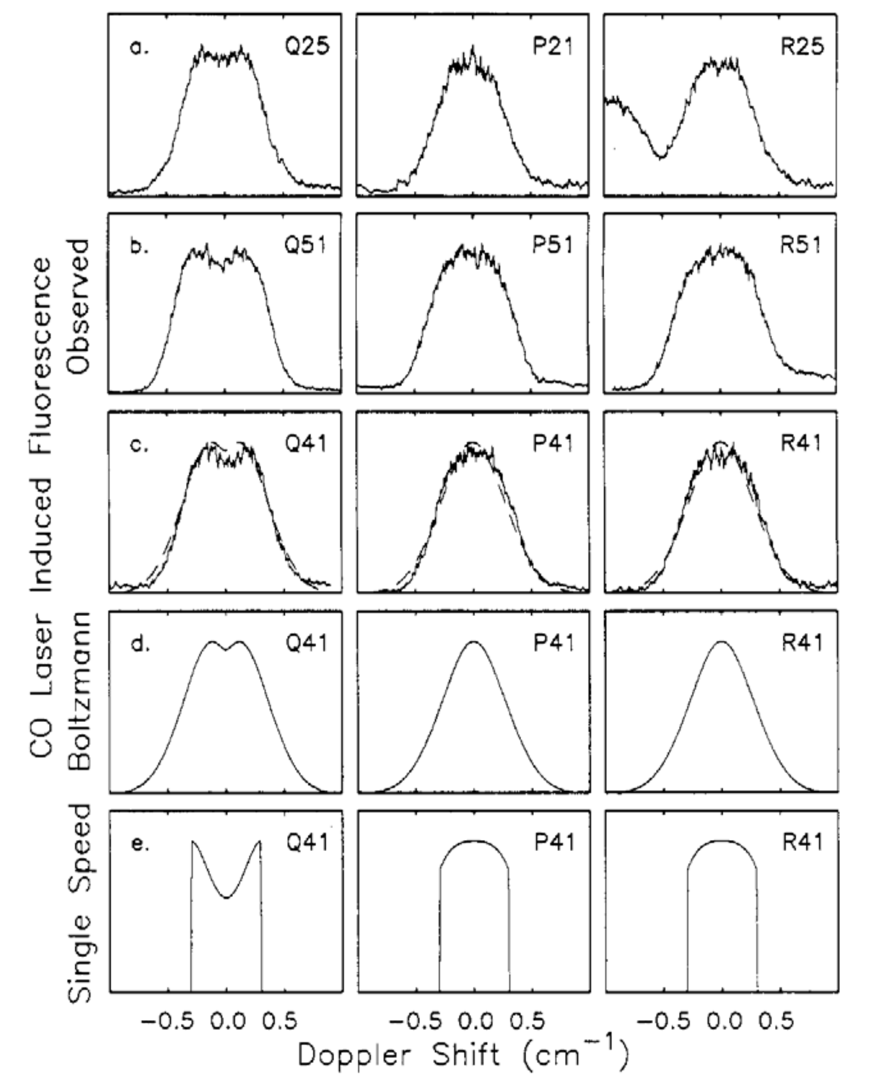


Evidence for Planar Dissociation

All the Q line profiles have "dips," while the P and R do not

NB: the glyoxal dissociation lifetime is ns!

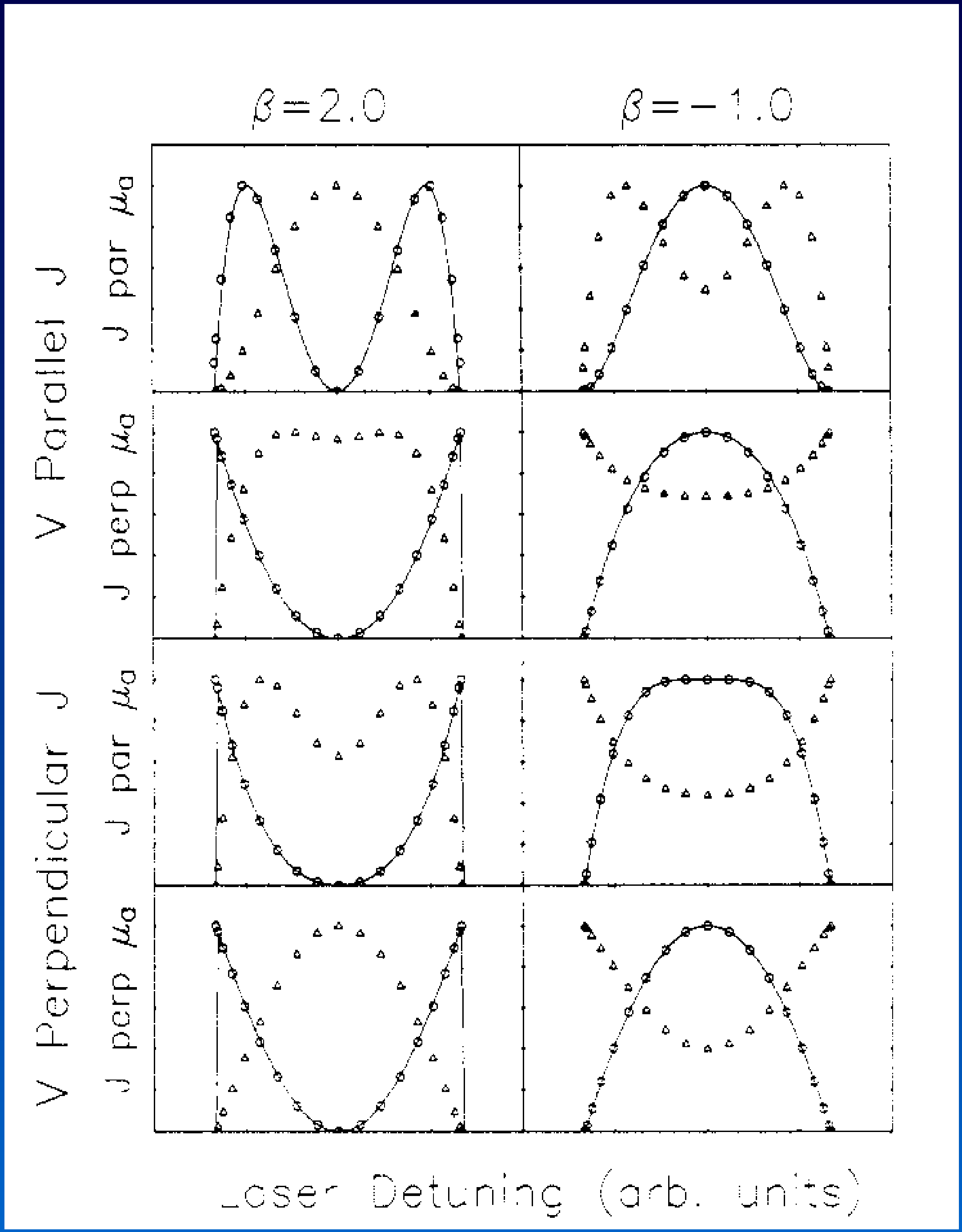
I. Burak, J. W. Hepburn, N. Sivakumar, G. E. Hall, G. Chawla, and P. L. Houston, J. Chem. Phys. 86, 1258 (1987)



Summary of Doppler Profiles

μ-*v*-*J* Correlation

See: Dixon, R. N. (J. Chem. Phys. 1986, 85, 1866) for description using bipolar moments



Conclusions

- Doppler Profiles are a one-dimensional projection of the velocity distribution (as opposed to our 2D projection images)
- Reveal speed and angle dist of products
- Reveal vector correlations between μ, v, and J