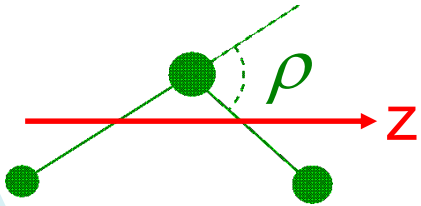
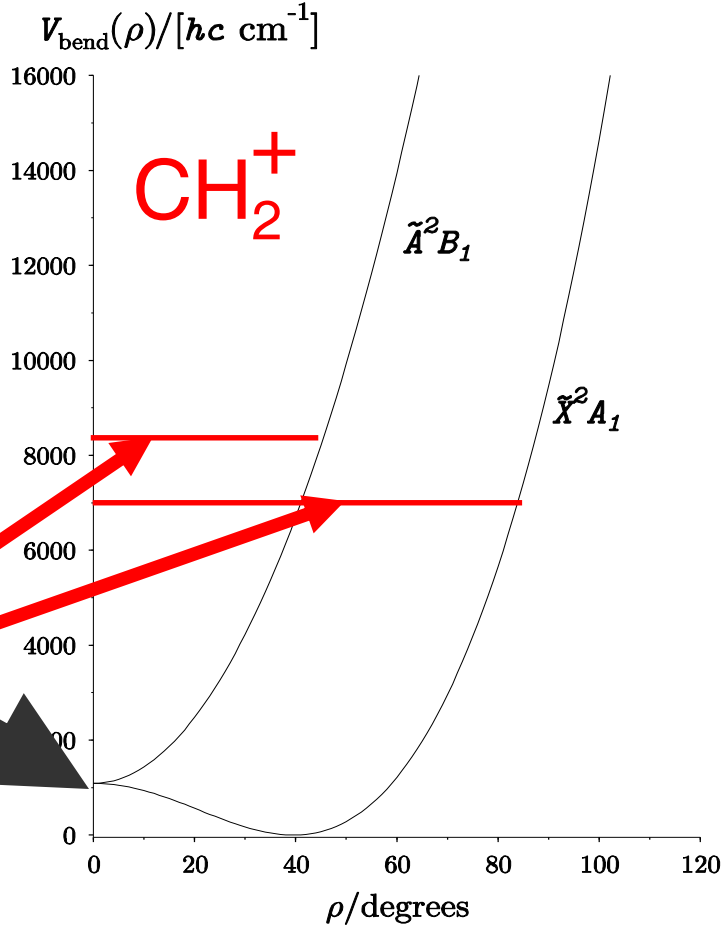
THE RENNER EFFECT



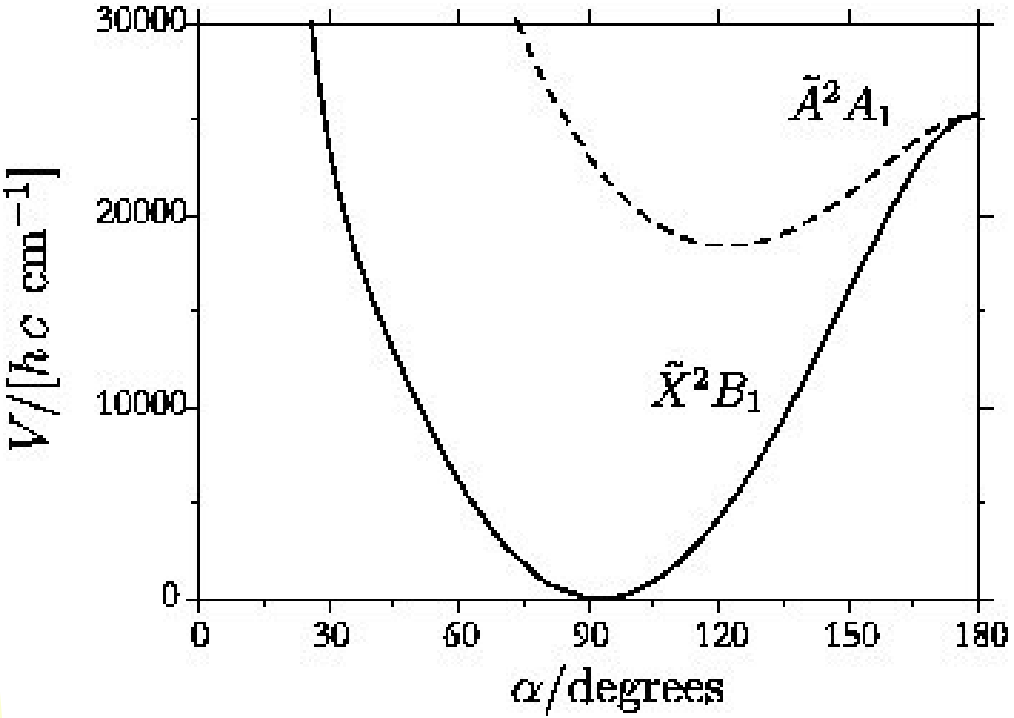
E_{elec} degeneracy at linearity.

Ψ_{rve} mixed by z-axis Coriolis ($N_z L_z$) +spin-orbit interaction.

$^2\Pi_u$



The PH_2 molecule



Term values for some N_{KaKc} states

3_{30}	F_1 104.0	
	F_2 103.3	
3_{31}	F_1 102.1	
	F_2 101.2	
3_{21}	F_1 95.6	
	F_2 95.3	
3_{22}	F_1 85.6	
	F_2 85.2	

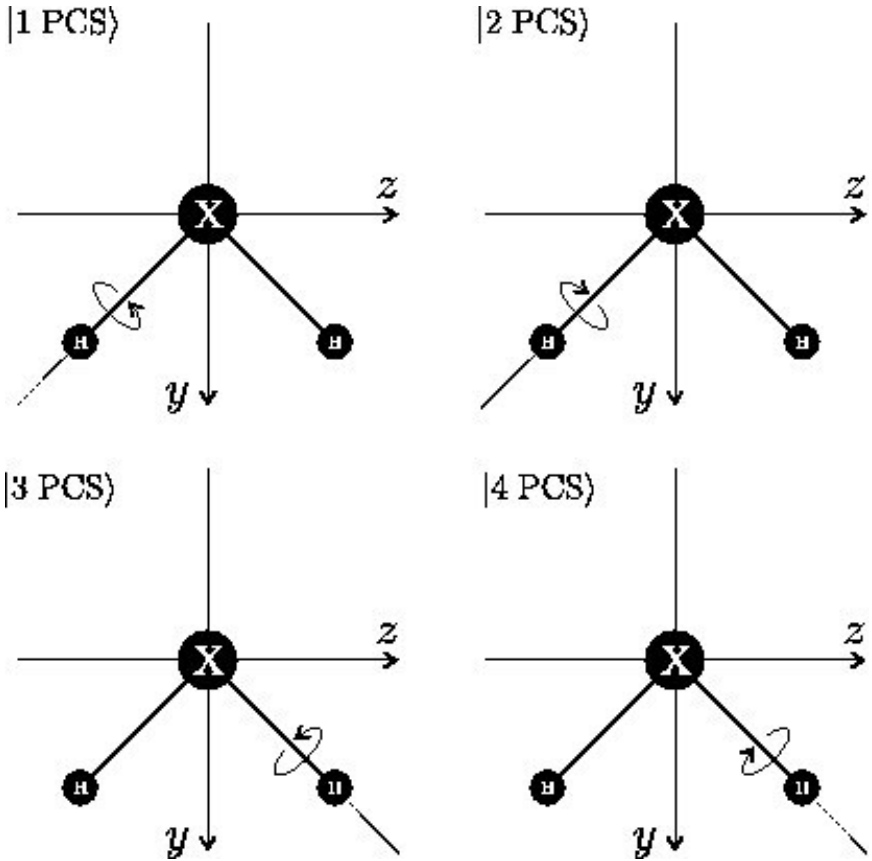
Term values for some N_{KaKc} states

3_{30} F_1 104.0	$10_{10,0}$ F_1 966.2
F_2 103.3	$10_{10,1}$ F_1 966.2
3_{31} F_1 102.1	$10_{10,0}$ F_2 963.3
F_2 101.2	$10_{10,1}$ F_2 963.3
3_{21} F_1 95.6	$10_{9,1}$ F_1 930.3
F_2 95.3	$10_{9,2}$ F_1 930.0
3_{22} F_1 85.6	$10_{9,1}$ F_2 928.2
F_2 85.2	$10_{9,2}$ F_2 927.8

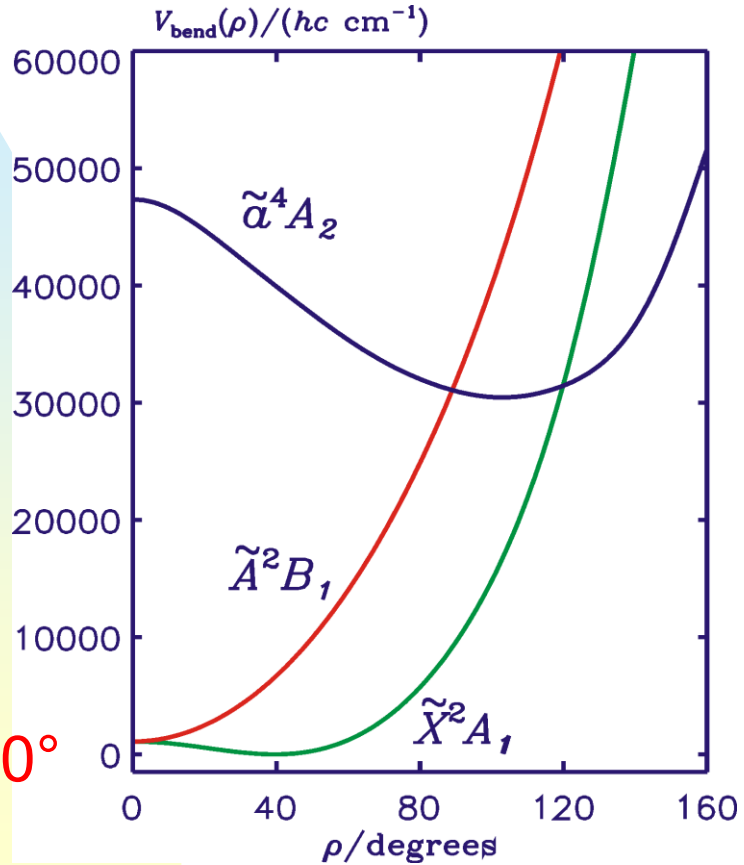
Term values for some N_{KaKc} states

3_{30} F_1 104.0	$10_{10,0}$ F_1 966.2	$30_{30,0}$ F_1 7579.8
F_2 103.3	$10_{10,1}$ F_1 966.2	$30_{30,1}$ F_1 7579.8
3_{31} F_1 102.1	$10_{10,0}$ F_2 963.3	$30_{29,1}$ F_1 7575.2
F_2 101.2	$10_{10,1}$ F_2 963.3	$30_{29,2}$ F_1 7575.2
3_{21} F_1 95.6	$10_{9,1}$ F_1 930.3	$30_{30,0}$ F_2 7573.9
F_2 95.3	$10_{9,2}$ F_1 930.0	$30_{30,1}$ F_2 7573.9
3_{22} F_1 85.6	$10_{9,1}$ F_2 928.2	$30_{29,1}$ F_2 7569.5
F_2 85.2	$10_{9,2}$ F_2 927.8	$30_{29,2}$ F_2 7569.5

Four localized Primitive Cluster States



CH_2^+ Potential energy surfaces



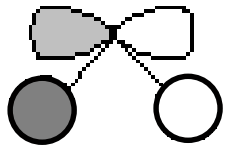
$\alpha_e = 77.1°$

$\alpha_e = 180°$

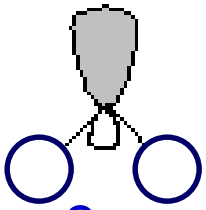
$\alpha_e = 140.5°$

Molecular Orbitals

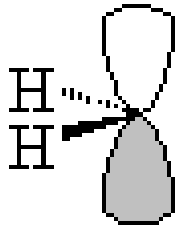
CH_2^+ $(1s)^2(2s)^2$ + 3 electrons



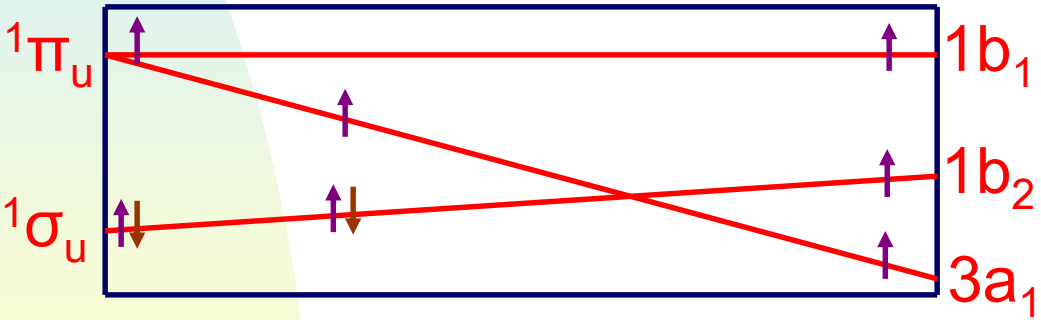
$1b_2$



$3a_1$



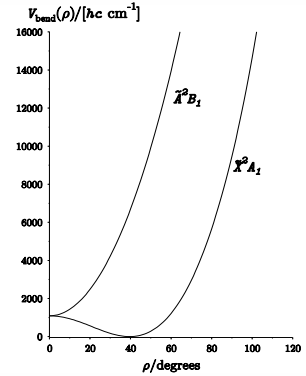
$1b_1$



α = 180° 140° 77°

$\tilde{A}\ ^2B_1$ $\tilde{X}\ ^2A_1$ $\tilde{a}\ ^4A_2$

Application to CH_2^+



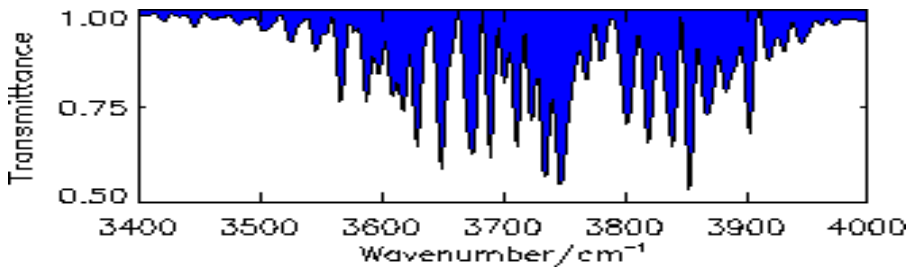
Potential surfaces
Spin-orbit coupling surface

Dipole moment surfaces

Transition moment surface

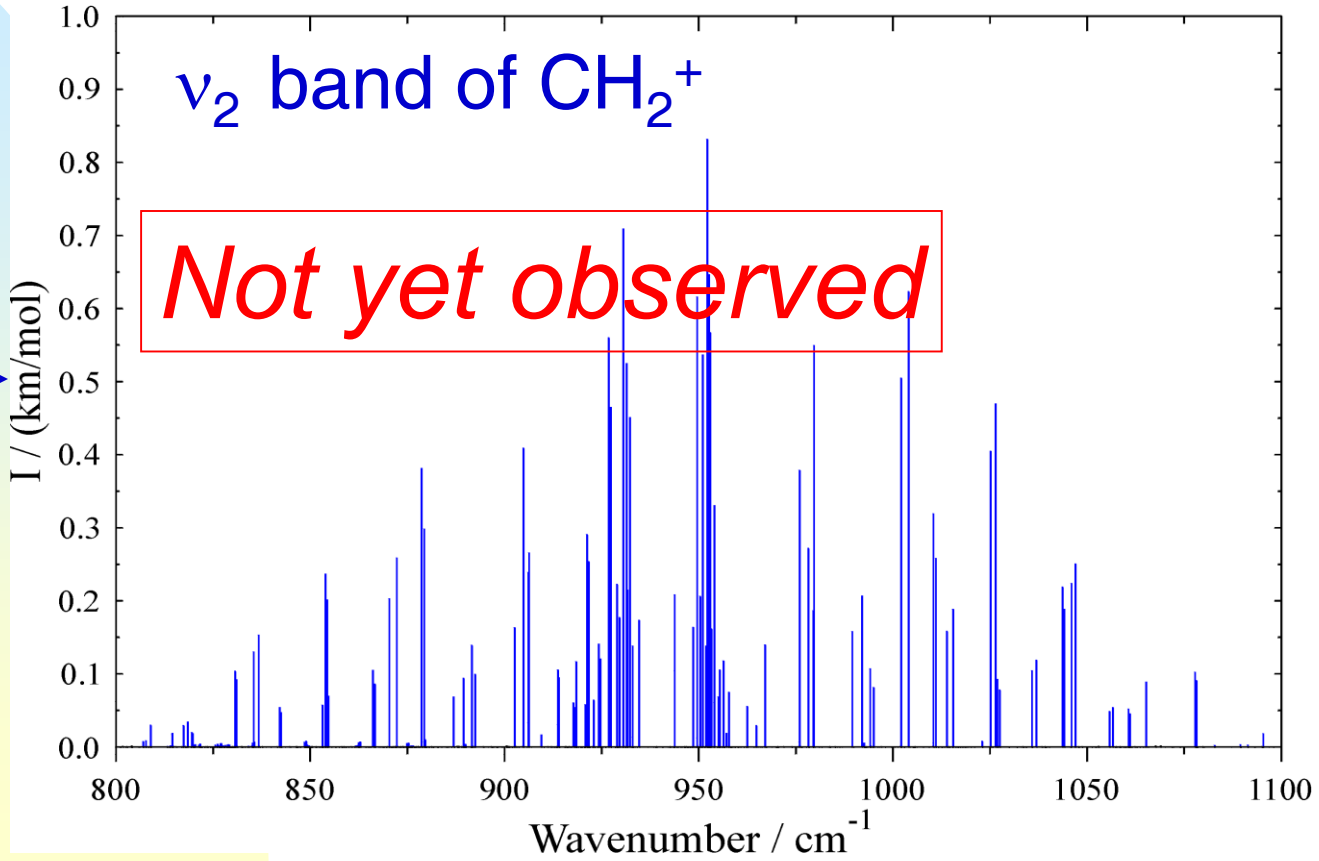
The RENNER computer program

Spectrum

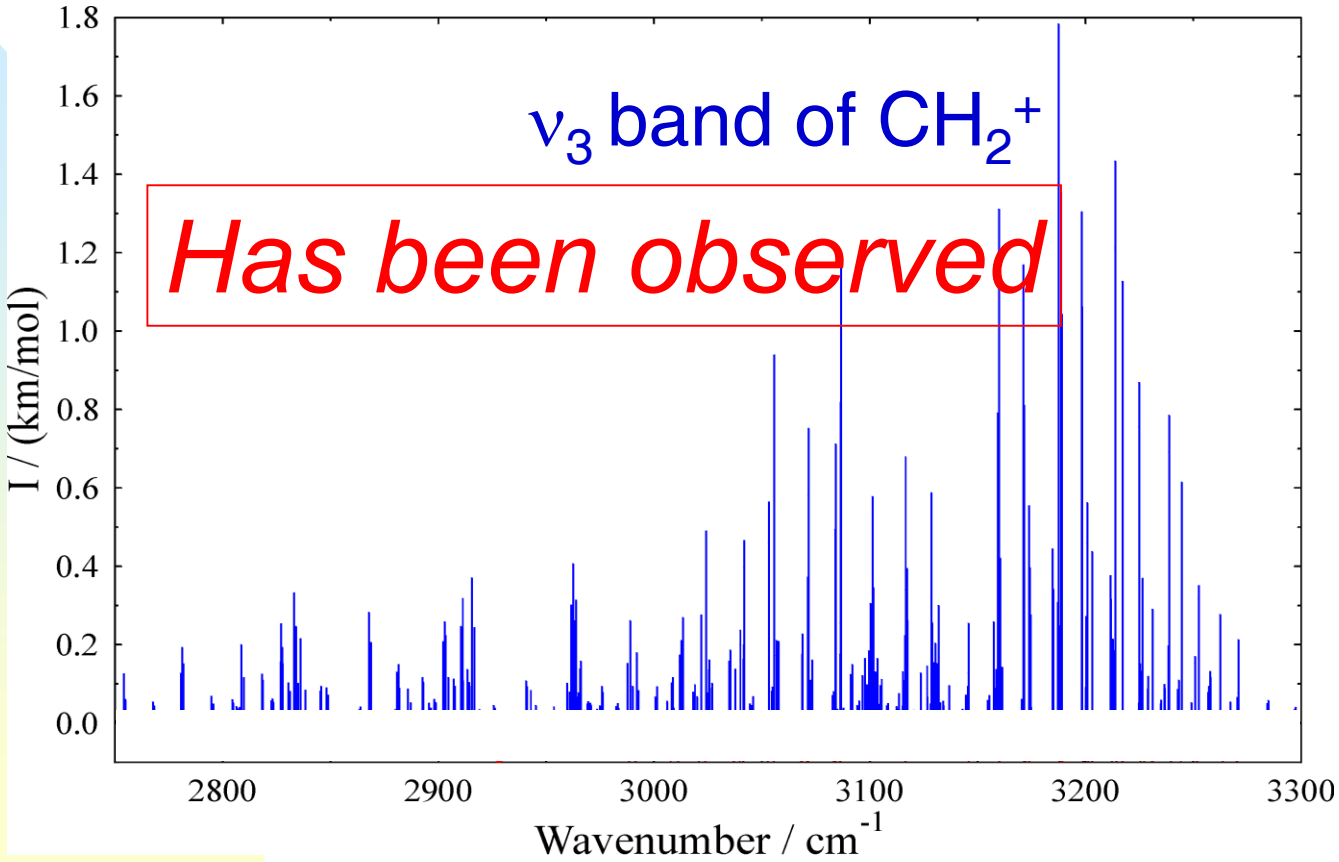


Simulation with $N < 11$ and T = 300 K

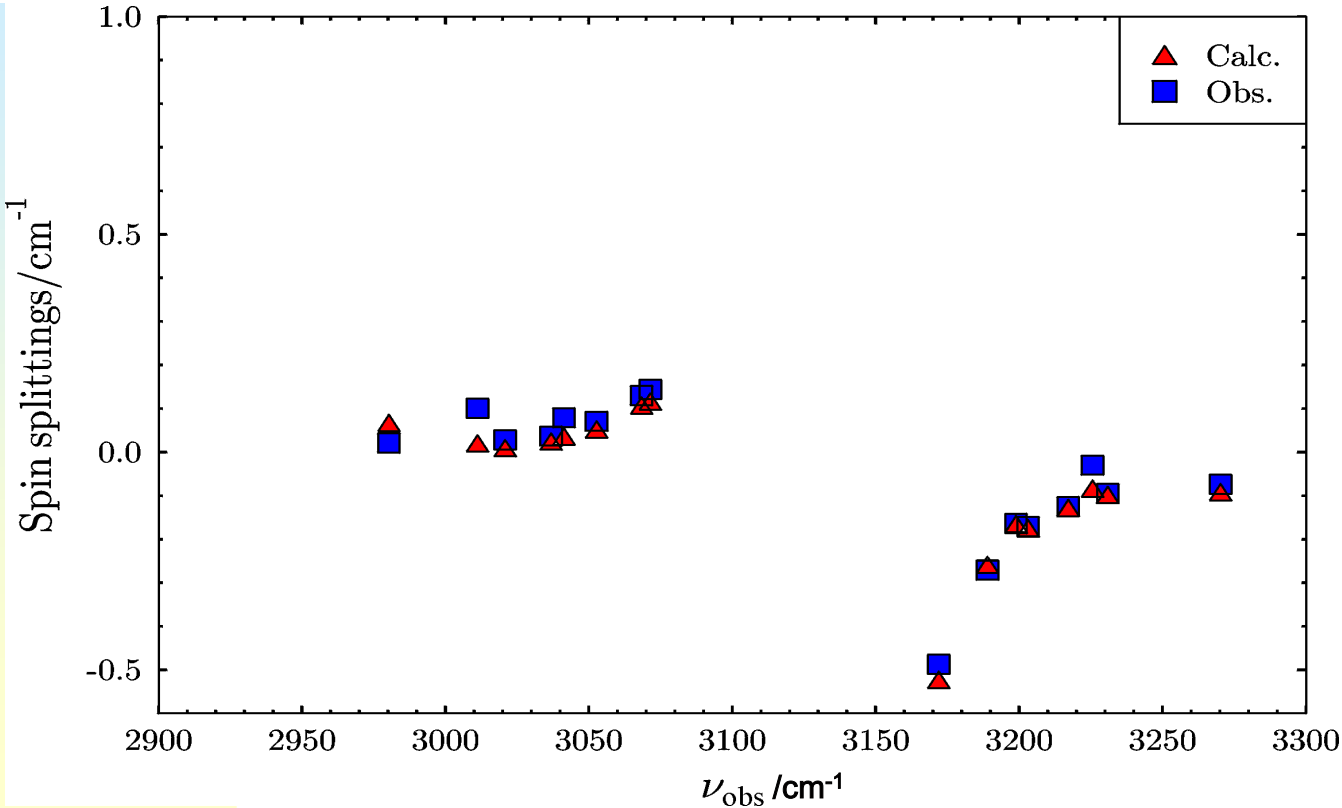
N.B. →



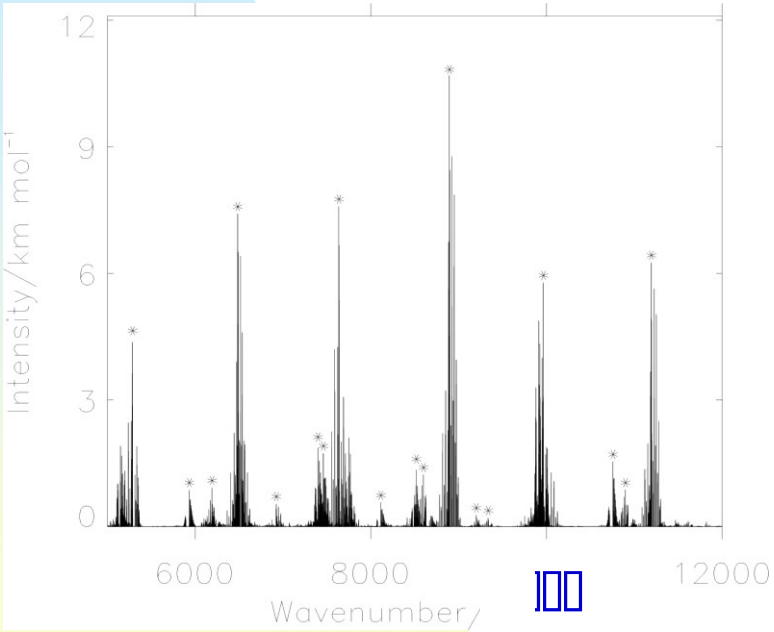
Simulation with $N < 11$ for $T = 300$ K

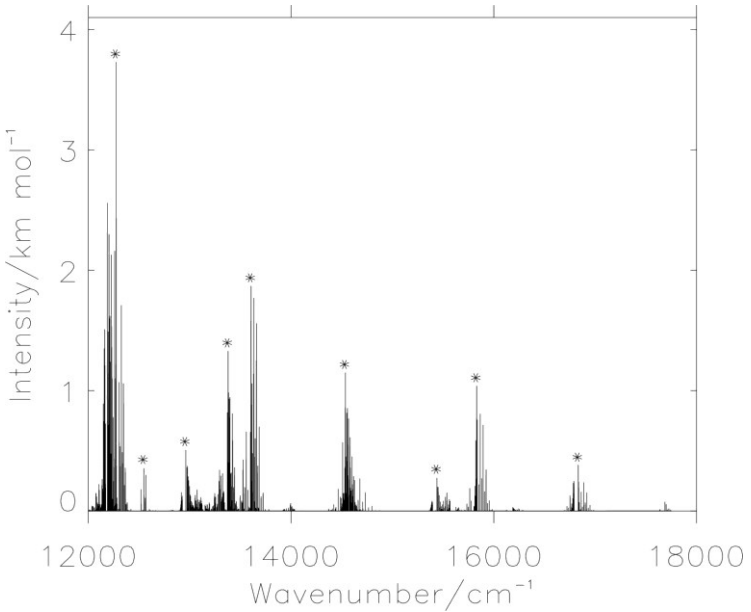


CH_2^+ spin splittings in v_3 band



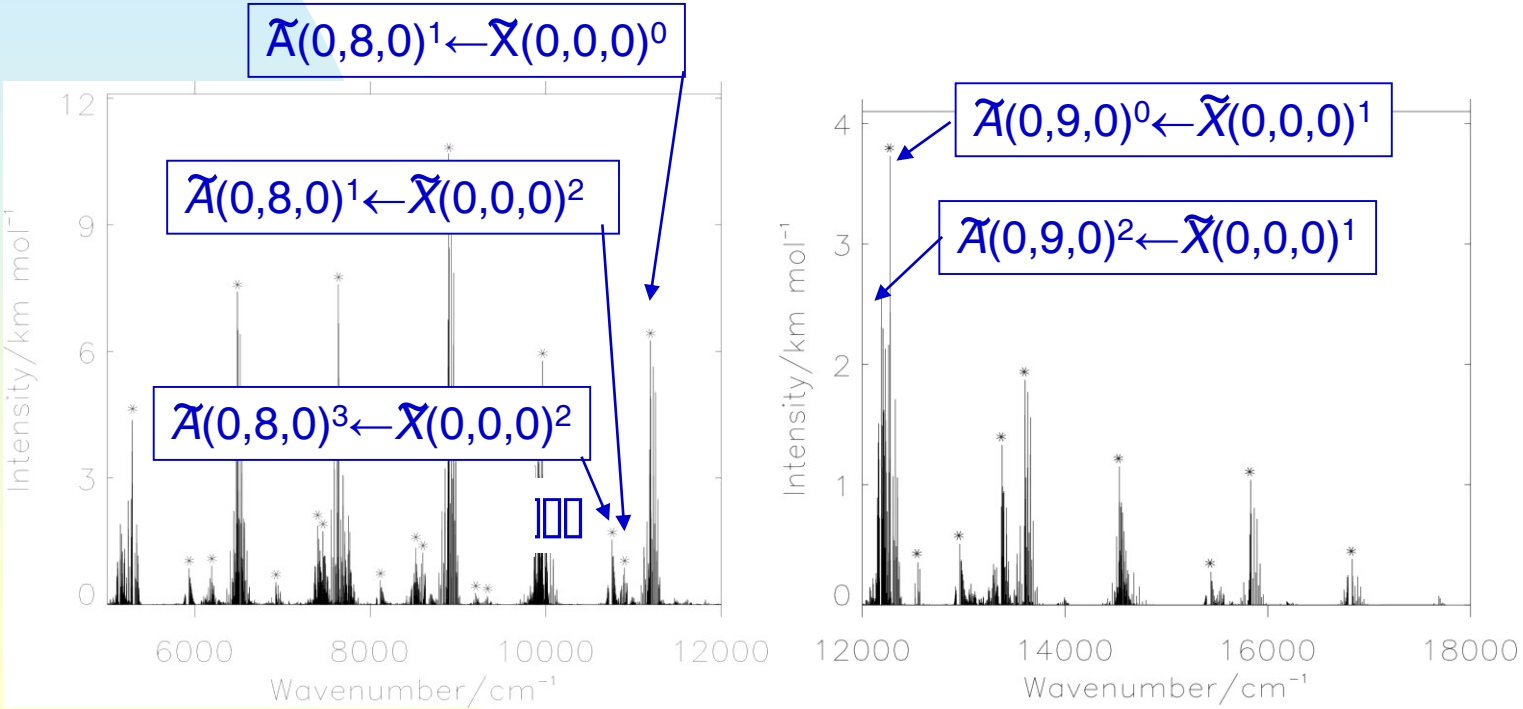
CH_2^+ $\tilde{A}\,^2B_1 \leftarrow \tilde{X}\,^2A_1$

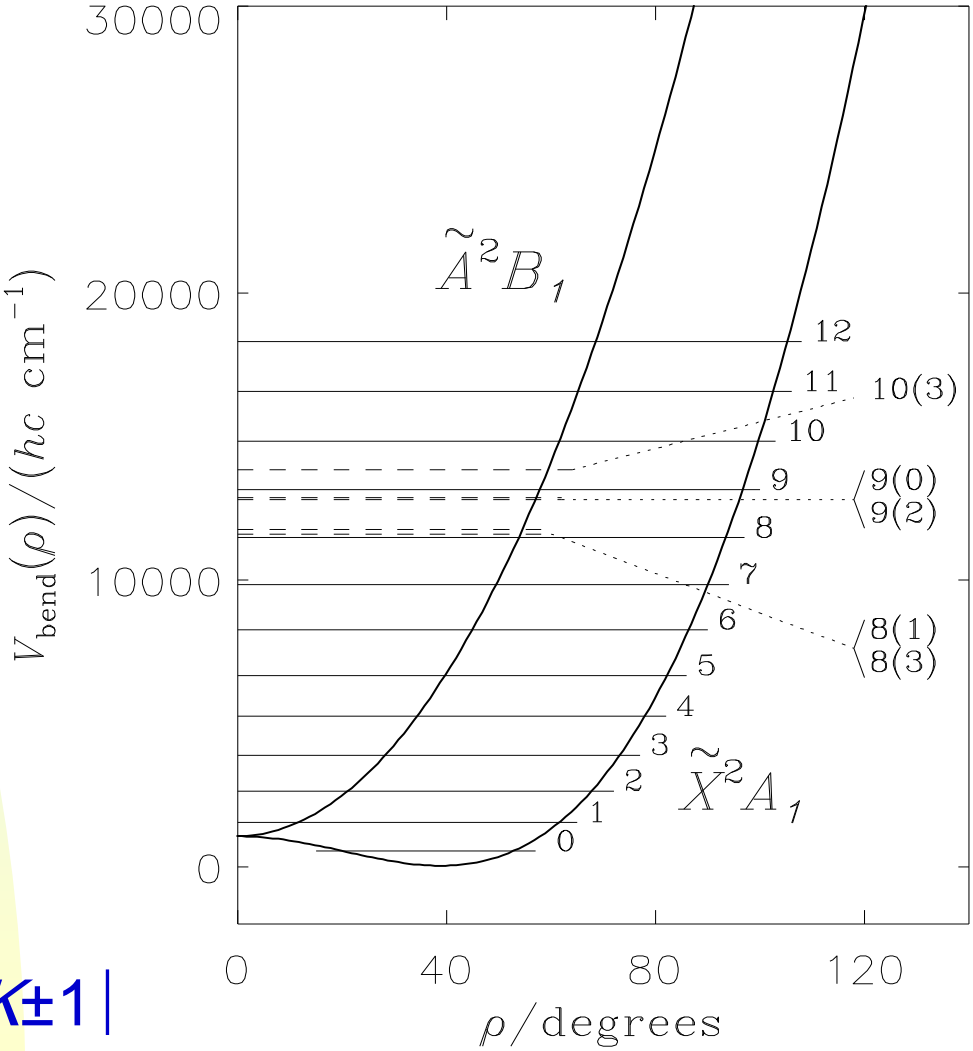




CH_2^+ $\tilde{A}\,^2B_1 \leftarrow \tilde{X}\,^2A_1$

Bands observed at high resolution





$$\nu_2^{\rm lin} = 2\nu_2^{\rm b} + |K \pm 1|$$

Observed - *ab initio* (cm^{-1})

$\tilde{X}$ K=2←0	4
$\tilde{X}$ ν_3	-1
$\tilde{A}$ 8^3	-30
$\tilde{A}$ 8^1	-69
$\tilde{A}$ 9^2	-26
$\tilde{A}$ 9^0	-30

MOLPRO2002 Program system

CCSD(T): aug-cc-pVTZ and pVQZ extrapolated → CBS.

A-state 263 geometries

X-state 429 geometries

E<25000 cm^{-1}

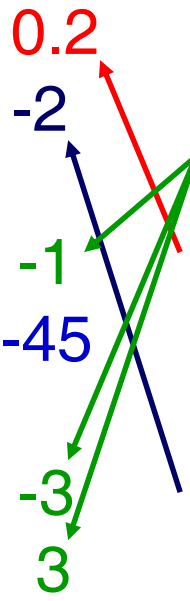
R_e = 1.093 Å

α_e = 140.4°

H = 1066 cm^{-1}

Observed - calculated (cm^{-1})

$\tilde{X}$	K=2←0	4
$\tilde{X}$	ν_3	-1
$\tilde{A}$	8^3	-30
$\tilde{A}$	8^1	-69
$\tilde{A}$	9^2	-26
$\tilde{A}$	9^0	-30



Just adjust the single parameter $G_{001}^{(-)}$ for X state to lower barrier.

Nice effect on K=2←0

But this has pushed ν_3 off a bit.

Observed - calculated (cm^{-1})

$\tilde{X}$	K=2←0	4	0.2	0.1
$\tilde{X}$	ν_3	-1	-2	-0.4
$\tilde{A}$	8^3	-30	-1	-1
$\tilde{A}$	8^1	-69	-45	?
$\tilde{A}$	9^2	-26	-3	-3
$\tilde{A}$	9^0	-30	3	3

Adjust $G^{(-)}_{001}$ and G_{110}

Perturbed by $\tilde{X}(3,3,0)$ $K = 1$

Dealing with a perturbation

If had V^{exact} and used H^{exact} with computer^{exact} would get $E^{exact} = E^{experiment}$ and no perturbations.

However, $V \neq V^{exact}$ so we adjust V. Problem is that a small change in V can make a big change for some E. Need enough "unperturbed" data to constrain V adjustments as try to make a fitting.

More X-state data needed, or, perhaps, we start with ab initio$^{closer\text{-}to\text{-}exact}$