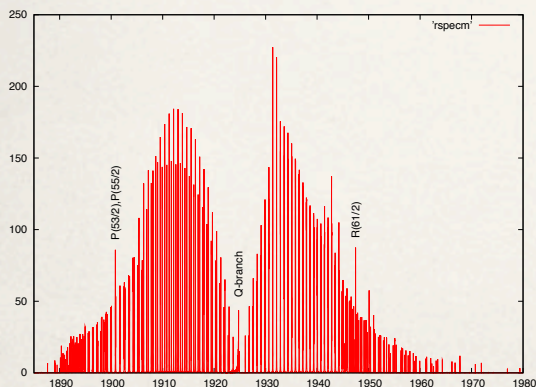


# Composite Approaches for ab Initio Spectroscopy: CCX (X=N, P, As, Sb) and HN<sub>2</sub>O radicals

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Dept. of Chemistry, Purdue University



Complete basis set (CBS)

Exact, BO, non-rel  
 $H\Psi = E\Psi$

Basis

204/atom cc-pV7Z

140/atom cc-pV6Z

91/atom cc-pV5Z

55/atom cc-pVQZ

30/atom cc-pVTZ

14/atom cc-pVDZ

N<sup>3</sup>

N<sup>6</sup>

N<sup>7</sup>

N<sup>8</sup>

N<sup>10</sup>

FCI

HF

CCSD

CCSD(T)

CCSDT

CCSDT<sub>Q</sub>

Method



Complete basis set (CBS)

Basis

204/atom cc-pV7Z

140/atom cc-pV6Z

91/atom cc-pV5Z

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N<sup>8</sup>

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HF

CCSD

CCSD(T)

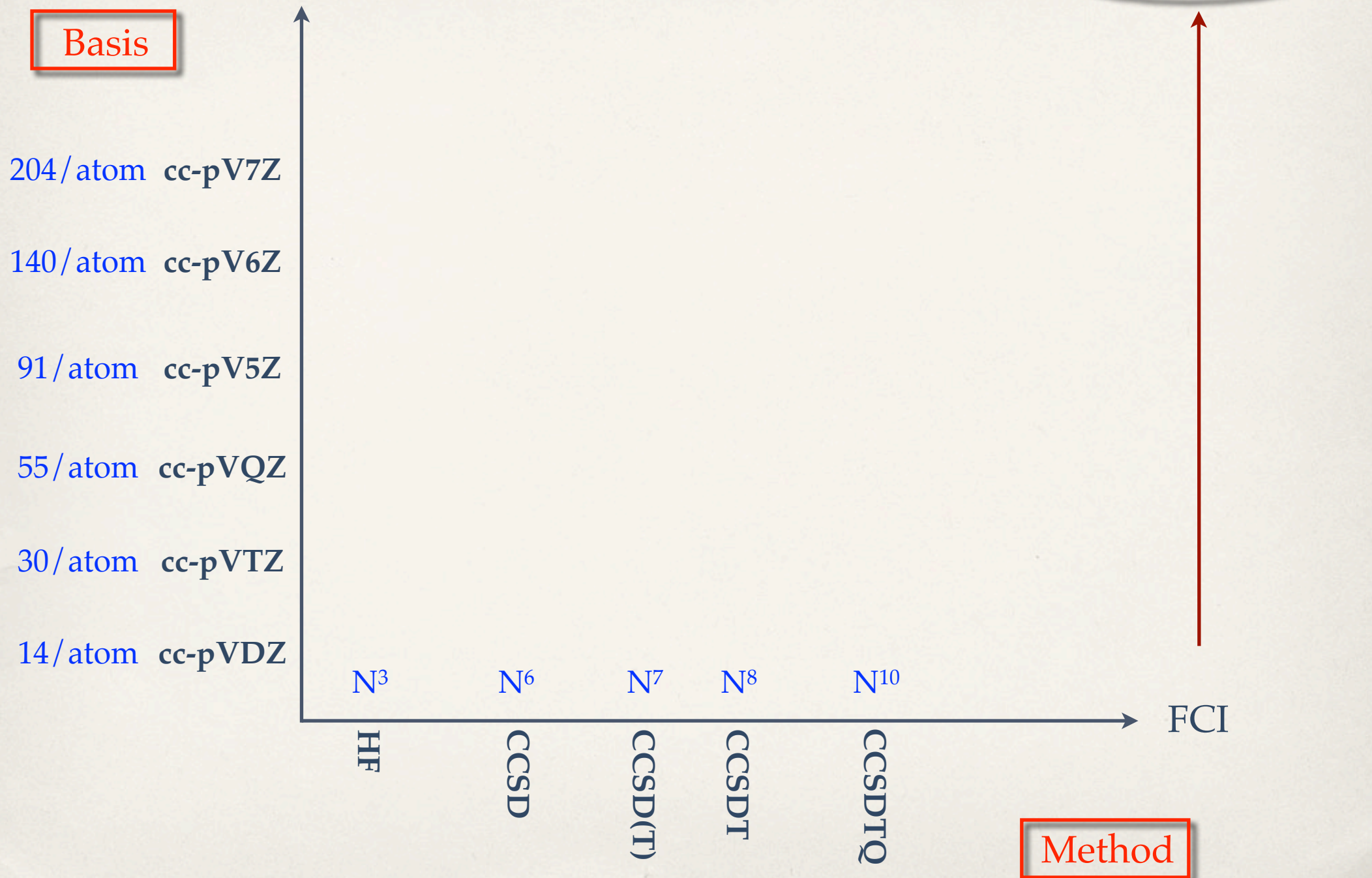
CCSDT

CCSDT<sub>Q</sub>

FCI

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HF

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CCSD(T)

CCSDT

CCSDT<sub>Q</sub>

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$N^3$

$N^6$

$N^7$

$N^8$

$N^{10}$

FCI

HF

CCSD

CCSD(T)

CCSDT

CCSDT $\tilde{Q}$

Method



# Methods for high accuracy work

---

## Multireference configuration interaction, MRCI



$$\psi_{CI} = \sum_{ref} \Phi_{ref} + \sum_i C_i^a \Phi_i^a + \sum_{ij} C_{ij}^{ab} \Phi_{ij}^{ab} + \dots$$

-  allows for correct dissociation of molecules, capable of very high accuracy, but can become intractable for large systems

## Coupled cluster methods

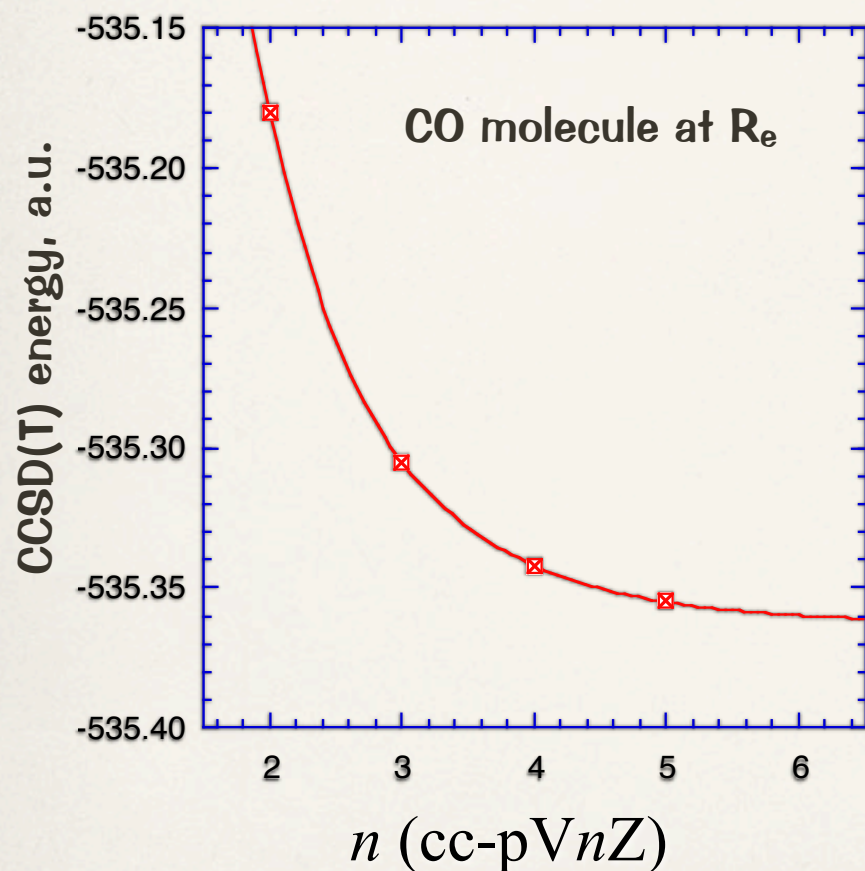
$$\Psi_{CC} = e^{\hat{T}} |0\rangle \quad \text{where} \quad \hat{T} = \hat{T}_1 + \hat{T}_2 + \dots$$

where CCSD corresponds to a coupled cluster method with  $\hat{T}$  truncated at  $\hat{T}_2$

-  Provides a hierarchy of methods that converges to the exact solution within a given 1-particle basis set
-  Inherently based on a single determinant wave function (HF), so can not in general describe dissociation

# Estimating the complete basis set limit

Systematic basis set convergence using **correlation consistent basis sets** allows for extrapolation of energies to the complete basis set (CBS) limit



**Hartree-Fock:**

$$E(n) = E_{\text{HF-limit}} + Ae^{-bn}$$

or

$$E(n) = E_{\text{HF-limit}} + A(n+1)e^{-9\sqrt{n}}$$

**Correlation:**

$$E(n) = E_{\text{CBS}} + \frac{a}{n^3}$$

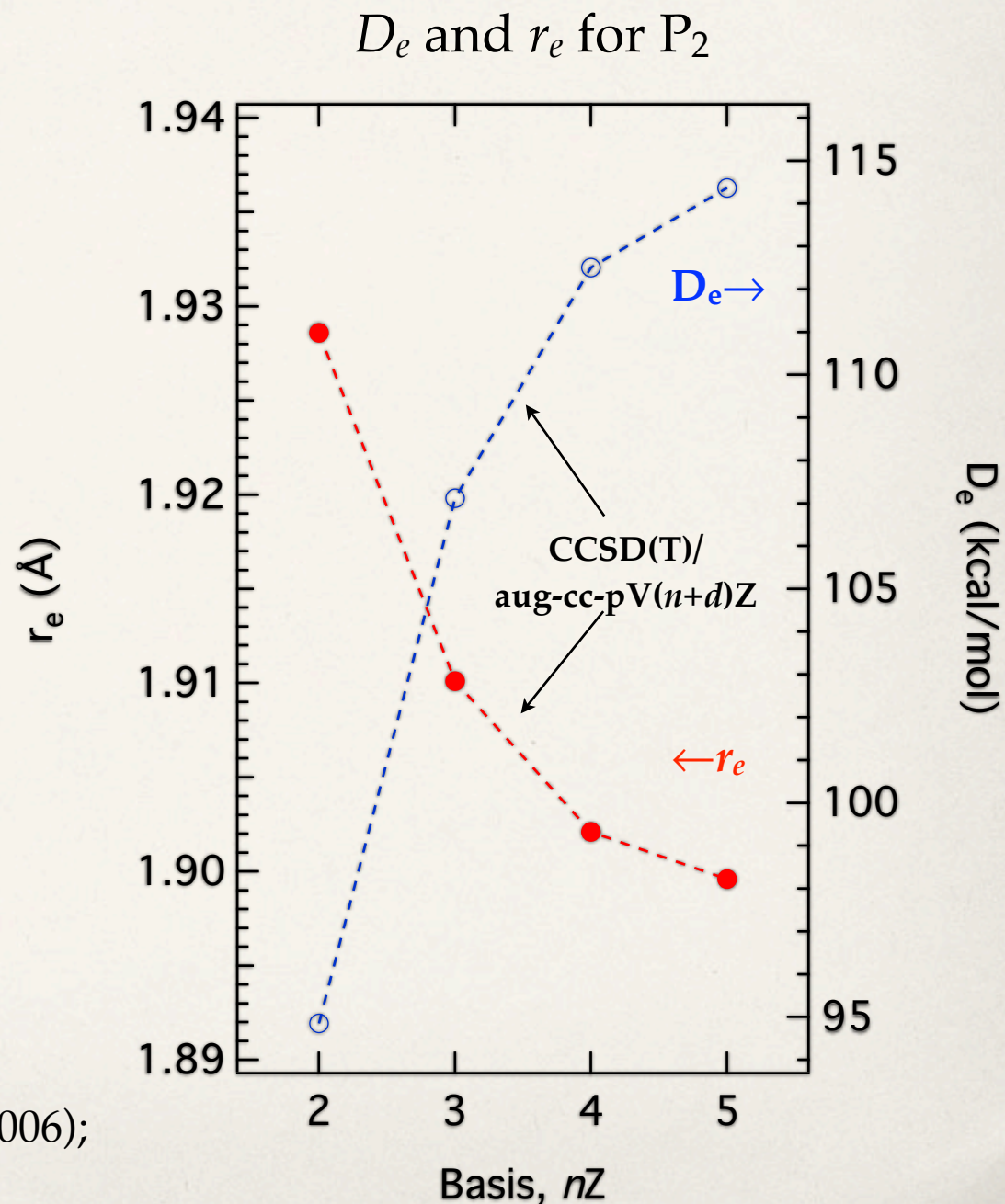
The CBS limit represents the exact solution for the particular choice of method



# Improving the basis set convergence rate

- Standard 1-particle basis sets yield very slow convergence due to a poor description of the 2-electron coalescence cusp
- Addition of a single function non-linear in  $r_{12}$  ( $e^{-\gamma r_{12}}$ ), results in substantially better convergence. Referred to as F12 methods.
- Over the last few years our group has been developing basis sets optimal for use in F12 calculations, cc-pVnZ-F12

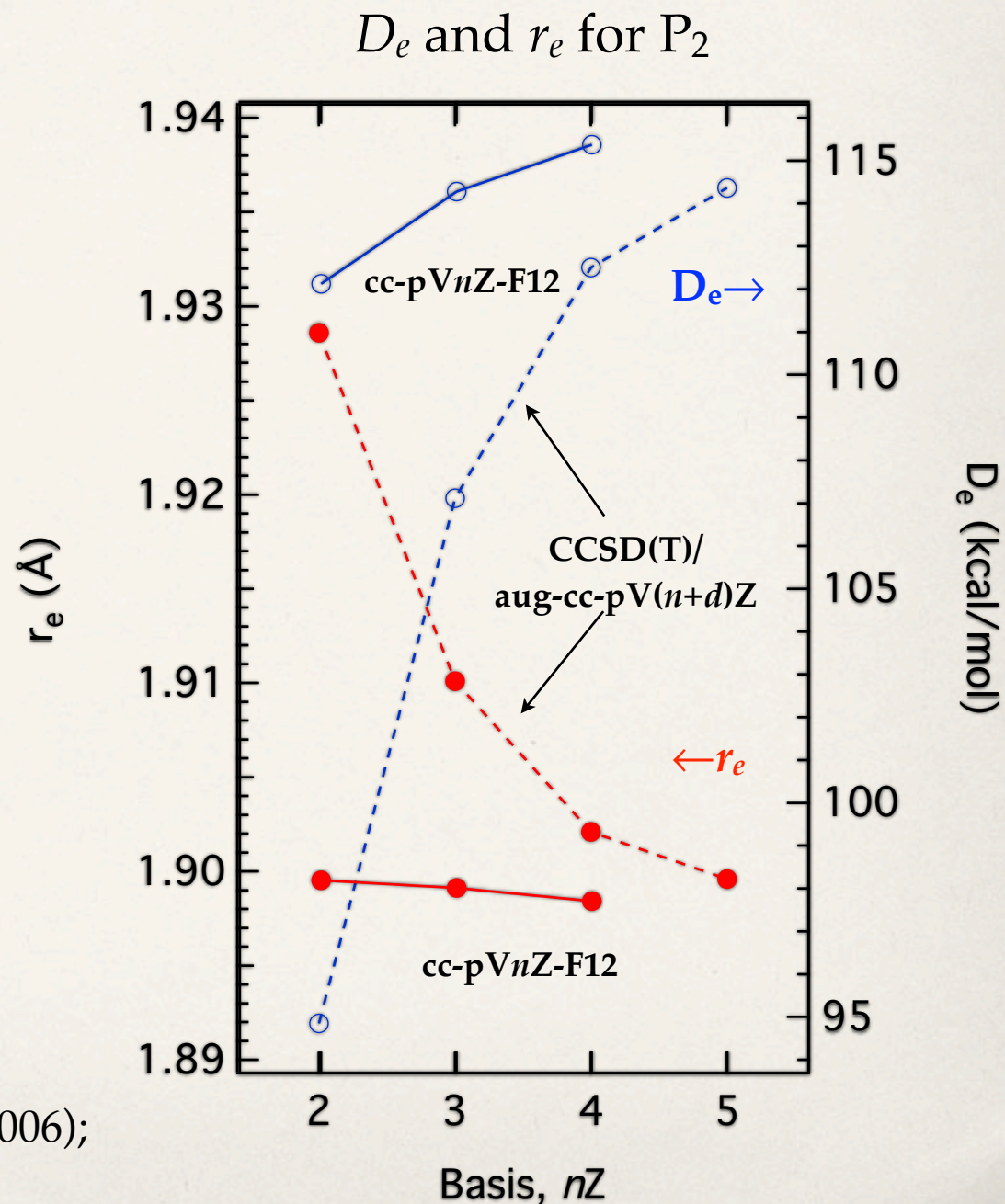
Klopper et al., Int. Rev. Phys. Chem. **25**, 427 (2006);  
Werner et al., Z. Phys. Chem. **224**, 493 (2010)



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# Composite Methods

---

- Assume additivity:

$$E = E(\text{base})$$

- Base calculation: highly correlated method with large correlation consistent basis set, e.g., CCSD(T)/aug-cc-pV5Z

# Composite Methods

---

- Assume additivity:

$$E = E(\text{base}) + \Delta\text{CBS}$$

- Base calculation: highly correlated method with large correlation consistent basis set, e.g., CCSD(T)/aug-cc-pV5Z
- Extrapolate to the CBS limit using energies from 2 consecutive basis sets



# Composite Methods

---

- Assume additivity:

$$E = E(\text{base}) + \Delta\text{CBS} + \Delta\text{CV}$$

- Base calculation: highly correlated method with large correlation consistent basis set, e.g., CCSD(T)/aug-cc-pV5Z
- Extrapolate to the CBS limit using energies from 2 consecutive basis sets
- Add contributions due to electron correlation of outer core electrons

**Goal: try to converge each contribution wrt to method and basis set**

# Composite Methods

---

🏆 Assume additivity:

$$E = E(\text{base}) + \Delta\text{CBS} + \Delta\text{CV} + \Delta\text{Rel}$$

- 📌 Base calculation: highly correlated method with large correlation consistent basis set, e.g., CCSD(T)/aug-cc-pV5Z
- 📌 Extrapolate to the CBS limit using energies from 2 consecutive basis sets
- 📌 Add contributions due to electron correlation of outer core electrons
- 📌 Add effects of scalar relativity on light atoms while including corrections for the pseudopotential approx. (if used)

**Goal: try to converge each contribution wrt to method and basis set**



# Composite Methods

---

🍌 Assume additivity:

$$E = E(\text{base}) + \Delta\text{CBS} + \Delta\text{CV} + \Delta\text{Rel} + \Delta\text{FCI}$$

- 🍌 Base calculation: highly correlated method with large correlation consistent basis set, e.g., CCSD(T)/aug-cc-pV5Z
- 🍌 Extrapolate to the CBS limit using energies from 2 consecutive basis sets
- 🍌 Add contributions due to electron correlation of outer core electrons
- 🍌 Add effects of scalar relativity on light atoms while including corrections for the pseudopotential approx. (if used)
- 🍌 If possible, include correction for high-level electron correlation

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# Composite Methods

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🏆 Assume additivity:

$$E = E(\text{base}) + \Delta\text{CBS} + \Delta\text{CV} + \Delta\text{Rel} + \Delta\text{FCI} + \Delta\text{SO}$$

- 📌 Base calculation: highly correlated method with large correlation consistent basis set, e.g., CCSD(T)/aug-cc-pV5Z
- 📌 Extrapolate to the CBS limit using energies from 2 consecutive basis sets
- 📌 Add contributions due to electron correlation of outer core electrons
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- 📌 If possible, include correction for high-level electron correlation
- 📌 Add contributions due to spin-orbit coupling

**Goal: try to converge each contribution wrt to method and basis set**



# Composite Methods

---

🍷 Assume additivity:

$$E = E(\text{base}) + \Delta\text{CBS} + \Delta\text{CV} + \Delta\text{Rel} + \Delta\text{FCI} + \Delta\text{SO} + \Delta\text{Misc}$$

- 🍷 Base calculation: highly correlated method with large correlation consistent basis set, e.g., CCSD(T)/aug-cc-pV5Z
- 🍷 Extrapolate to the CBS limit using energies from 2 consecutive basis sets
- 🍷 Add contributions due to electron correlation of outer core electrons
- 🍷 Add effects of scalar relativity on light atoms while including corrections for the pseudopotential approx. (if used)
- 🍷 If possible, include correction for high-level electron correlation
- 🍷 Add contributions due to spin-orbit coupling
- 🍷 Add anything else that comes to mind!

**Goal: try to converge each contribution wrt to method and basis set**

# Consider H<sub>2</sub>O

---

- PES defined by 50 symmetry-unique points accurately fit to polynomials in displacement coordinates
- The following contributions were investigated:
  - extrapolations to the CCSD(T)/CBS limit (frozen-core and CV)
  - relativistic effects via Douglas-Kroll-Hess CCSD(T) calculations
  - higher-order correlation via CCSDT/CBS(TQ) and CCSDT(Q)/aVTZ
    - ◆ both FC and CV (the latter with cc-pwCVTZ and cc-pwCVDZ)
  - Born-Oppenheimer diagonal corrections (MRCI)
  - choice of masses (nuclear vs. atomic), Breit interaction, QED, etc.
- Fully anharmonic vibrational energies (for total J=0) were obtained via a variational approach using the full triatomic hamiltonian



## Errors from experiment in $\text{cm}^{-1}$

[illegible]

## Errors from experiment in $\text{cm}^{-1}$

	$\nu_1 (a_1)$	$\nu_2 (a_1)$	$\nu_3 (b_1)$	(020)	(101)
CCSD(T)/aVQZ	-1.7	+1.8	-3.5	+4.2	-4.1
Expt'l	3657.1	1594.8	3755.9	3151.6	7249.8



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CCSD(T)/CBS	+2.4	+0.8	+1.8	+1.9	+5.4
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CCSD(T)/CBS	+2.4	+0.8	+1.8	+1.9	+5.4
+ $\Delta\text{CV}$	+9.2	+0.0	+9.1	-0.1	+19.2
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+ $\Delta\text{Rel}$	+6.6	+1.3	+6.4	+2.6	+13.9
+ $\Delta\text{FCI (FC)}$	-0.7	+0.7	-0.5	+1.5	-1.1
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+ $\Delta$ FCI (FC)	-0.7	+0.7	-0.5	+1.5	-1.1
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+ $\Delta\text{FCI (CV)}$	-1.0	+0.5	-0.9	+0.6	-2.0
Nuc. masses	-0.1	+0.9	+0.0	+1.4	-0.2
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Nuc. masses	-0.1	+0.9	+0.0	+1.4	-0.2
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+ $\Delta\text{FCI (FC)}$	-0.7	+0.7	-0.5	+1.5	-1.1
+ $\Delta\text{FCI (CV)}$	-1.0	+0.5	-0.9	+0.6	-2.0
Nuc. masses	-0.1	+0.9	+0.0	+1.4	-0.2
+BODC	+0.3	+0.5	+0.6	+0.5	+0.9
+Breit,QED,etc.	-0.2	+0.4	+0.1	+0.3	-0.1
Expt'l	3657.1	1594.8	3755.9	3151.6	7249.8



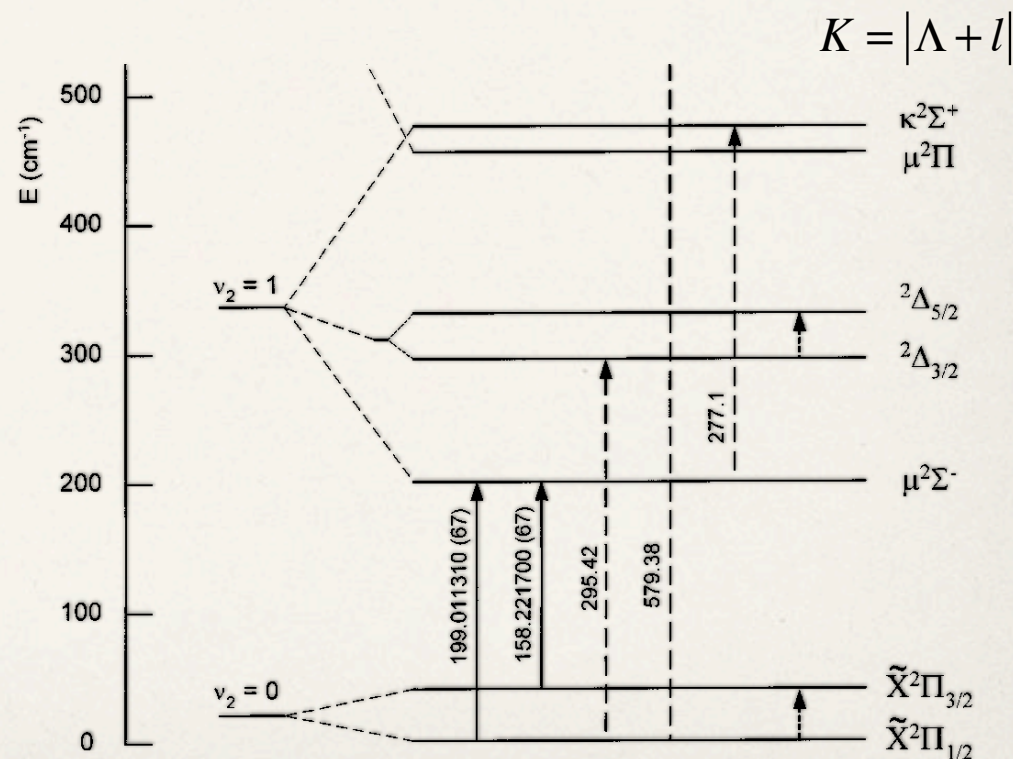
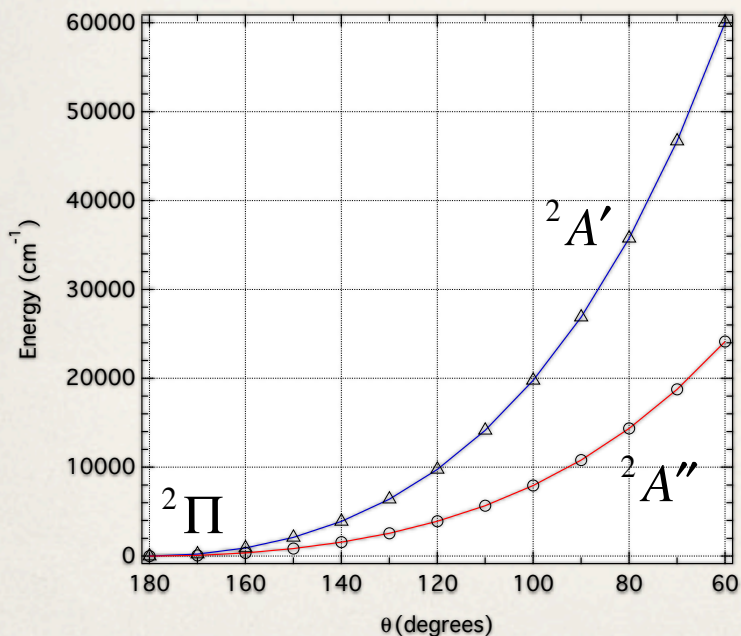
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+Breit,QED,etc.	-0.2	+0.4	+0.1	+0.3	-0.1
Total	3656.9	1595.0	3756.1	3151.9	7249.7
Expt'l	3657.1	1594.8	3755.9	3151.6	7249.8

# The $X^2\Pi$ CCN radical

- Should be important species in interstellar medium but not observed due to small permanent dipole moment
- Strong vibronic Renner-Teller effect on bending mode has motivated numerous spectroscopic investigations

$$\varepsilon = \frac{\omega_{2,A'}^2 - \omega_{2,A''}^2}{\omega_{2,A'}^2 + \omega_{2,A''}^2} = 0.43$$





# Details of the PES Calculations for CCN

---

- PES defined by 50 symmetry-unique points for both RT components accurately fit to polynomials in displacement coordinates
- The following contributions were included:
  - CCSD(T)-F12b for both valence and CV with CBS extrapolations
  - relativistic effects via Douglas-Kroll-Hess CCSD(T) calculations
  - higher-order correlation via CAS-MRCI+Q/cc-pVTZ
- All of these calculations were also carried out for the excited  $^4\Sigma^-$  state
- In addition the following were also calculated at each point on the PES:
  - Spin-orbit matrix elements at the CASSCF level
  - Permanent and transition dipole moments at CCSD(T) and CASSCF levels of theory, respectively (aug-cc-pVTZ)

# Contributions to the Composite Surface: CCN

Å and  $\text{cm}^{-1}$  ; average surface,  $(A' + A'')/2$

2nd-order VPT

	$r_e(\text{CC})$	$r_e(\text{CN})$	$\nu_1 (\text{CN})$	$\nu_2 (\text{bend})$	$\nu_3 (\text{CC})$

<sup>a</sup> Expt: Gillett and Brown, Can. J. Phys. **72**, 1001 (1994); Oliphant et al., J. Chem. Phys. **92**, 2244 (1990)



# Contributions to the Composite Surface: C<sub>2</sub>N

Å and cm<sup>-1</sup> ; average surface,  $(A' + A'')/2$

2nd-order VPT

	$r_e(\text{CC})$	$r_e(\text{CN})$	$\nu_1(\text{CN})$	$\nu_2(\text{bend})$	$\nu_3(\text{CC})$
VDZ-F12	1.382 5	1.185 7	1922.9	318.3	1033.6

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+ΔVQZ-F12	-0.000 4	-0.000 3	+2.0	+0.8	+0.4

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+ΔVTZ-F12	-0.001 7	-0.000 8	+7.4	+1.6	+5.3
+ΔVQZ-F12	-0.000 4	-0.000 3	+2.0	+0.8	+0.4
+ΔCBS	-0.000 1	+0.000 0	+0.2	+0.4	+0.2

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# Contributions to the Composite Surface: CCN

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+ΔVQZ-F12	-0.000 4	-0.000 3	+2.0	+0.8	+0.4
+ΔCBS	-0.000 1	+0.000 0	+0.2	+0.4	+0.2
+ΔCV	-0.003 8	-0.002 6	+9.7	+2.7	+6.4

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2nd-order VPT

	$r_e(\text{CC})$	$r_e(\text{CN})$	$\nu_1(\text{CN})$	$\nu_2(\text{bend})$	$\nu_3(\text{CC})$
VDZ-F12	1.382 5	1.185 7	1922.9	318.3	1033.6
+ΔVTZ-F12	-0.001 7	-0.000 8	+7.4	+1.6	+5.3
+ΔVQZ-F12	-0.000 4	-0.000 3	+2.0	+0.8	+0.4
+ΔCBS	-0.000 1	+0.000 0	+0.2	+0.4	+0.2
+ΔCV	-0.003 8	-0.002 6	+9.7	+2.7	+6.4
+ΔRel	-0.000 2	-0.000 2	-0.8	-0.1	-0.5

<sup>a</sup> Expt: Gillett and Brown, Can. J. Phys. **72**, 1001 (1994); Oliphant et al., J. Chem. Phys. **92**, 2244 (1990)



# Contributions to the Composite Surface: CCN

Å and cm<sup>-1</sup> ; average surface, (A' + A'')/2

2nd-order VPT

	$r_e(\text{CC})$	$r_e(\text{CN})$	$\nu_1 (\text{CN})$	$\nu_2 (\text{bend})$	$\nu_3 (\text{CC})$
VDZ-F12	1.382 5	1.185 7	1922.9	318.3	1033.6
+ΔVTZ-F12	-0.001 7	-0.000 8	+7.4	+1.6	+5.3
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+ΔCBS	-0.000 1	+0.000 0	+0.2	+0.4	+0.2
+ΔCV	-0.003 8	-0.002 6	+9.7	+2.7	+6.4
+ΔRel	-0.000 2	-0.000 2	-0.8	-0.1	-0.5
+ΔFCI	-0.001 5	+0.002 9	-18.1	-3.4	+5.2

<sup>a</sup> Expt: Gillett and Brown, Can. J. Phys. **72**, 1001 (1994); Oliphant et al., J. Chem. Phys. **92**, 2244 (1990)

# Contributions to the Composite Surface: CCN

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2nd-order VPT

	$r_e(\text{CC})$	$r_e(\text{CN})$	$\nu_1(\text{CN})$	$\nu_2(\text{bend})$	$\nu_3(\text{CC})$
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+ΔCBS	-0.000 1	+0.000 0	+0.2	+0.4	+0.2
+ΔCV	-0.003 8	-0.002 6	+9.7	+2.7	+6.4
+ΔRel	-0.000 2	-0.000 2	-0.8	-0.1	-0.5
+ΔFCI	-0.001 5	+0.002 9	-18.1	-3.4	+5.2
Total	1.374 9	1.184 7	1923.3	322.3	1050.4

<sup>a</sup> Expt: Gillett and Brown, Can. J. Phys. **72**, 1001 (1994); Oliphant et al., J. Chem. Phys. **92**, 2244 (1990)



# Contributions to the Composite Surface: CCN

Å and cm<sup>-1</sup> ; average surface,  $(A' + A'')/2$

2nd-order VPT

	$r_e(\text{CC})$	$r_e(\text{CN})$	$\nu_1 (\text{CN})$	$\nu_2 (\text{bend})$	$\nu_3 (\text{CC})$
VDZ-F12	1.382 5	1.185 7	1922.9	318.3	1033.6
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+ΔVQZ-F12	-0.000 4	-0.000 3	+2.0	+0.8	+0.4
+ΔCBS	-0.000 1	+0.000 0	+0.2	+0.4	+0.2
+ΔCV	-0.003 8	-0.002 6	+9.7	+2.7	+6.4
+ΔRel	-0.000 2	-0.000 2	-0.8	-0.1	-0.5
+ΔFCI	-0.001 5	+0.002 9	-18.1	-3.4	+5.2
Total	1.374 9	1.184 7	1923.3	322.3	1050.4
Expt'l <sup>a</sup>			1923.25		1050.76

<sup>a</sup> Expt: Gillett and Brown, Can. J. Phys. **72**, 1001 (1994); Oliphant et al., J. Chem. Phys. **92**, 2244 (1990)

# Full variational treatment of the ro-vibronic problem

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- Fully anharmonic ro-vibronic energies and transition intensities were calculated variationally using the YART code of Mitrushchenkov in a 2-step procedure:
- rotationless vibronic equation solved by 3-dim. diagonalization of  $\hat{T}_K + V$  for  $K \leq 20$ . For  $K > 0$  the coupled equations for the RT pairs were solved by diagonalizing:

$$\begin{pmatrix} \hat{T}_{|K-\Lambda|} + V_+ & V_- \\ V_- & \hat{T}_{|K+\Lambda|} + V_+ \end{pmatrix} \quad \text{where} \quad V_{\pm} = \frac{1}{2}(V_{A'} \pm V_{A''})$$
$$K = |\Lambda + l| \quad ; \quad \Lambda = \pm 1$$
$$l = \pm v_2, \pm(v_2 - 2), \dots, \pm 1 \text{ or } 0$$

- the exact  $\hat{T}_K$  was employed, no contraction of the basis was used, and states 7000 cm<sup>-1</sup> above the (000) of the X<sup>2</sup>Π and 4000 cm<sup>-1</sup> above the *a*<sup>4</sup>Σ<sup>-</sup> were included.
- resulting vibronic states were then used as a basis for the full ro-vibrational diagonalization including spin-orbit and rotation up to  $J=155/2$ .



# Energy level structure of the ro-vibronic levels ( $J=P, K=0-3$ )

where

$$P = |K + \Sigma|$$

with

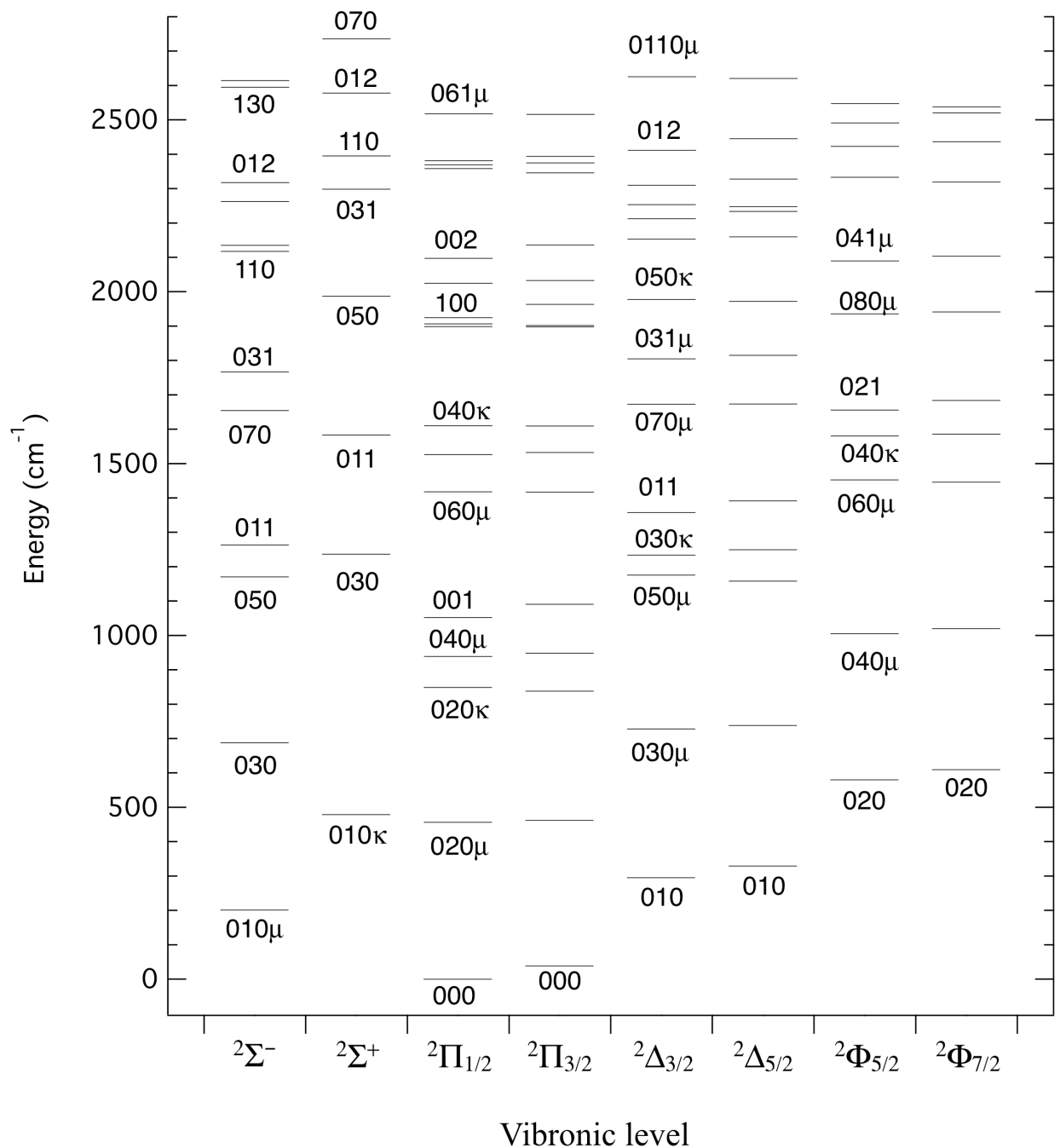
$$K = |\Lambda + l|$$

for a  $^2\Pi$  state:

$$\Lambda = \pm 1$$

$$\Sigma = \pm \frac{1}{2}$$

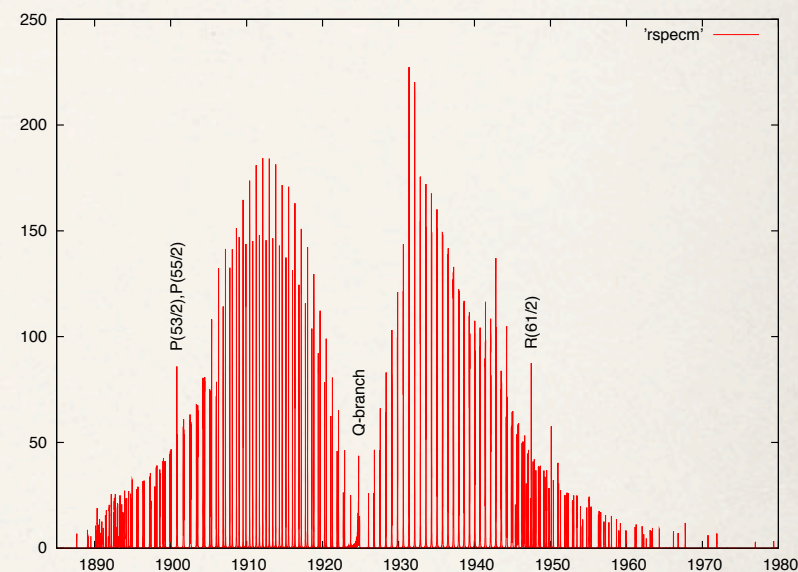
$$l = \pm v_2, \pm(v_2 - 2), \dots, \pm 1 \text{ or } 0$$



# Selected Ro-vibronic Transition Energies for CCN

	Theory	Expt.
<b>The (100) band</b>		
$(100) \ ^2\Pi_{1/2} \leftarrow (000) \ ^2\Pi_{1/2}; P(9/2)$	1921.29	1919.69
$(100) \ ^2\Pi_{1/2} \leftarrow (000) \ ^2\Pi_{1/2}; R(5/2)$	1927.60	1925.99
$(100) \ ^2\Pi_{3/2} \leftarrow (000) \ ^2\Pi_{3/2}; P(29/2)$	1912.56	1911.04
$(100) \ ^2\Pi_{3/2} \leftarrow (000) \ ^2\Pi_{3/2}; R(9/2)$	1929.08	1927.55
<b>The (010) band</b>		
$(010) \ \mu^2\Sigma^- \leftarrow (000) \ ^2\Pi_{1/2}; Q(1/2)$	200.99	199.06
$(010) \ \mu^2\Sigma^- \leftarrow (000) \ ^2\Pi_{3/2}; P(3/2)$	162.09	158.28
$(010) \ \kappa^2\Sigma^+ \leftarrow (010) \ \mu^2\Sigma^-; Q(1/2)$	277.77	277.10
$(010) \ ^2\Delta_{3/2} \leftarrow (000) \ ^2\Pi_{1/2}; R(1/2)$	295.26	295.42
$(020) \ ^2\Phi_{5/2} \leftarrow (000) \ ^2\Pi_{1/2}; S(1/2)$	580.31	579.38
<b>Spin-orbit transitions</b>		
$(000) \ ^2\Pi_{3/2} \leftarrow (000) \ ^2\Pi_{1/2}; P(7/2)$	35.00	36.89
$(000) \ ^2\Pi_{3/2} \leftarrow (000) \ ^2\Pi_{1/2}; Q(3/2)$	37.72	39.60
$(000) \ ^2\Pi_{3/2} \leftarrow (000) \ ^2\Pi_{1/2}; R(19/2)$	46.97	48.82
<b>The <math>1_0^1 2_1^1</math> hot band</b>		
$(110)\mu^2\Sigma^- \leftarrow (010)\mu^2\Sigma^-; P(7), F_1$	1913.4571	1911.3882
$(110)^2\Delta \leftarrow (010)^2\Delta; R(17/2), F_1$	1924.8741	1922.9424

Theoretical (100) band at 300 K



## Experiment

**(100):** Gillett and Brown, Can. J. Phys. **72**, 1001 (1994)

**(010) & SO:** Allen et al., J. Mol. Spectrosc. **201**, 17 (2000).

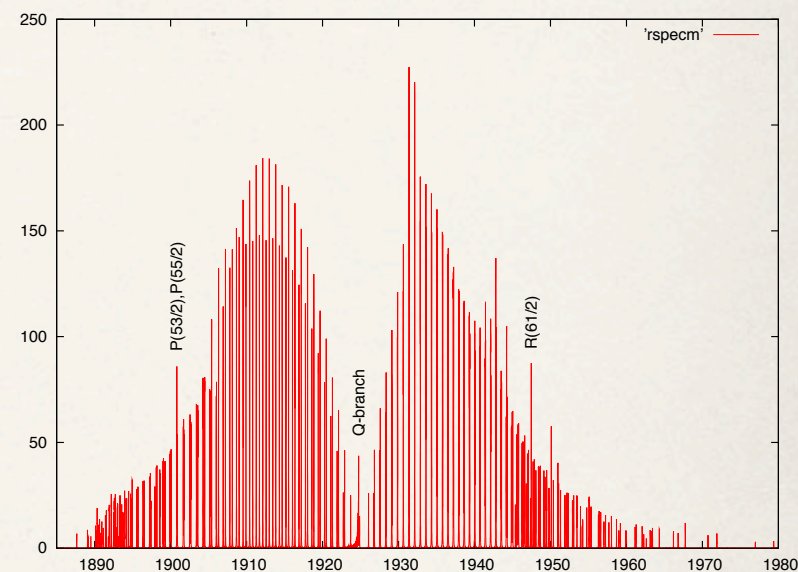
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$(010) \ \mu^2\Sigma^- \leftarrow (000) \ ^2\Pi_{3/2}; P(3/2)$	162.09	158.28
$(010) \ \kappa^2\Sigma^+ \leftarrow (010) \ \mu^2\Sigma^-; Q(1/2)$	277.77	277.10
$(010) \ ^2\Delta_{3/2} \leftarrow (000) \ ^2\Pi_{1/2}; R(1/2)$	295.26	295.42
$(020) \ ^2\Phi_{5/2} \leftarrow (000) \ ^2\Pi_{1/2}; S(1/2)$	580.31	579.38
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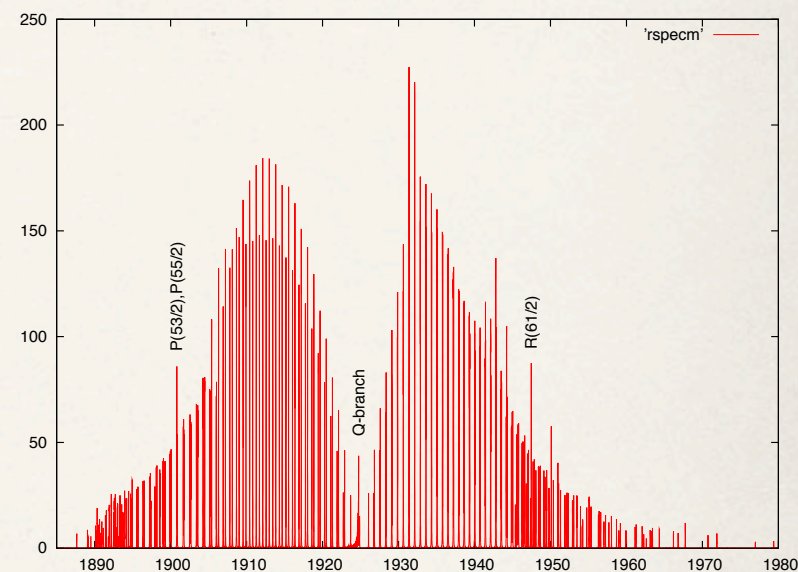
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**Hot band:** Beaton et al., J. Mol. Spectrosc. **209**, 60 (2001)



# The $X^2\Pi$ CCP radical: Preliminary Results

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- Jet-cooled LIF spectrum of  $C_2P$  reported by Clouthier and co-workers
  - Assigned ground state vibrational frequencies and Renner-Teller effect
- High resolution microwave spectrum reported by Ziurys, Clouthier, and co-workers
  - Yielded  $r_0$ ,  $r_s$ , and  $r_m^{(1)}$  structures
- Detected in the circumstellar envelope of IRC+10216
- All calculations of this work mostly analogous to those of CCN
  - •C-C-P resonance structure causes problems for ROHF (same for CCAs)
    - Use full-valence CASSCF orbitals in the CCSD(T) calculations
  - Full variational calculations are currently just underway

F.X. Sunahori, J. Wei, & D.J. Clouthier, J. Chem. Phys. 128, 4311 (2008)

D.T. Halfen, M. Sun, D.J. Clouthier, & L.M. Ziurys, J. Chem. Phys. 130, 014305 (2009);

D.T. Halfen, D.J. Clouthier, & L.M. Ziurys, Astrophys. J. Lett. 677 L101 (2008).

# Contributions to the Composite Surface: CCP

Å and cm<sup>-1</sup> ; average surface,  $(A' + A'')/2$

2nd-order VPT

	$r_e(\text{CC})$	$r_e(\text{CP})$	$\nu_1(\text{CC})$	$\nu_2(\text{bend})$	$\nu_3(\text{CP})$
VTZ-F12	1.310 5	1.613 2	1671.5	205.2	833.1
+ΔVQZ-F12	-0.000 3	-0.000 5	+1.3	+2.8	+0.6
+ΔCBS	+0.000 0	-0.000 1	+0.3	+0.6	+0.0
+ΔCV	-0.003 7	-0.005 1	+9.1	+0.6	+5.7
+ΔRel	-0.000 2	-0.000 2	-1.0	-0.5	-0.9
+ΔFCI	+0.001 6	+0.001 9	-10.8	-0.3	-7.0
Total	1.307 9	1.609 2	1670.4	208.4	831.5
Expt'l <sup>a</sup>	1.289	1.621	1644.3		834.8

$B_0 = 6361$  MHz vs. expt'l value of 6392.41 MHz

$B_e = 6354$  MHz vs. approx. expt'l value of 6366 MHz

<sup>a</sup>  $r_m^{(1)}$  structure



# Contributions to the Composite Surface: CCP

Å and cm<sup>-1</sup> ; average surface,  $(A' + A'')/2$

2nd-order VPT

	$r_e(\text{CC})$	$r_e(\text{CP})$	$\nu_1(\text{CC})$	$\nu_2(\text{bend})$	$\nu_3(\text{CP})$	(002)
VTZ-F12	1.310 5	1.613 2	1671.5	205.2	833.1	1654.7
+ $\Delta$ VQZ-F12	-0.000 3	-0.000 5	+1.3	+2.8	+0.6	+1.3
+ $\Delta$ CBS	+0.000 0	-0.000 1	+0.3	+0.6	+0.0	+0.1
+ $\Delta$ CV	-0.003 7	-0.005 1	+9.1	+0.6	+5.7	+10.8
+ $\Delta$ Rel	-0.000 2	-0.000 2	-1.0	-0.5	-0.9	-1.7
+ $\Delta$ FCI	+0.001 6	+0.001 9	-10.8	-0.3	-7.0	-13.7
Total	1.307 9	1.609 2	1670.4	208.4	831.5	1651.5
Expt'l <sup>a</sup>	1.289	1.621	1644.3		834.8	1677.7

$B_0 = 6361$  MHz vs. expt'l value of 6392.41 MHz

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+ $\Delta\text{CV}$	-0.003 7	-0.005 1	+9.1	+0.6	+5.7	+10.8
+ $\Delta\text{Rel}$	-0.000 2	-0.000 2	-1.0	-0.5	-0.9	-1.7
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$B_e = 6354$  MHz vs. approx. expt'l value of 6366 MHz

<sup>a</sup>  $r_m^{(1)}$  structure



# The $X^2\Pi$ CCAs and CCSb radicals: Preliminary Results

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- Jet-cooled LIF spectrum of  $C_2As$  reported by Clouthier and co-workers
  - Assigned ground state vibrational frequencies and Renner-Teller effect
  - Spin-orbit coupling now large enough to nearly overwhelm the RT interaction
- For these calculations, relativistic effects must now be included at the outset
  - Choose relativistic effective core potentials on As and Sb with new cc-pVnZ-F12-PP basis sets in F12 calculations
  - Use DKH calculations to account for the small pseudopotential errors and account for scalar relativistic effects from the carbon atoms
- For both  $C_2As$  and  $C_2Sb$  low-lying cyclic minima exist on the PES
  - after including spin-orbit, these lie above the linear configuration by 4.5 kcal/mol for  $C_2As$  and 1.0 kcal/mol for  $C_2Sb$

# Contributions to the Composite Surface: CCAs

Å and cm<sup>-1</sup> ; average surface, (A' + A'')/2

2nd-order VPT

	$r_e(\text{CC})$	$r_e(\text{CAs})$	$\nu_1(\text{CC})$	$\nu_2(\text{bend})$	$\nu_3(\text{CAs})$
VTZ-F12	1.302 7	1.741 5	1690.1	153.4	659.5
+ΔVQZ-F12	-0.000 3	-0.000 6	+0.8	+2.9	+0.9
+ΔCBS	-0.000 0	-0.000 1	+0.0	+2.0	+0.3

Expt'l <sup>a</sup>			1691.7		661.0
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<sup>a</sup> Wei et al., J. Chem. Phys. **129**, 4307 (2008). Data from the  $\Omega=1/2$  state was used.

J. Shearouse and K.A. Peterson, in preparation



# Contributions to the Composite Surface: CCAs

Å and cm<sup>-1</sup> ; average surface,  $(A' + A'')/2$

2nd-order VPT

	$r_e(\text{CC})$	$r_e(\text{CAs})$	$\nu_1(\text{CC})$	$\nu_2(\text{bend})$	$\nu_3(\text{CAs})$
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+ΔVQZ-F12	-0.000 3	-0.000 6	+0.8	+2.9	+0.9
+ΔCBS	-0.000 0	-0.000 1	+0.0	+2.0	+0.3
+ΔCV	-0.004 5	-0.009 7	+9.6	-11.4	+2.3

Expt'l <sup>a</sup>			1691.7		661.0
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# Contributions to the Composite Surface: CCAs

Å and  $\text{cm}^{-1}$  ; average surface,  $(A' + A'')/2$

2nd-order VPT

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+ $\Delta\text{VQZ-F12}$	-0.000 3	-0.000 6	+0.8	+2.9	+0.9
+ $\Delta\text{CBS}$	-0.000 0	-0.000 1	+0.0	+2.0	+0.3
+ $\Delta\text{CV}$	-0.004 5	-0.009 7	+9.6	-11.4	+2.3
+ $\Delta\text{Rel}$	-0.000 1	+0.000 8	-0.5	+2.9	-1.7

Expt'l <sup>a</sup>			1691.7		661.0
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Å and cm<sup>-1</sup> ; average surface,  $(A' + A'')/2$

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+ $\Delta$ VQZ-F12	-0.000 3	-0.000 6	+0.8	+2.9	+0.9
+ $\Delta$ CBS	-0.000 0	-0.000 1	+0.0	+2.0	+0.3
+ $\Delta$ CV	-0.004 5	-0.009 7	+9.6	-11.4	+2.3
+ $\Delta$ Rel	-0.000 1	+0.000 8	-0.5	+2.9	-1.7
+ $\Delta$ FCI	+0.001 5	+0.001 6	-13.9	+0.5	-3.7

Expt'l <sup>a</sup>			1691.7		661.0
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2nd-order VPT

	$r_e(\text{CC})$	$r_e(\text{CAs})$	$\nu_1(\text{CC})$	$\nu_2(\text{bend})$	$\nu_3(\text{CAs})$
VTZ-F12	1.302 7	1.741 5	1690.1	153.4	659.5
+ΔVQZ-F12	-0.000 3	-0.000 6	+0.8	+2.9	+0.9
+ΔCBS	-0.000 0	-0.000 1	+0.0	+2.0	+0.3
+ΔCV	-0.004 5	-0.009 7	+9.6	-11.4	+2.3
+ΔRel	-0.000 1	+0.000 8	-0.5	+2.9	-1.7
+ΔFCI	+0.001 5	+0.001 6	-13.9	+0.5	-3.7
Total	1.2993	1.7335	1686.1	150.3	657.6
Expt'l <sup>a</sup>			1691.7		661.0

<sup>a</sup> Wei et al., J. Chem. Phys. **129**, 4307 (2008). Data from the  $\Omega=1/2$  state was used.



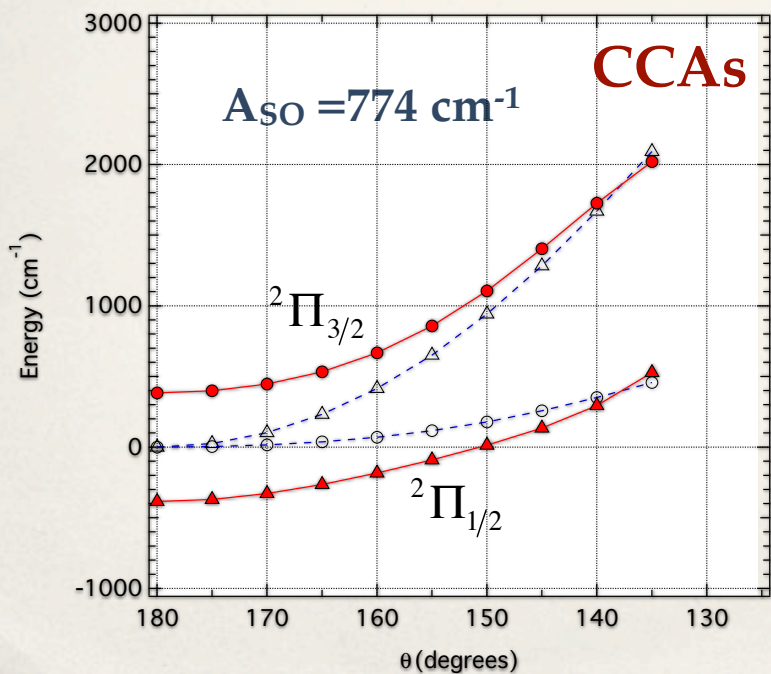
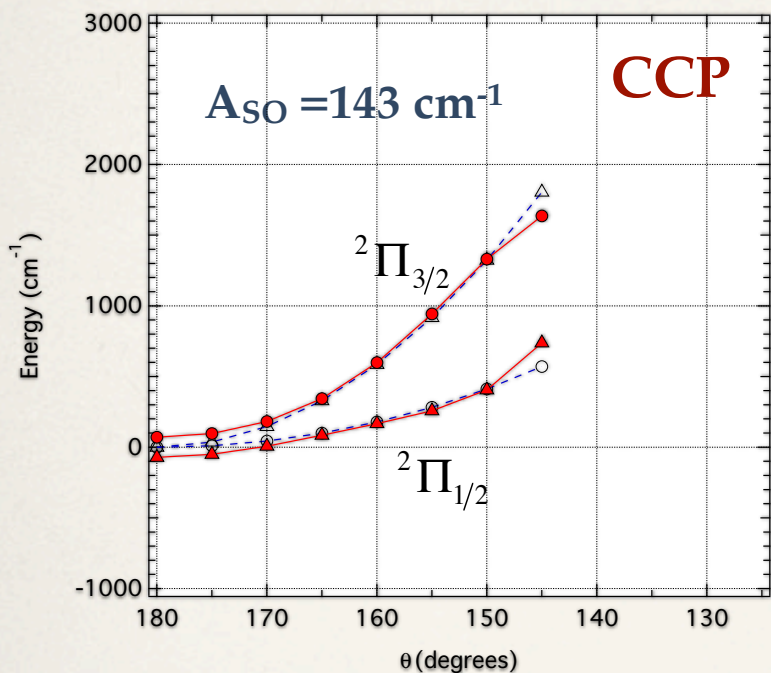
# Contributions to the Composite Surface: CCSb

Å and cm<sup>-1</sup> ; average surface,  $(A' + A'')/2$

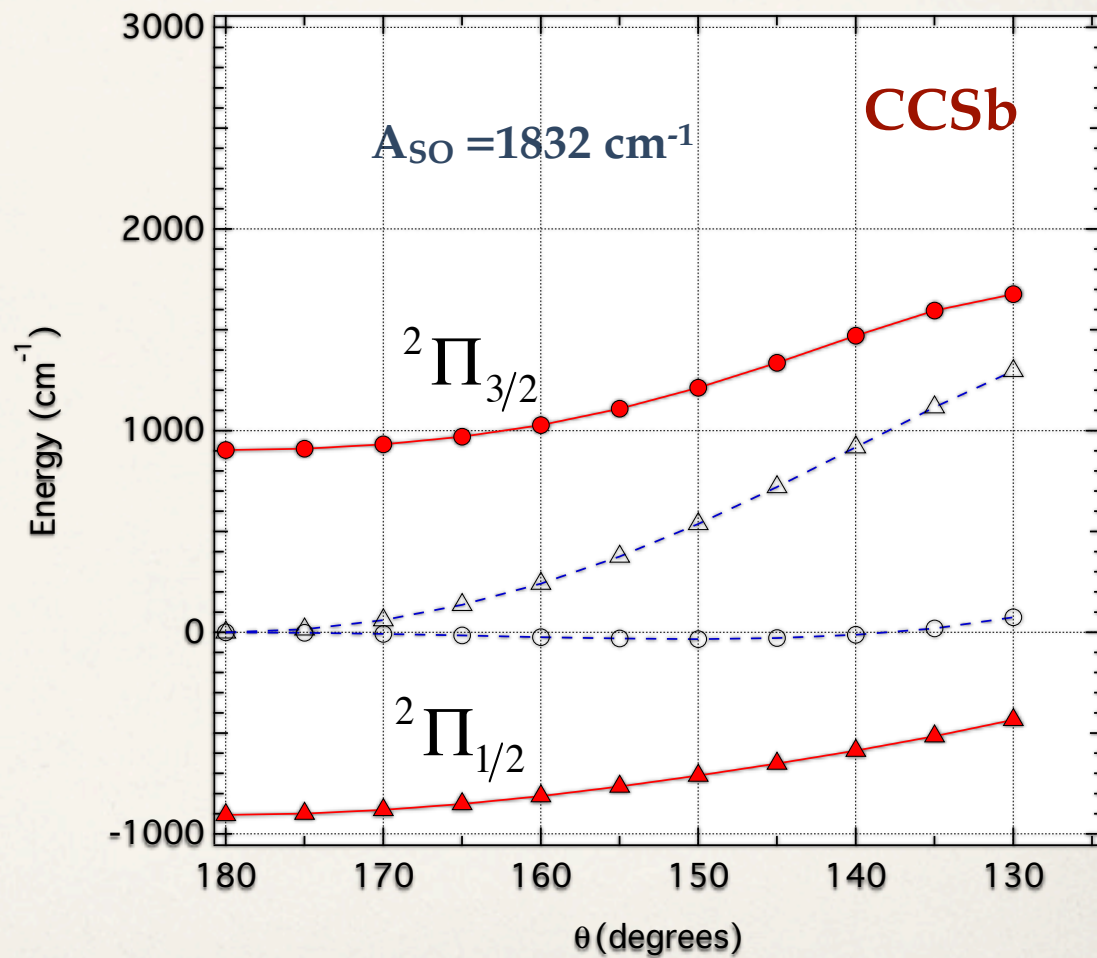
2nd-order VPT

	$r_e(\text{CC})$	$r_e(\text{CSb})$	$\nu_1(\text{CC})$	$\nu_2(\text{bend})$	$\nu_3(\text{CSb})$
VTZ-F12	1.293 3	1.953 3	1742.6	98.5	566.0
+ΔVQZ-F12	-0.000 3	-0.000 8	+1.4	+2.8	+0.6
+ΔCBS	+0.000 1	-0.000 1	+0.0	+1.6	-0.1
+ΔCV	-0.002 3	-0.021 4	+2.5	+8.5	+7.8
+ΔRel	+0.000 4	+0.000 2	+1.7	+2.8	-0.7
+ΔFCI	+0.002 4	+0.000 8	-13.2	+2.7	-8.8
Total	1.293 5	1.932 1	1735.0	116.9	564.8

# Impact of Spin-Orbit on Bending Potentials



MRCI+Q PESs with  
CASSCF SO matrix elements





# Moving from N to Sb

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Å and cm<sup>-1</sup>

	$r_{CC}$	$r_{CX}$	$\omega(CC)$	$\omega_2$	$\omega(CX)$	$\mu$ (D)
CCN	1.375	1.185	1058	322	1967	0.30
CCP	1.308	1.609	1700	217	830	3.11
CCAs	1.299	1.734	1720	108	652	3.87
CCSb	1.294	1.932	1766	117	556	5.01

# Spectroscopic Properties of the $X^2A'$ $\text{HN}_2\text{O}$ Radical

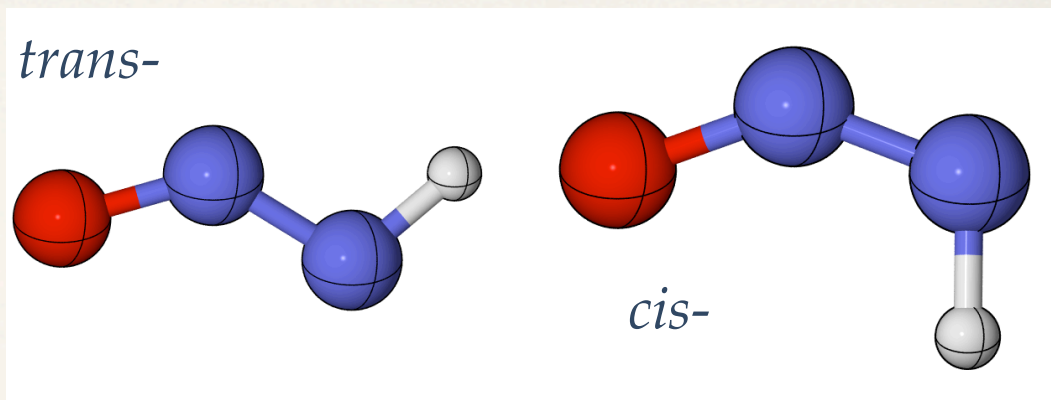
Proposed to be important in the planetary atmosphere of Saturn's rings; formed by reaction of  $\text{NH}$  with  $\text{NO}$ .

*trans*- isomer lower than *cis*- by 6.9 kcal/mol

Composite approach:

CCSD(T)/CBS +  $\Delta\text{CV}$  +  $\Delta\text{DK}$   
+  $\Delta\text{CCSDT}$  +  $\Delta\text{CCSDT}(\text{Q})$

Large contribution from (Q)



<i>trans</i> -	$\Delta\text{T}$	$\Delta(\text{Q})$	Theory	Matrix IR
$\nu_1$	+30.2	-49.6	3286.9	3254.0
$\nu_2$	-20.4	-37.1	1629.6	1628.9
$\nu_3$	+8.1	-69.5	1279.0	1294.5
$\nu_4$	-5.1	-66.2	1172.1	1213.4
$\nu_5$	0.0	-34.4	638.7	---
$\nu_6$	-16.7	-13.5	740.4	746.5



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● Dr. Gerald Knizia and Prof. Hans-Joachim Werner (Uni. Stuttgart)

● Most CCSD(T) and all F12 calculations were carried out with the MOLPRO suite of ab initio programs (v2010.1).

● The CFOUR program was used for the CCSD(T) frequencies of HNNO.

● The MRCC program was used for all higher order coupled cluster calculations

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