# *Ab Initio Spin-Orbit Coupling in Spectroscopy and Dynamics*

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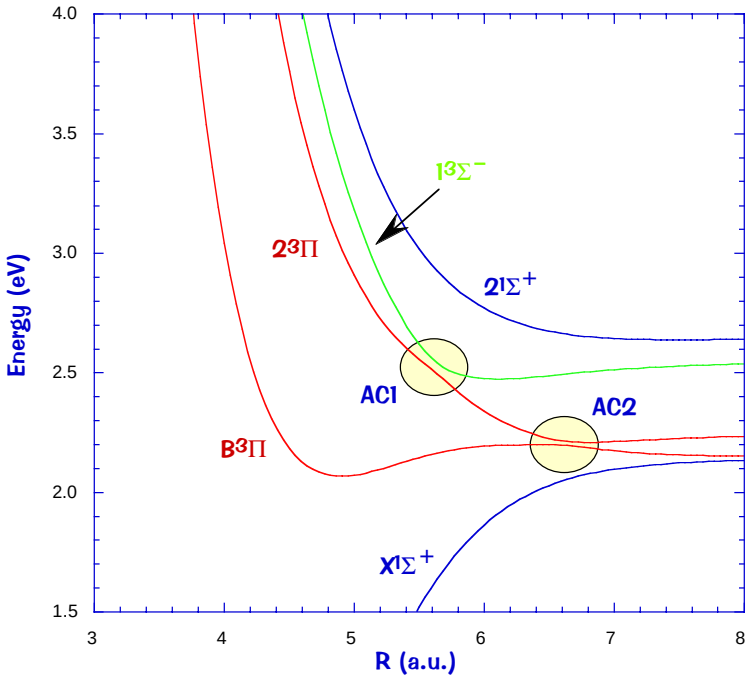


# Outline of Talk

- Methods of computing spin-orbit effects

- Basis sets and electron correlation

  All-electron benchmark calculations: Atoms and light diatomics

  Effective 1-electron operators: Pseudopotentials vs. all-electron

- Applications

  BrO : low-lying electronic states: predissociation of $A^2\Pi_{3/2}$

  HOBr: Singlet-triplet interactions in the UV/Vis absorption spectrum

  BrCl: preliminary results for the $B^3\Pi(0^+) \leftarrow X^1\Sigma^+$ system

# Spin-Orbit Coupling: It's Not Just for Heavy Atoms

- Predissociation of excited electronic states by states of different spin multiplicity
- Intersystem crossing and phosphorescence of excited triplet states in organic molecules
- Altering the shape of potential energy surfaces in exit and/or entrance channels
- Fine structure in high resolution spectroscopy
- Altering ground state chemical reactions by inducing transitions between different potential energy surfaces
- Thermochemistry to within "chemical accuracy"

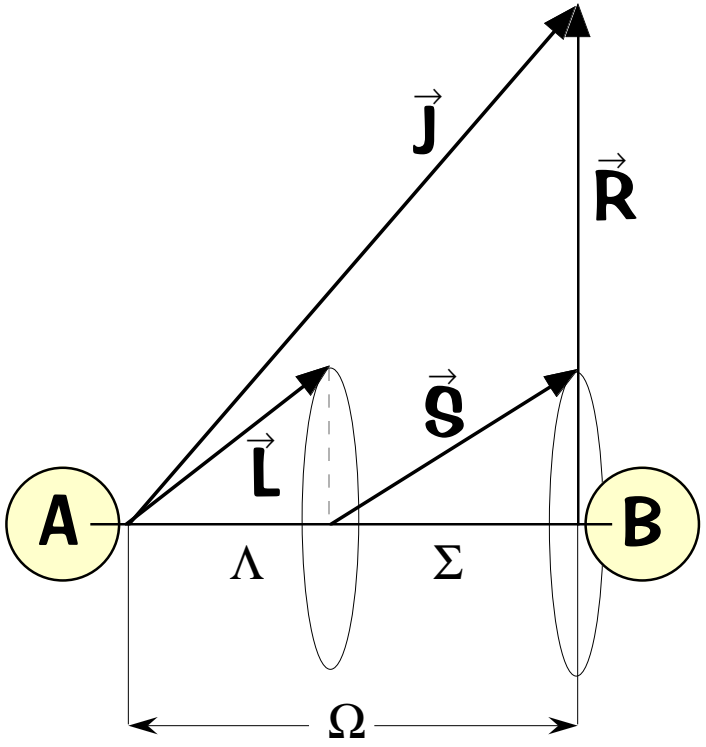
# Options for Computing Spin-orbit Effects *ab Initio*

- 4-component methods based on the Dirac equation
  - computationally very expensive; few programs available
- 2-component spin-orbit schemes
  - incorporates SO effects into the orbitals
  - requires significant work to implement into standard *ab initio* codes
- Perturbation treatments
  - include SO when setting up the CI matrix
  - calculate SO matrix elements between small number of spin-free states

operators:

1- and 2-electron Breit-Pauli; Douglas-Kroll-Hess; effective 1-electron

$$\hat{H}_{SO} = A\,\mathbf{L}\cdot\mathbf{S}$$




## Angular momenta in a diatomic molecule

J (total) = L (orbital) + S (spin) + R (rotational)

# Operators Used in the Present Work

## 1) The Breit-Pauli spin-orbit operator

$$H_{SO} = \frac{1}{2}\alpha^2 \sum_{i\lambda}\left[\frac{Z_\lambda}{r_{i\lambda}^3}\left(\mathbf{r}_{i\lambda}\times\mathbf{p}_i\right)\cdot\mathbf{s}_i\right] - \frac{1}{2}\alpha^2 \sum_{i\neq j}\left[\frac{1}{r_{ij}^3}\left(\mathbf{r}_{ij}\times\mathbf{p}_i\right)\cdot\left(\mathbf{s}_i + 2\mathbf{s}_j\right)\right]$$

1-electron
$Z_\lambda$ is the actual nuclear charge

2-electron
spin-same-orbit &
spin-other-orbit

## 2) Effective 1-electron operator via quasi-relativistic pseudopotentials

$$H_{SO} = \sum_{i\lambda}\left[\sum_{l}^{L-1}\frac{2\Delta V_l^\lambda(r_{i\lambda})}{2l+1}P_l^\lambda(i)\mathbf{l}_{\lambda i}\mathbf{s}_i P_l^\lambda(i)\right]$$

Contains the difference between 2-component relativistic pseudopotentials

* Includes scalar relativistic & some 2-electron effects

# Calculation of Spin-Orbit Coupled Eigenstates

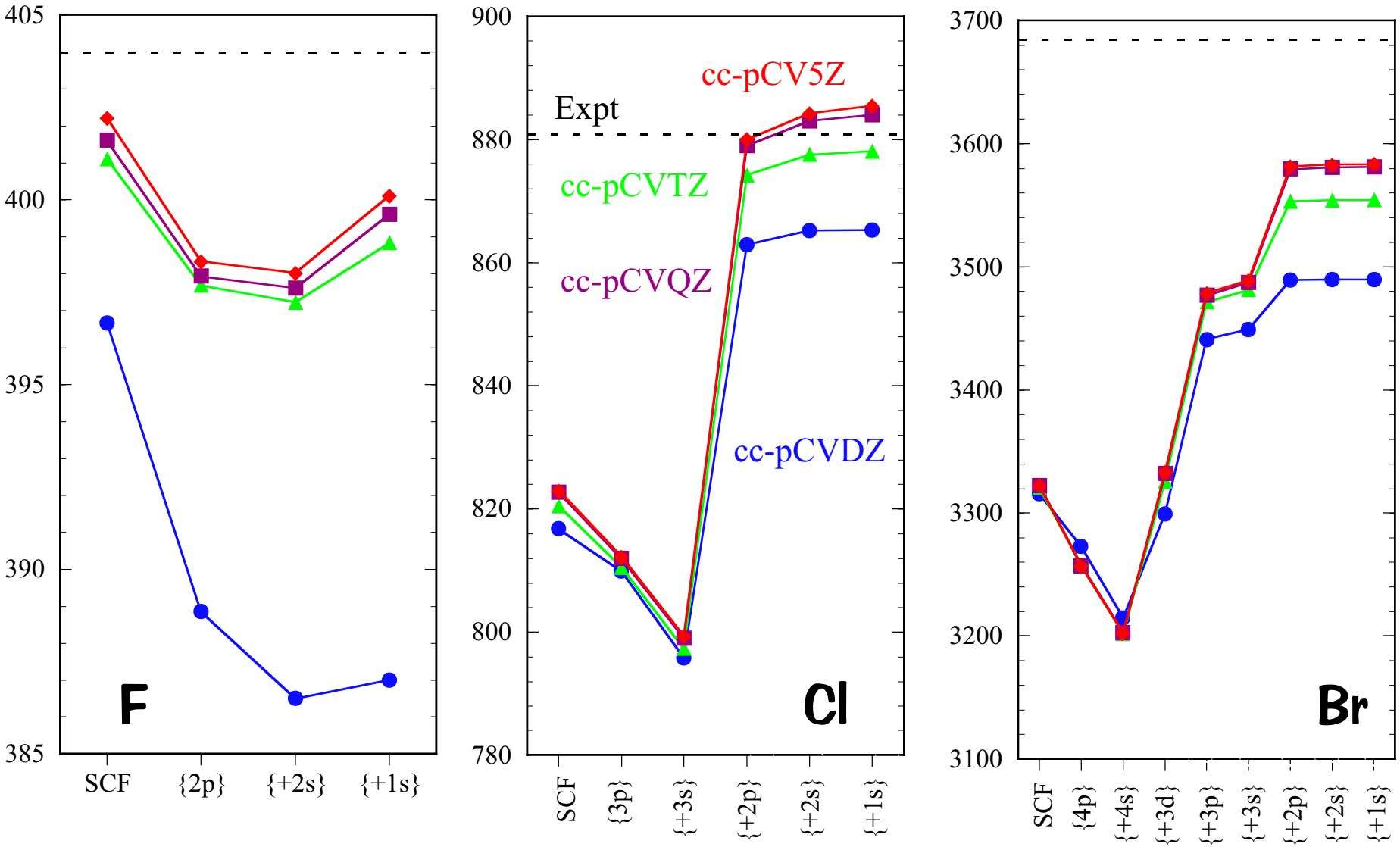
Diagonalize $H_{el} + H_{SO}$ in a basis of spin-free ($\Lambda$-S) eigenfunctions

**Example: HOBr**

use a basis of the lowest 5 valence states: $X^1A'$, $2^1A'$, $1^1A''$, $1^3A'$, $1^3A''$ (labeled by S and $M_S$)

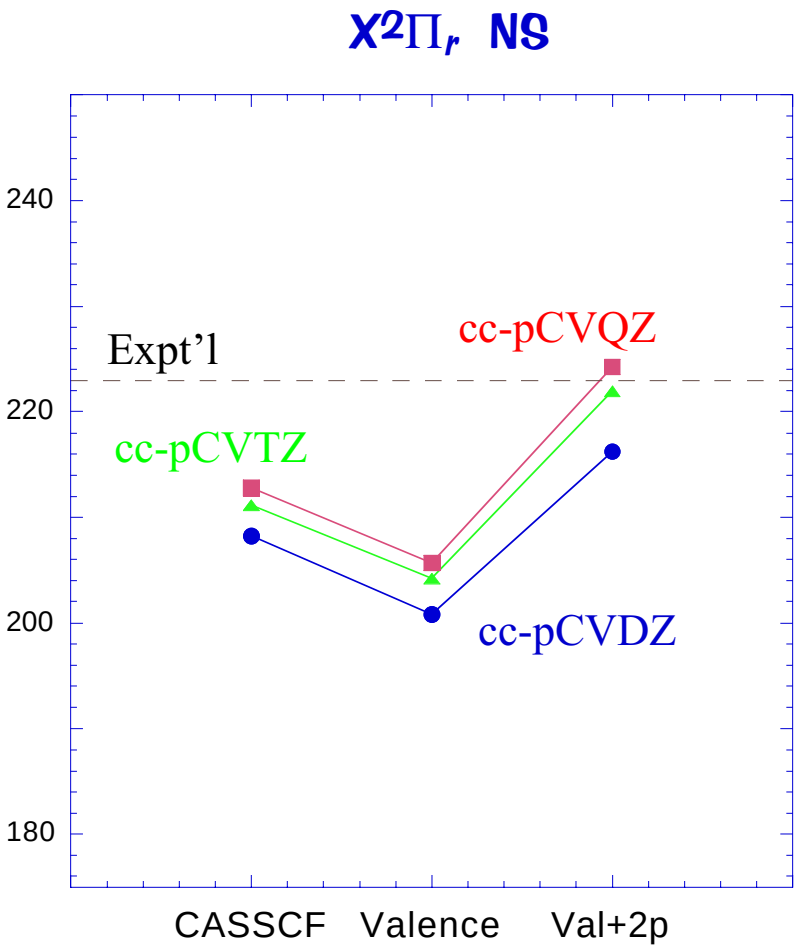
| | $\lvert 1^1A', 0,0\rangle$ | $\lvert 2^1A', 0,0\rangle$ | $\lvert 1^1A'', 0,0\rangle$ | $\lvert 1^3A', 1,1\rangle$ | $\lvert 1^3A', 1,0\rangle$ | $\lvert 1^3A', 1,-1\rangle$ | $\lvert 1^3A'', 1,1\rangle$ | $\lvert 1^3A'', 1,0\rangle$ | $\lvert 1^1A'', 1,-1\rangle$ |
|---|---|---|---|---|---|---|---|---|---|
| $\langle 1^1A', 0,0\rvert$ | $E(1^1A')$ | | | | | | | | |
| $\langle 2^1A', 0,0\rvert$ | 0 | $E(2^1A')$ | | | | | | | |
| $\langle 1^1A'', 0,0\rvert$ | 0 | 0 | $E(1^1A'')$ | | | | | | |
| $\langle 1^3A', 1,1\rvert$ | $(LS)_x$ | $(LS)_x$ | $(LS)_y$ | $E(1^3A')$ | | | | | |
| $\langle 1^3A', 1,0\rvert$ | 0 | 0 | $(LS)_z$ | 0 | $E(1^3A')$ | | | | |
| $\langle 1^3A', 1,-1\rvert$ | $(LS)_x$ | $(LS)_x$ | $(LS)_y$ | 0 | 0 | $E(1^3A')$ | | | |
| $\langle 1^3A'', 1,1\rvert$ | $(LS)_y$ | $(LS)_y$ | $(LS)_x$ | $(LS)_z$ | $(LS)_y$ | 0 | $E(1^3A'')$ | | |
| $\langle 1^3A'', 1,0\rvert$ | $(LS)_z$ | $(LS)_z$ | 0 | $(LS)_y$ | $(LS)_z$ | $(LS)_y$ | 0 | $E(1^3A'')$ | |
| $\langle 1^1A'', 1,-1\rvert$ | $(LS)_y$ | $(LS)_y$ | $(LS)_x$ | 0 | $(LS)_y$ | $(LS)_z$ | 0 | 0 | $E(1^3A'')$ |

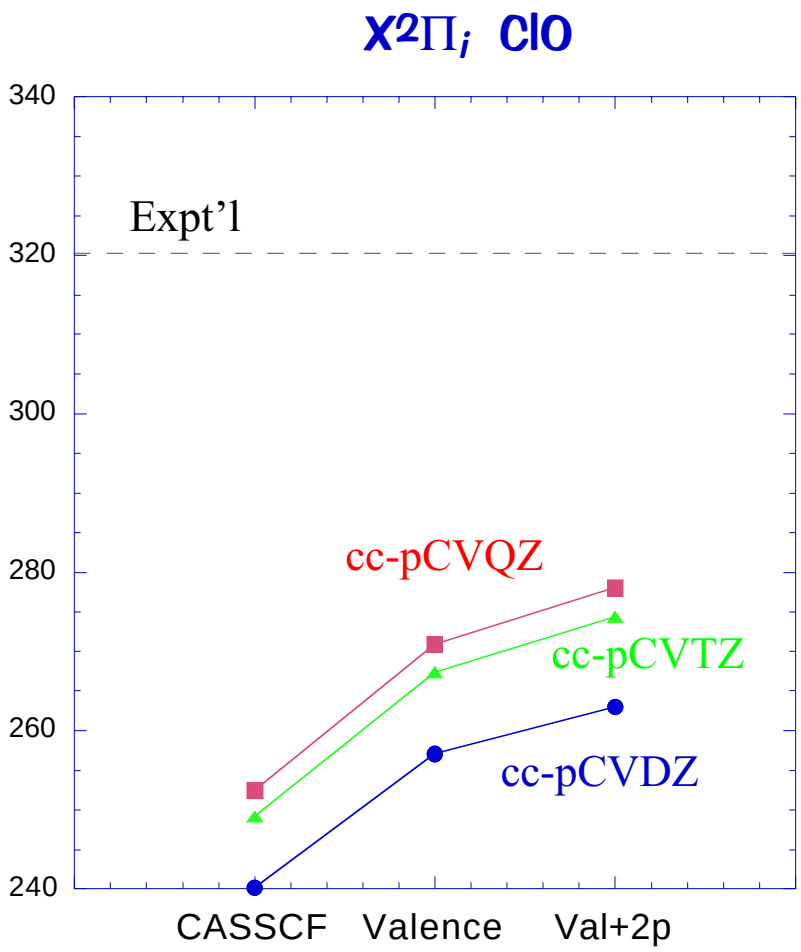
# The all-electron Breit-Pauli operator: Basis Set and Electron Correlation Effects for the Spin-Orbit Splittings of F, Cl, Br




Splittings in $cm^{-1}$ , CISD wavefunctions

# Basis Set and Electron Correlation Effects for the Spin-Orbit Splittings of Small (Light) Molecules



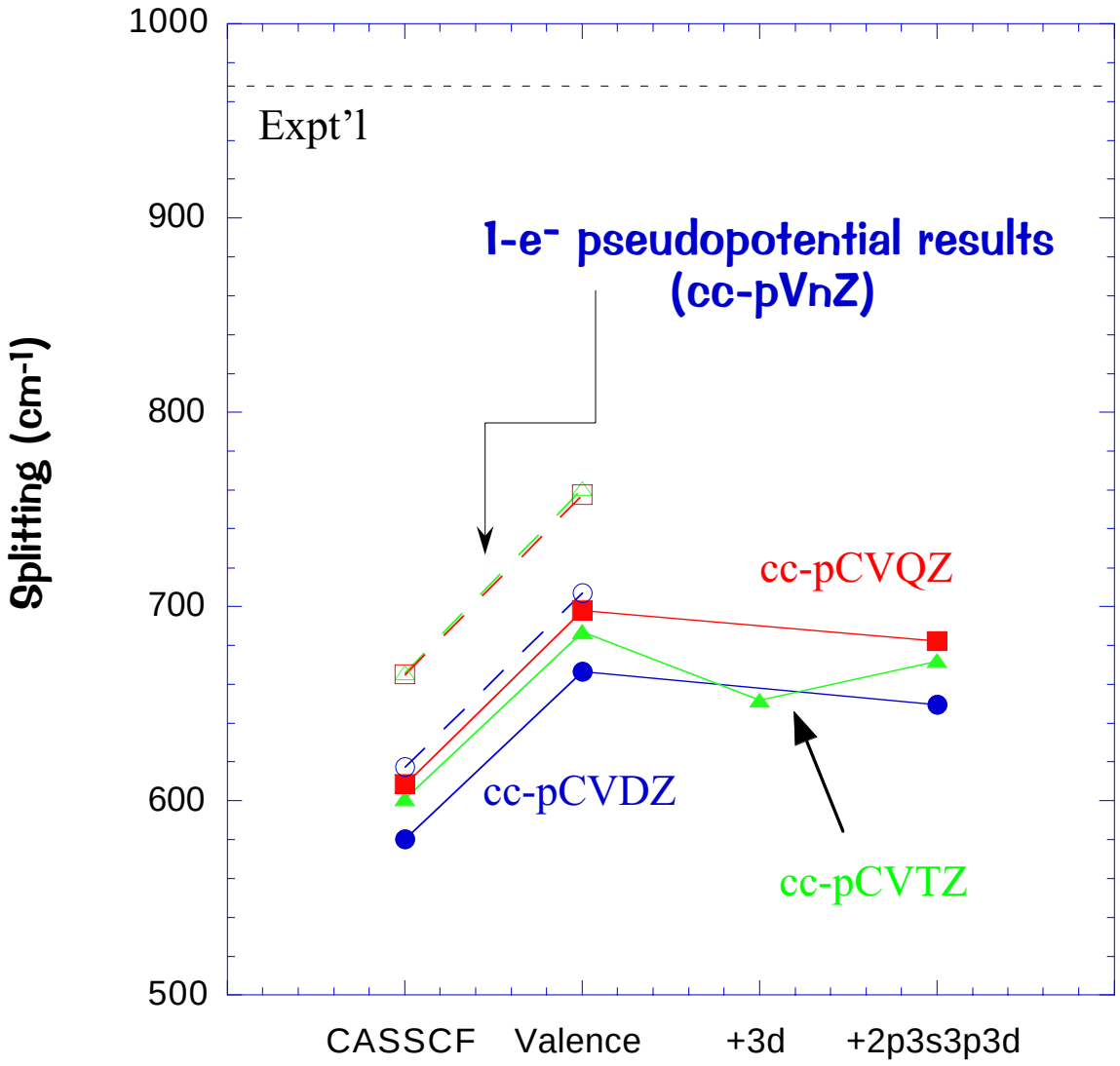

**Effects of Valence-state Spin-Orbit CI:**

+0.01 $cm^{-1}$

+10.4 $cm^{-1}$

(Splittings in $cm^{-1}$)

# All-electron Breit-Pauli vs. pseudopotentials: The X $^2\Pi$ state of BrO




**Effects of Valence-state Spin-Orbit CI:** + 60–70 cm$^{-1}$

**Atomic Br($^2$P) results:**

| | |
|---|---|
| "best" all-electron*: | 3583 cm$^{-1}$ |
| Rel. Pseudopotential: | 3670 cm$^{-1}$ |
| Expt'l: | 3685 cm$^{-1}$ |

* cc-pCV5Z, all electrons corr.

# Bromine Monoxide: low-lying valence electronic states

( >50% of all stratospheric bromine is in the form of BrO )

Previous Experimental Work:

(i) Numerous high-res. studies on the $X^2\Pi_{3/2}$ state (JPL, NOAA, Ottawa)

$\rightarrow$ equil. geom., IR freq., SO splitting, etc.

(ii) near-UV region dominated by the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ transition

emission, absorption $\rightarrow$ UV cross sections for atmospheric monitoring

- with high res.: Barnett et al. (Ottawa), Wheeler et al. (Bristol), and Wilmouth et al. (Harvard)

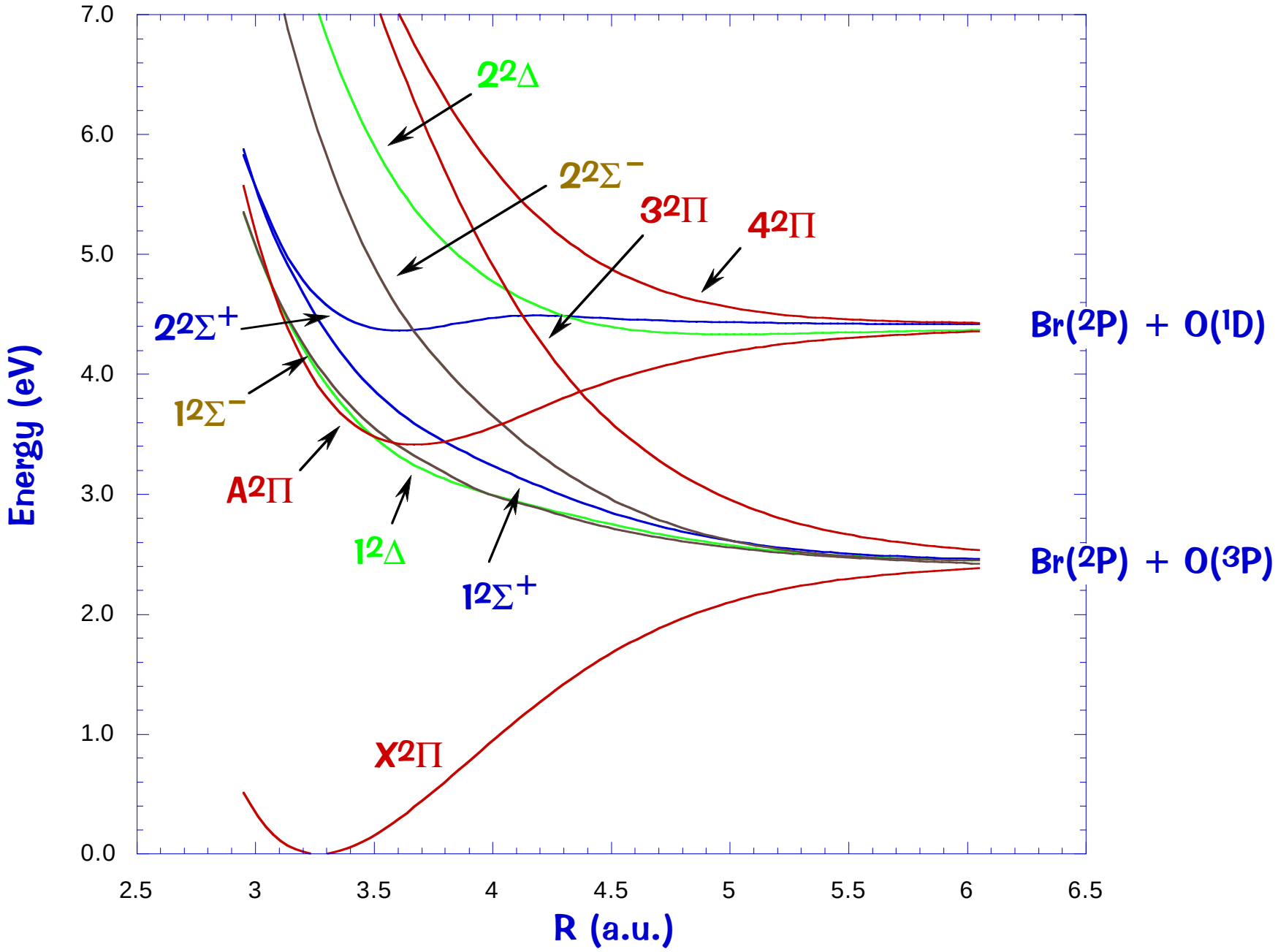
Previous Theoretical Work:

Nothing on the excited states of BrO. Recent calculations on ClO by Orr-Ewing and co-workers (Bristol) and Toniolo et al (Milan).

# Valence States of BrO

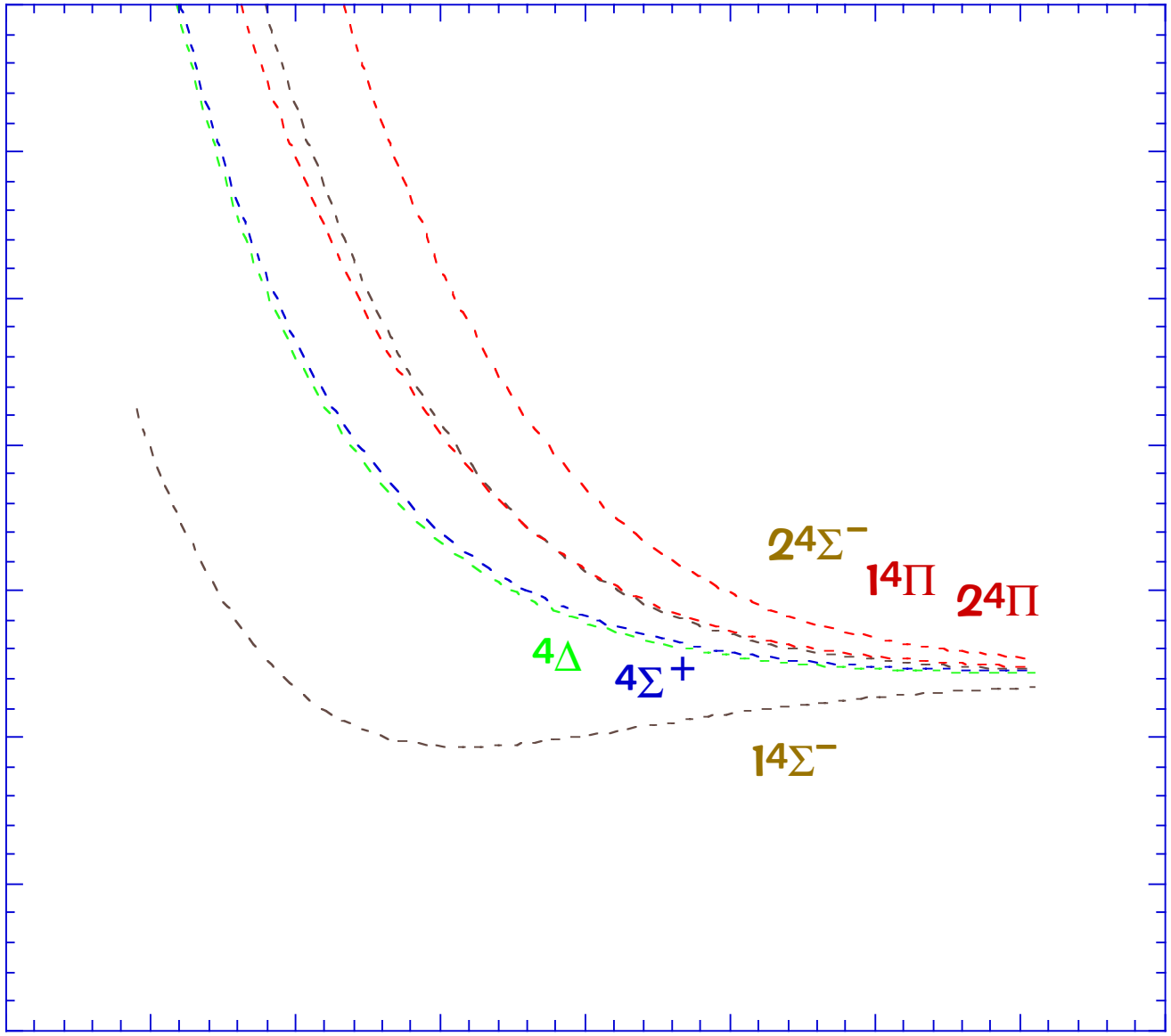
| | | Λ-S State | Ω = \|Λ+Σ\| |
|---|---|---|---|
| $Br(^2P_u) + O(^3P_g)$ | 2 x | $^2\Sigma^-$ | 1/2 |
| | 1 x | $^2\Sigma^+$ | 1/2 |
| | 2 x | $^2\Pi$ | 3/2, 1/2 |
| | 1 x | $^2\Delta$ | 5/2, 3/2 |
| | 2 x | $^4\Sigma^-$ | 3/2, 1/2 |
| | 1 x | $^4\Sigma^+$ | 3/2, 1/2 |
| | 2 x | $^4\Pi$ | 5/2, 3/2, 1/2, 1/2 |
| | 1 x | $^4\Delta$ | 7/2, 5/2, 3/2, 1/2 |
| | | | (27 total) |
| $Br(^2P_u) + O(^1D_g)$ | 1 x | $^2\Sigma^-$ | 1/2 |
| | 2 x | $^2\Sigma^+$ | 1/2 |
| | 3 x | $^2\Pi$ | 3/2, 1/2 |
| | 2 x | $^2\Delta$ | 5/2, 3/2 |
| | 1 x | $^2\Phi$ | 7/2, 5/2 |
| | | | (42 total) |

# The Doublet States (Λ-S) of BrO

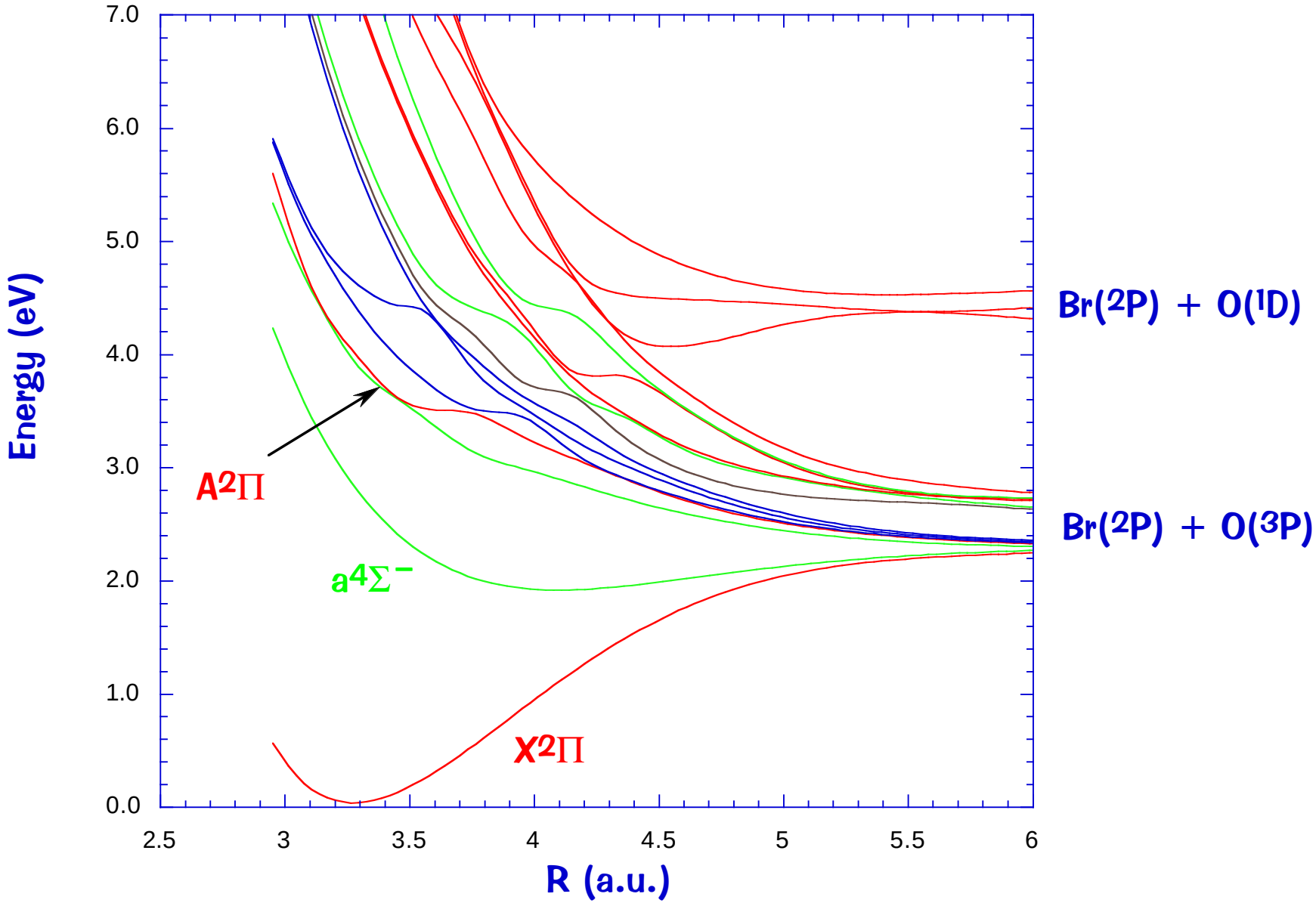



(obtained via MRCI+Q/aug-cc-pVQZ calculations)

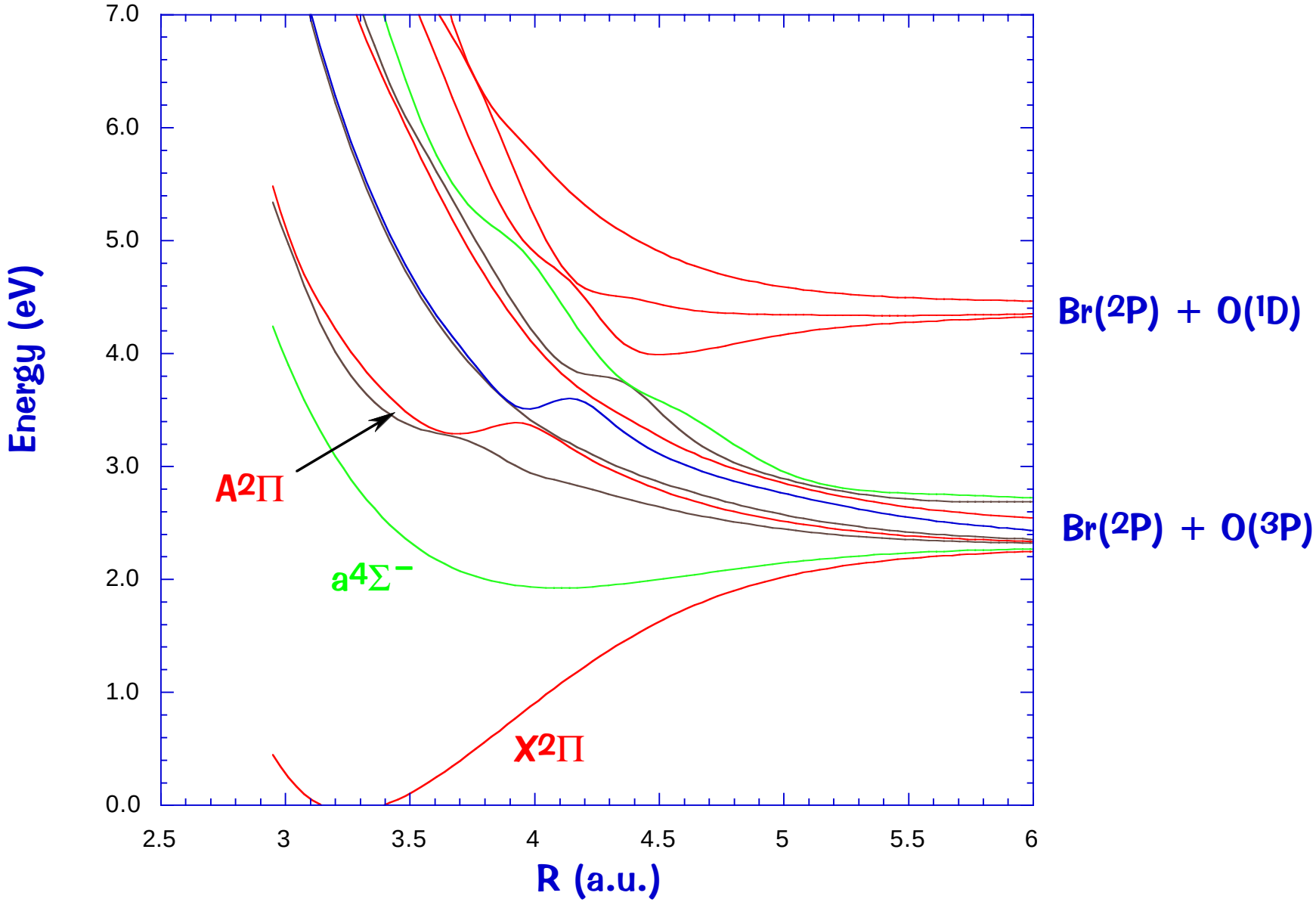
# + Quartet States



# Ω=1/2 States [ Case (c) coupling throughout ]



# Ω=3/2 States [ Case (c) coupling throughout ]



# Spectroscopic Constants of the X $^2\Pi_{3/2}$ and A $^2\Pi_{3/2}$ states

| | $T_e$ (eV) | $r_e$ (Å) | $\omega_e$ ($cm^{-1}$) | $\omega_e x_e$ ($cm^{-1}$) |
|---|---|---|---|---|
| $X^2\Pi$ | 0 | 1.726 | 729 | 4.9 |
| $X^2\Pi_{3/2}$ | 0 | 1.724<br>(1.717) | 734<br>(733) | 4.9 |
| $\Delta$(1/2–3/2) | 848 $cm^{-1}$<br>(968) | +0.007<br>(+0.007) | –13.0<br>(-15) | +0.2 |
| $A^2\Pi$ | 3.42 | 1.941 | 533 | 5.6 |
| $A^2\Pi_{3/2}$ | 3.28<br>(3.27) | | | |

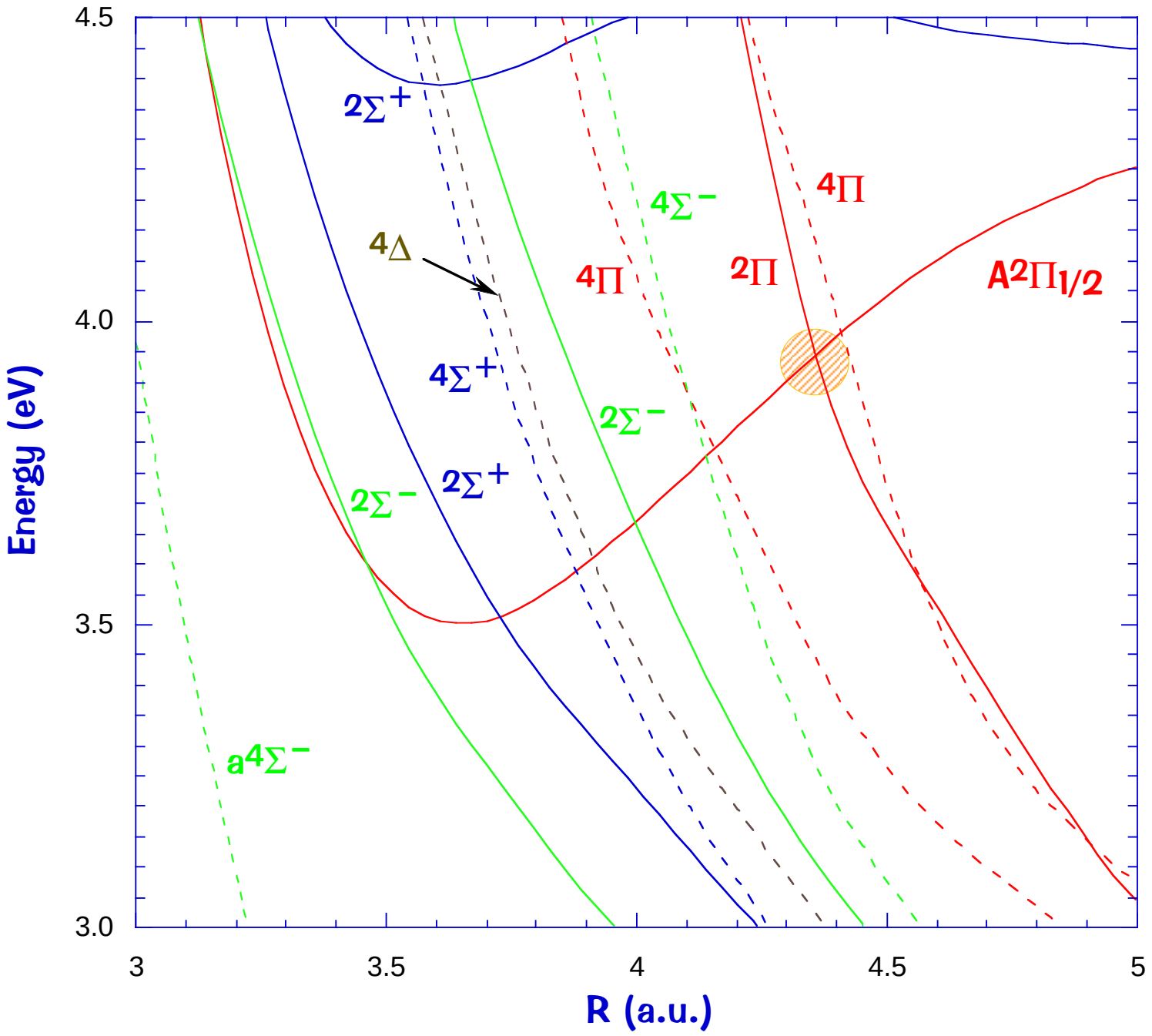
All values at the MRCI+Q/aug-cc-pV5Z level of theory

# Predissociation of the BrO $A^2\Pi_{3/2}$ State

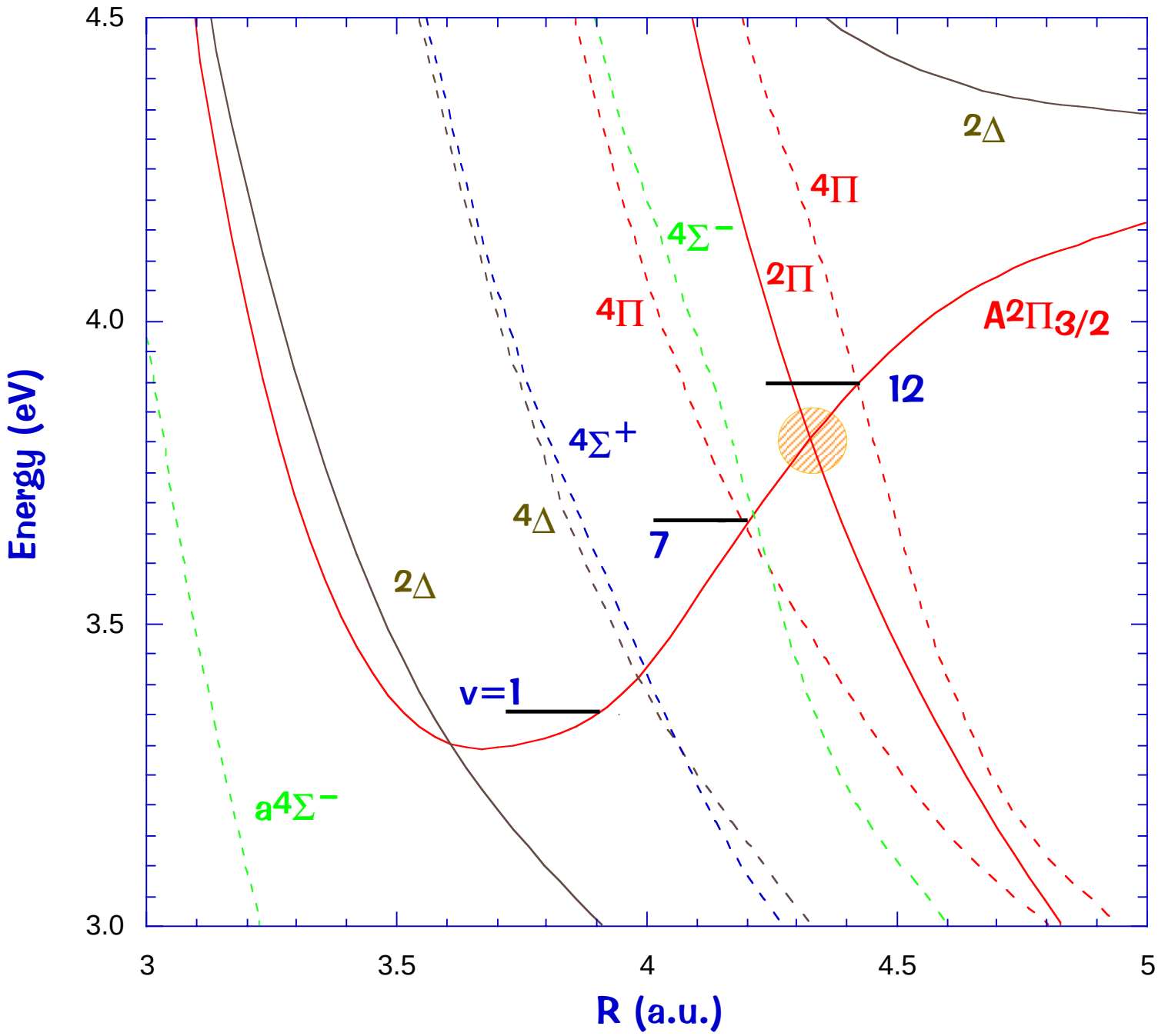
The 3 high resolution studies performed to date indicate that:

- The only bands showing rotational structure are the v',v''=7,0 & 12,0 and perhaps higher v',0
- Bands with v'=0 & 1 are very diffuse; v'=1 is strongly perturbed
- With increasing J, the 7,0 band tunes towards a crossing while the 12,0 band first tunes away and then into another crossing (linewidth minimum at 3.887 eV) ;
  12,0 has a slightly shorter lifetime than the 7,0 (2 vs. 2.5 ps)
- $D_0(A) = 1.107 \pm 0.017$ eV ; $D_0(X) = 2.394 \pm 0.017$ eV (Wilmouth et al.)

# The $A^2\Pi_{1/2}$ State with possible $\Omega=1/2$ perturbers



# The $A^2\Pi_{3/2}$ State with possible $\Omega=3/2$ perturbers



# Interaction of the $A^2\Pi$ and $3^2\Pi$ states: a weakly avoided crossing

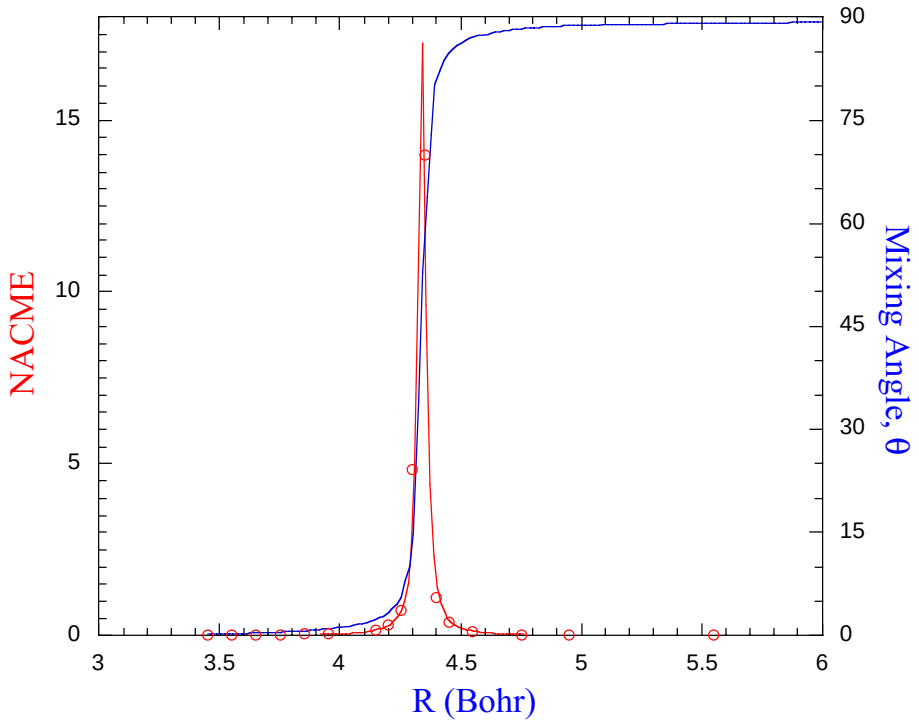
- non-adiabatic coupling matrix elements (NACMEs) were calculated as a function of $R$ by numerical differentiation of the MRCI wavefunctions with an aug-cc-pV5Z basis set

- These were integrated to yield the mixing angles $\theta(R)$, i.e., the transformation between the adiabatic and diabatic basis.

$$\begin{pmatrix} \Psi_1^d \\ \Psi_2^d \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \Psi_1^{ad} \\ \Psi_2^{ad} \end{pmatrix}$$

$$\frac{\partial\theta}{\partial R} = \left\langle \Psi_2^{ad} \left| \frac{\partial}{\partial R} \right| \Psi_1^{ad} \right\rangle$$

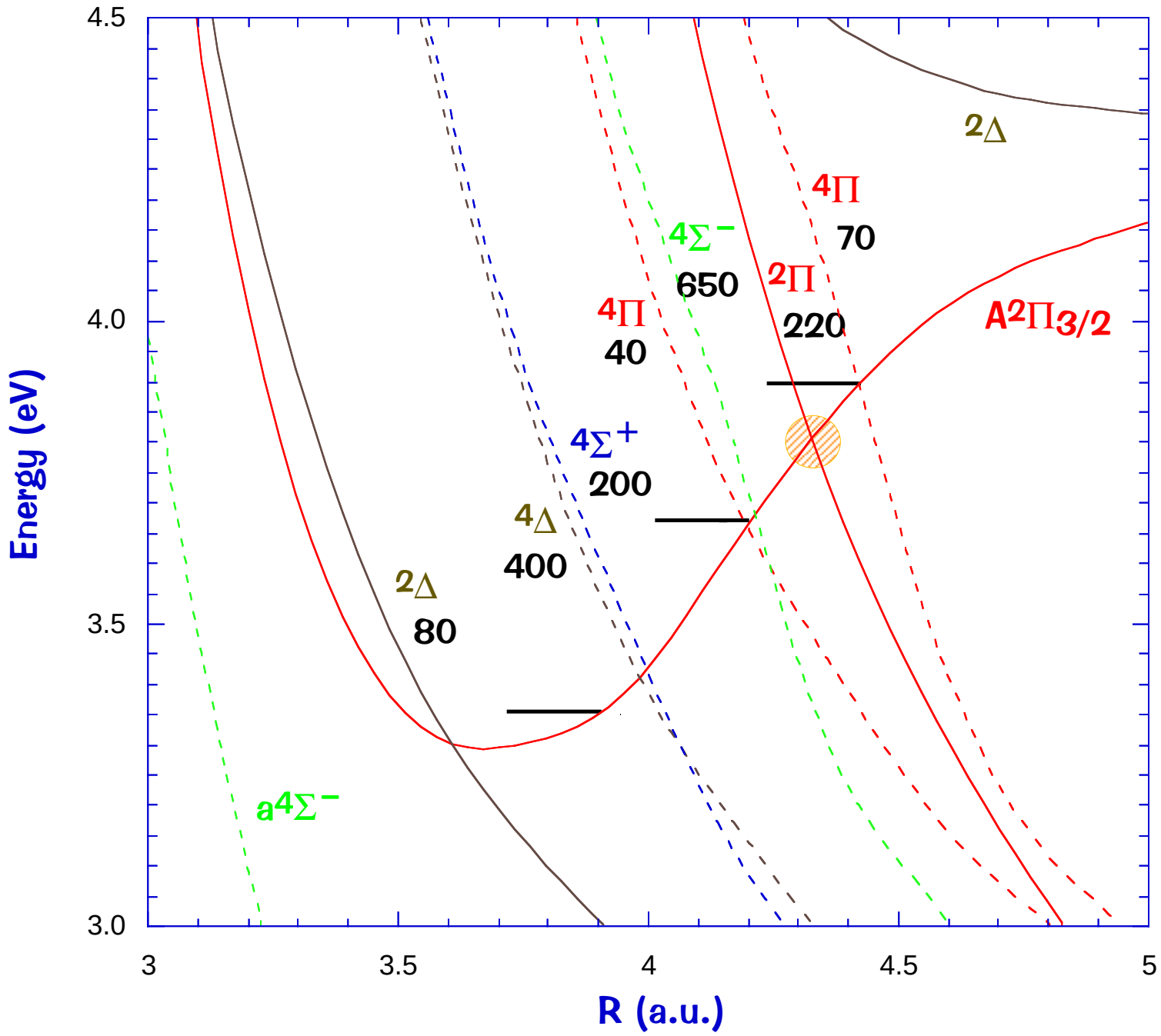
$$\theta(R) = \theta_{R_0} + \int_{R_0}^{R} \left\langle \Psi_2^{ad} \left| \frac{\partial}{\partial R'} \right| \Psi_1^{ad} \right\rangle dR'$$




**At the crossing (r=4.34 bohr) θ=52°**

**and $H_{12}^{(d)} = \cos\theta \sin\theta\, [E(3^2\Pi) - E(A^2\Pi)] = 200\ cm^{-1}$**

# The $A^2\Pi_{3/2}$ State with possible $\Omega=3/2$ perturbers & coupling ME's



# The Low-Lying Electronic States of BrCl: preliminary results

3-4 excited electronic states are involved in the UV and near-UV spectrum

– the $A^3\Pi(1)$, $B^3\Pi(0^+)$, $C^1\Pi(1)$ & $D(0^+)$ states (~550 - 235 nm)

Several non-adiabatic interactions have been observed

Recent Experimental Work

Cao et al. (1994)

Cooper et al. (1998)

Park et al. (2000)

At $\lambda$~235 nm: $D(0^+)$ absorption

3 product channels observed:

$Br^* + Cl$ (0.6), $Br + Cl^*$ (0.2), $Br + Cl$ (.2)

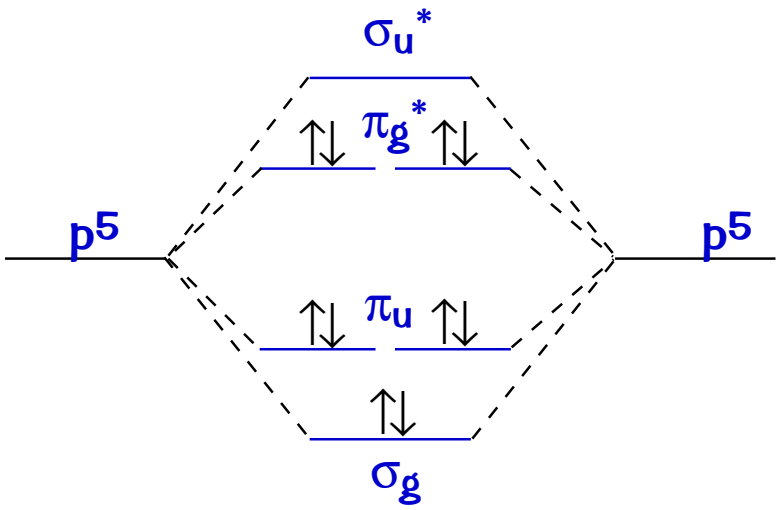
(∥) (⊥) (∥)

$\lambda$~310-410 nm: $C^1\Pi(1)$ absorption; Br+Cl formed

$\lambda$>410 nm: absorption via $B^3\Pi(0^+)$ with a ⊥ contribution; Cl*/Cl branching ratio increases

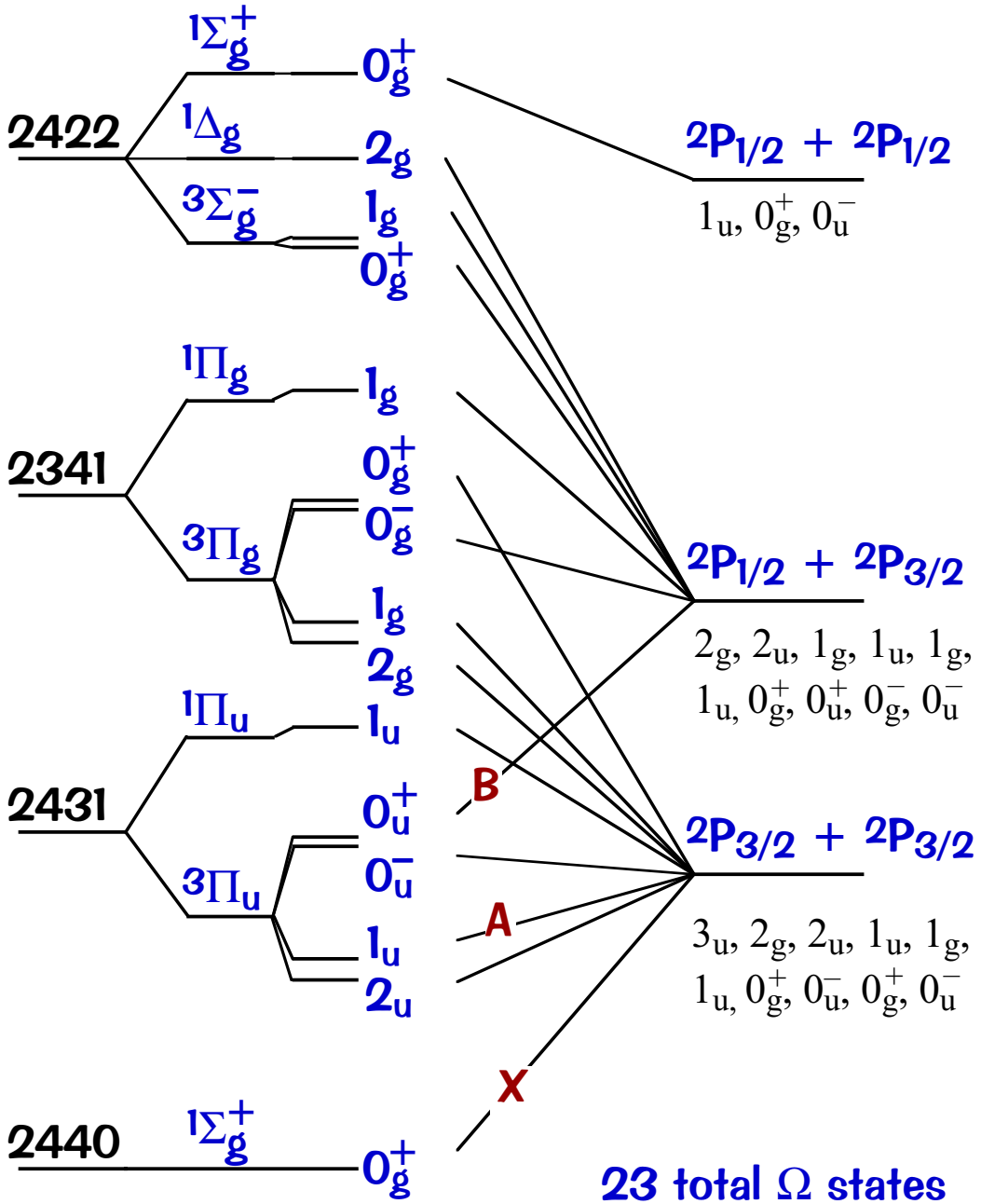
# Expected Low-Lying Electronic States of BrCl

## For the Homonuclear Halogens, e.g., $Br_2$:




2440 $X^1\Sigma_g^+$

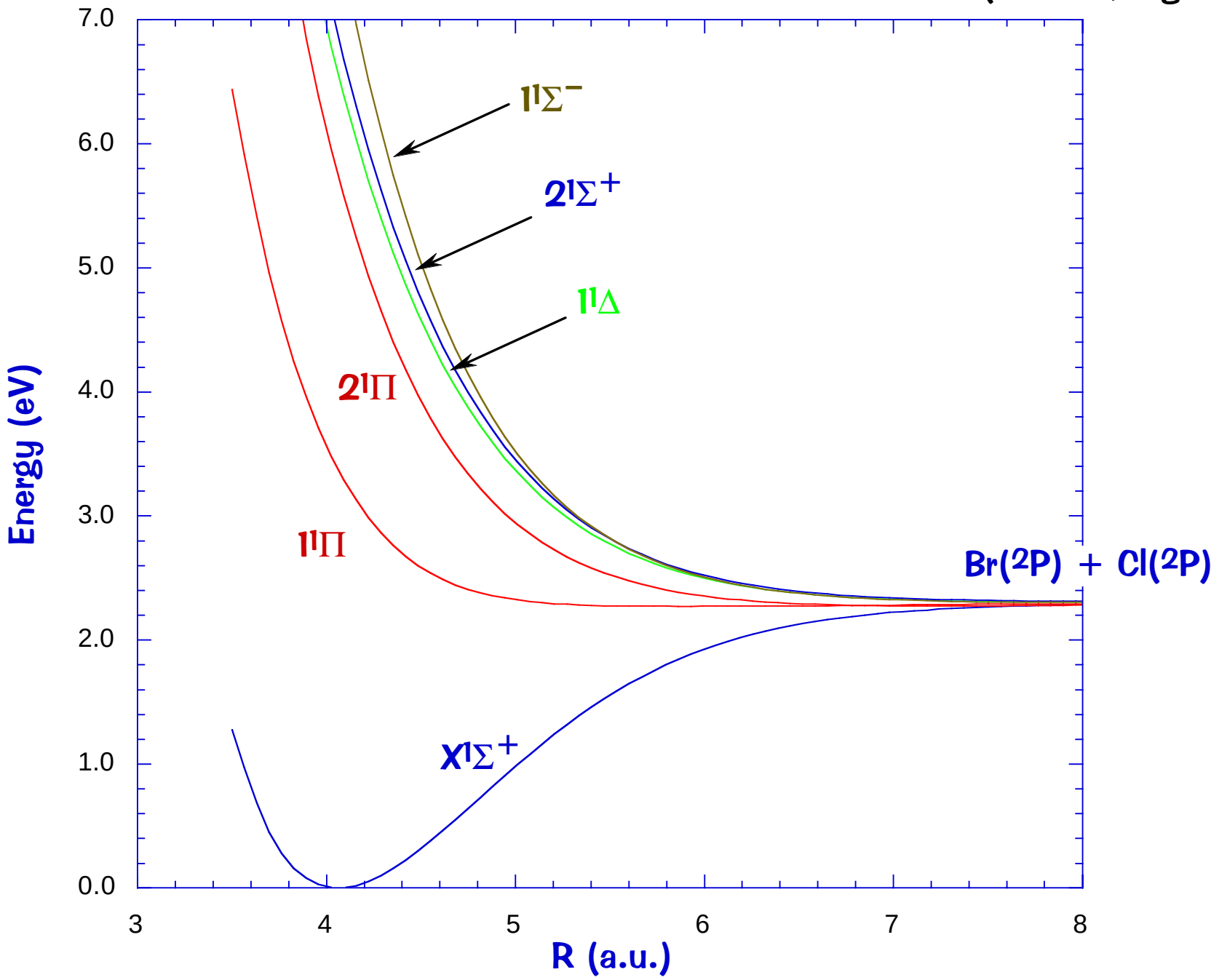
Mulliken label



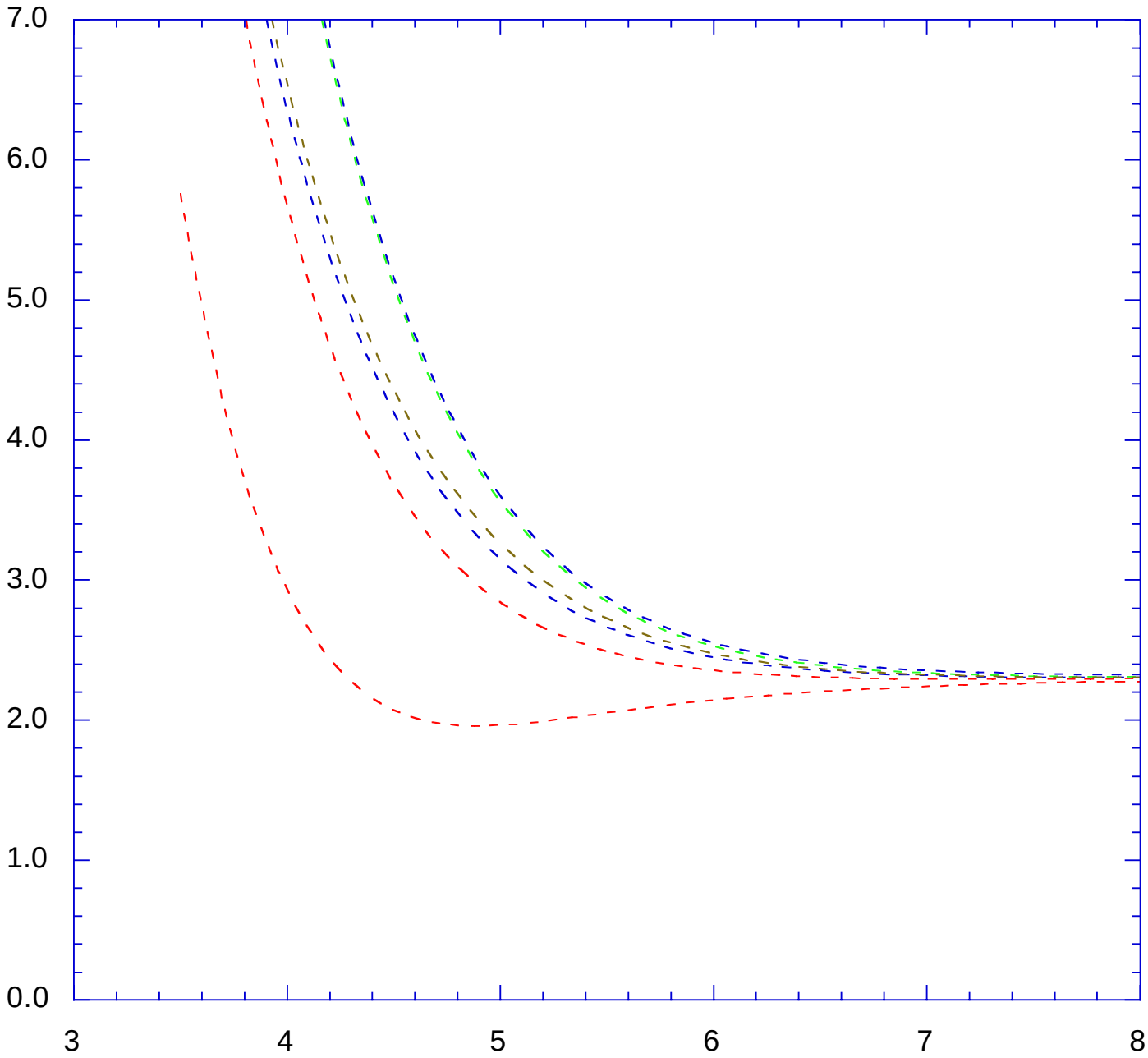

23 total Ω states

# The Singlet States (Λ-S) of BrCl

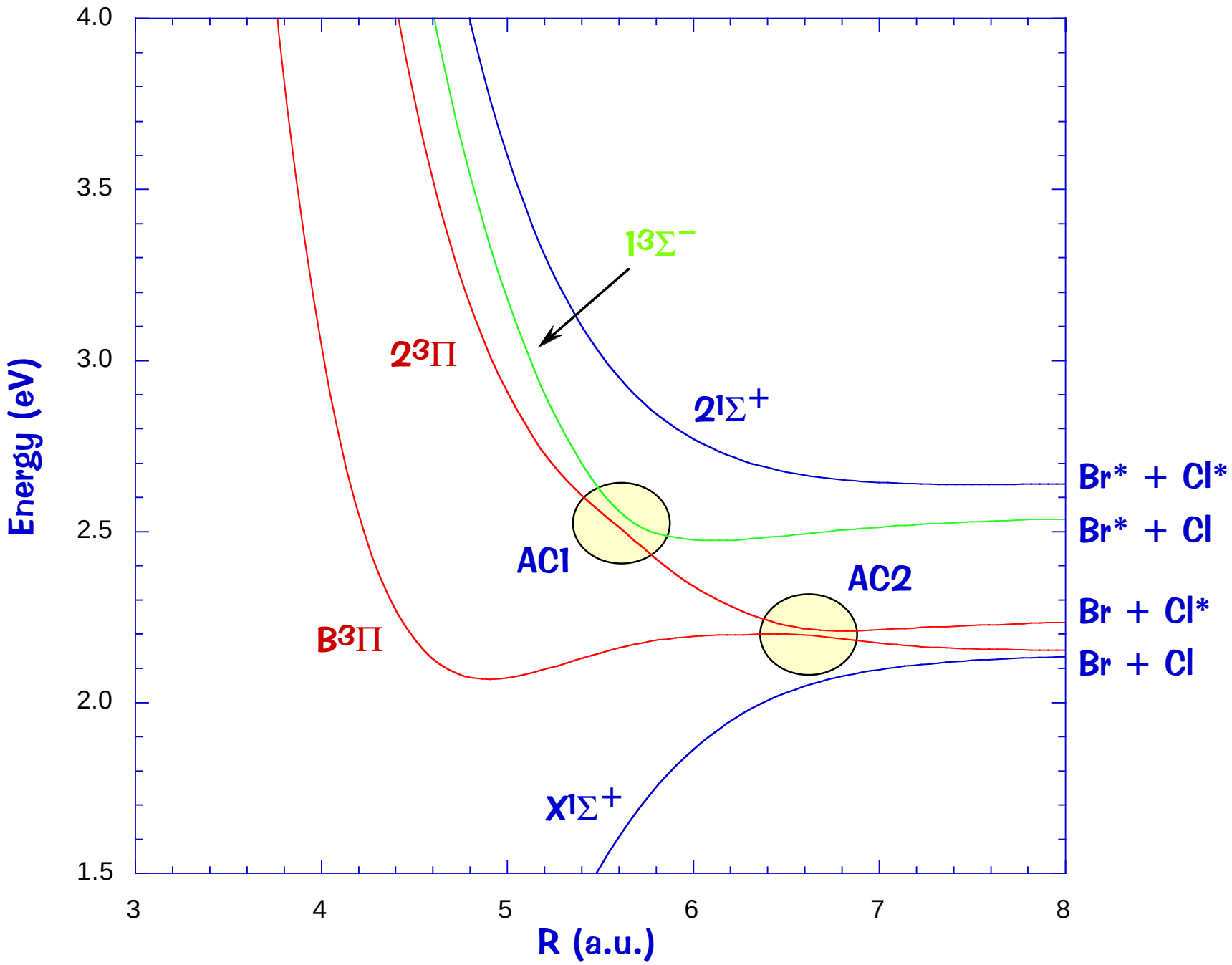
(MRCI+Q/aug-cc-pVQZ)



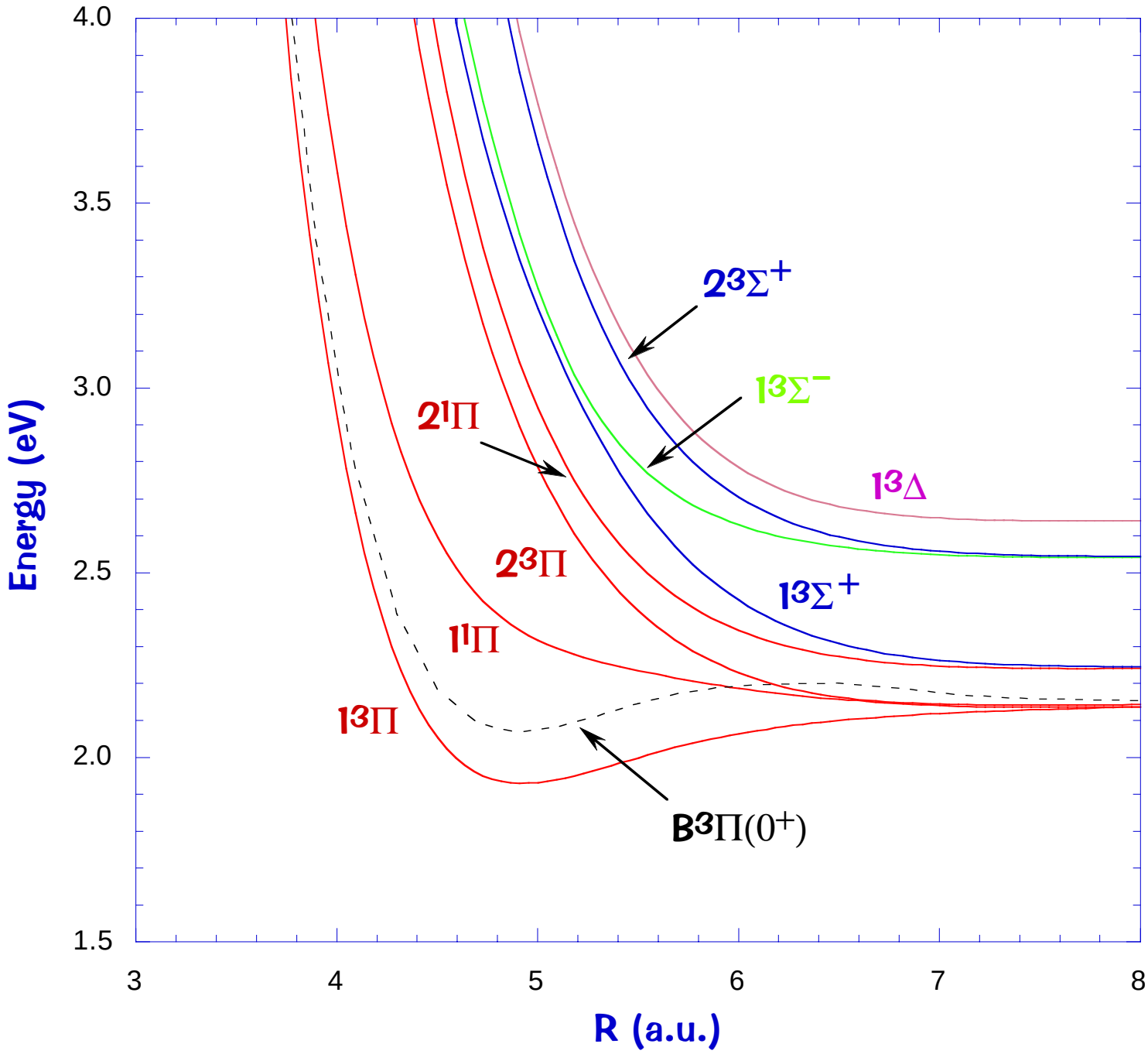
# Triplet States



# The Ω=0+ states of BrCl



# The Ω=1 states of BrCl



## Near $R_e$ the $1^3\Pi$ state has large SO matrix elements with low-lying singlets:

$\langle 1^3\Pi \mid H_{SO} \mid X^1\Sigma^+ \rangle = 601\ cm^{-1}$

$\langle 1^3\Pi \mid H_{SO} \mid 1^1\Pi \rangle = 937\ cm^{-1}$

$\langle 1^3\Pi \mid H_{SO} \mid 2^1\Pi \rangle = 453\ cm^{-1}$

$\langle 1^3\Pi \mid H_{SO} \mid 2^1\Sigma^+ \rangle = 371\ cm^{-1}$

$\langle X^1\Sigma^+ \mid \mu \mid 1^3\Sigma^-(0^+) \rangle = 0.017$ Debye

$\langle X^1\Sigma^+ \mid \mu \mid A^3\Pi(1) \rangle = 0.024$ Debye

$\langle X^1\Sigma^+ \mid \mu \mid B^3\Pi(0^+) \rangle = 0.071$ Debye

$\langle X^1\Sigma^+ \mid \mu \mid C^1\Pi(1) \rangle = 0.148$ Debye

## At AC2 the composition of the two $0^+$ states are:

II $0^+$ : 62% $1^3\Sigma^-$ 1% $1^3\Pi$ 32% $2^1\Sigma^+$ 2% $2^3\Pi$

III $0^+$ : 54% $1^3\Pi$ 2% $1^3\Sigma^-$ 27% $2^1\Sigma^+$ 16% $2^3\Pi$

# Hypobromous Acid (HOBr)

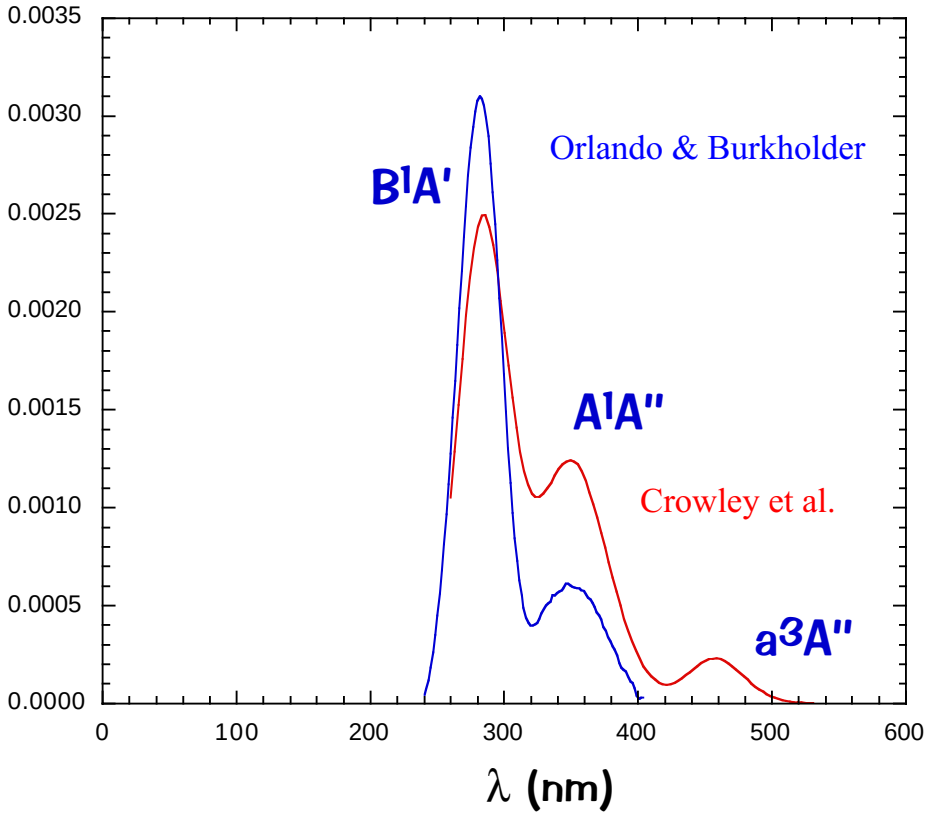
## UV/Vis Absorption Spectrum and Photodissociation Dynamics

Important contributor to both homogeneous and heterogeneous removal processes of stratospheric ozone

- Several studies of UV-Vis absorption X-sections
- First observation of the lowest triplet state of HOBr by Sinha and co-workers
- Photodissociation study of OH+Br (product distributions, vector correlation, etc.) by Sinha and co-workers at ~500 nm

$a^3A''$ state borrows intensity from $B^1A'$

Dissociation is rapid →



## *HOBr Computational Details*

Correlation treatment : full valence CAS-reference multireference CI with Davidson correction

- 246 reference configurations, all single and double excitations wrt to these
- Davidson correction added for approximate treatment of higher excitations
- Calculate a total of 5 electronic states: $X^1A'$, $a^3A''$, $B^1A''$, $b^3A'$, and $A^1A'$
- Relativistic effective core potential on Br

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Basis set(s) : series of 3 correlation consistent basis sets:

cc-pVDZ + diffuse + *spd/sp* : 54 contracted functions

cc-pVTZ + diffuse + *spd/sp* : 95 contracted functions

cc-pVQZ + diffuse + *spd/sp* : 161 contracted functions (~2 hrs CPU per point)

!! pointwise extrapolate to complete basis set (CBS) limit

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Grid: ~1000 points calculated with each of the 3 basis sets (~3000 calculations)

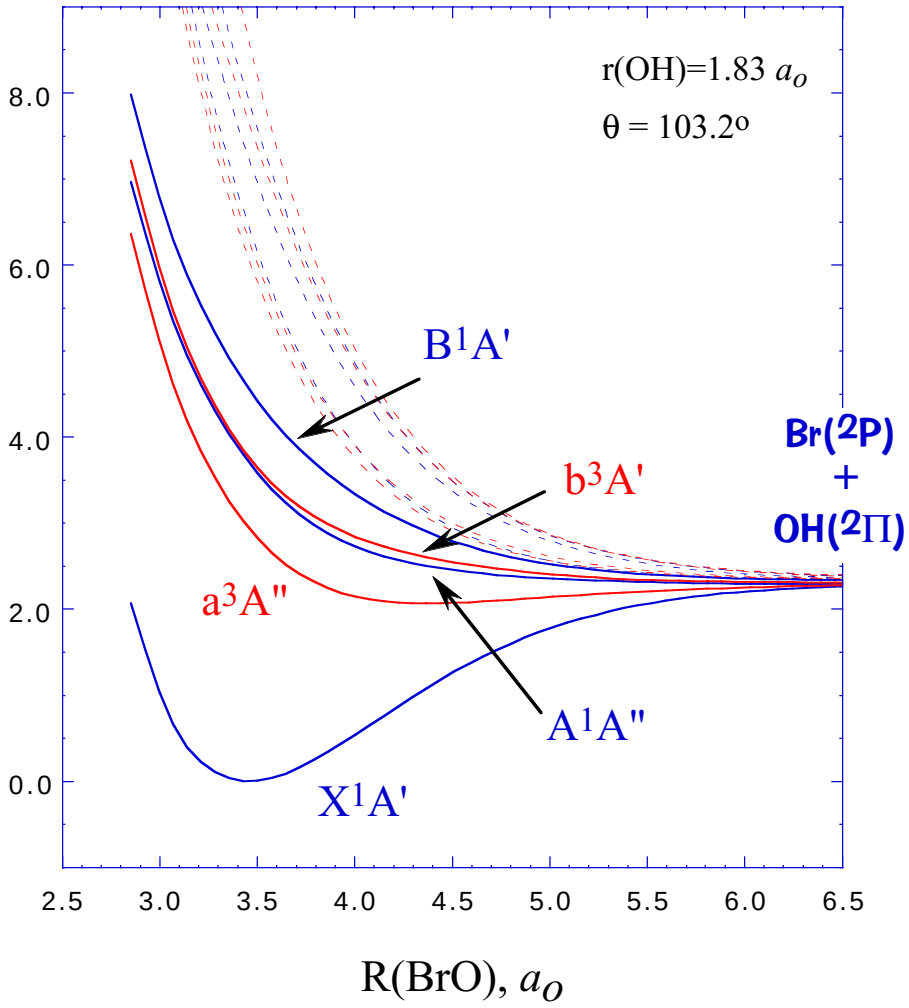
$R_{OH}$ ($a_o$) = 1.4 – 3.0; $R_{BrO}$ ($a_o$) = 2.6 – 10.0; $\theta_{HOBr}$ = 0 – 180°

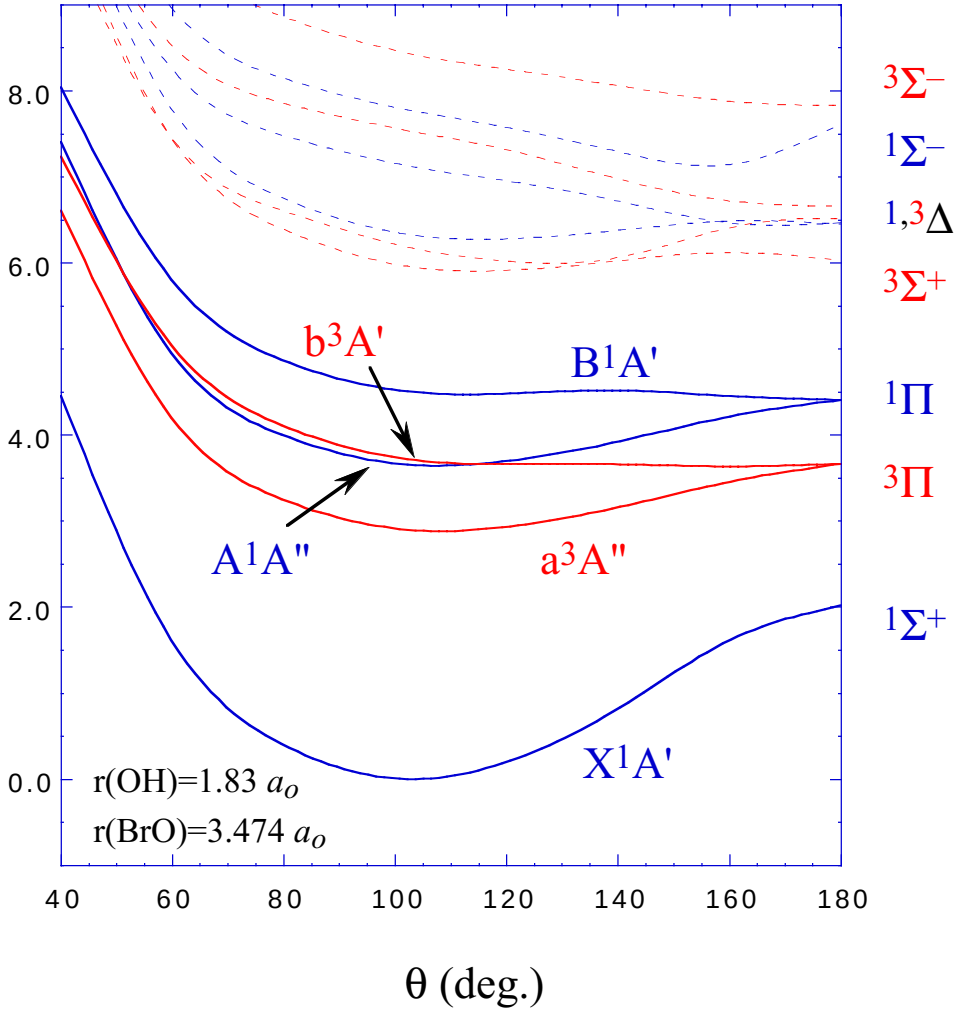
+ near-equilibrium data for HOBr, HBrO, and the HOBr → HBrO TS

+ additional $R_{OH}$ for $\theta \leq 80°$

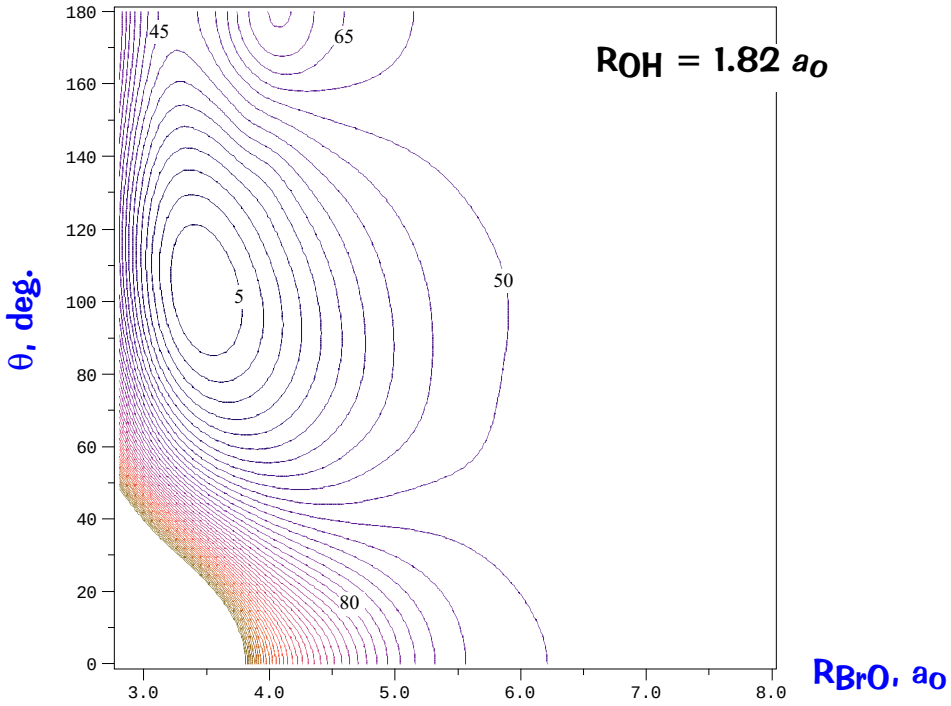
# The low-lying excited states of HOBr (Λ-S states)

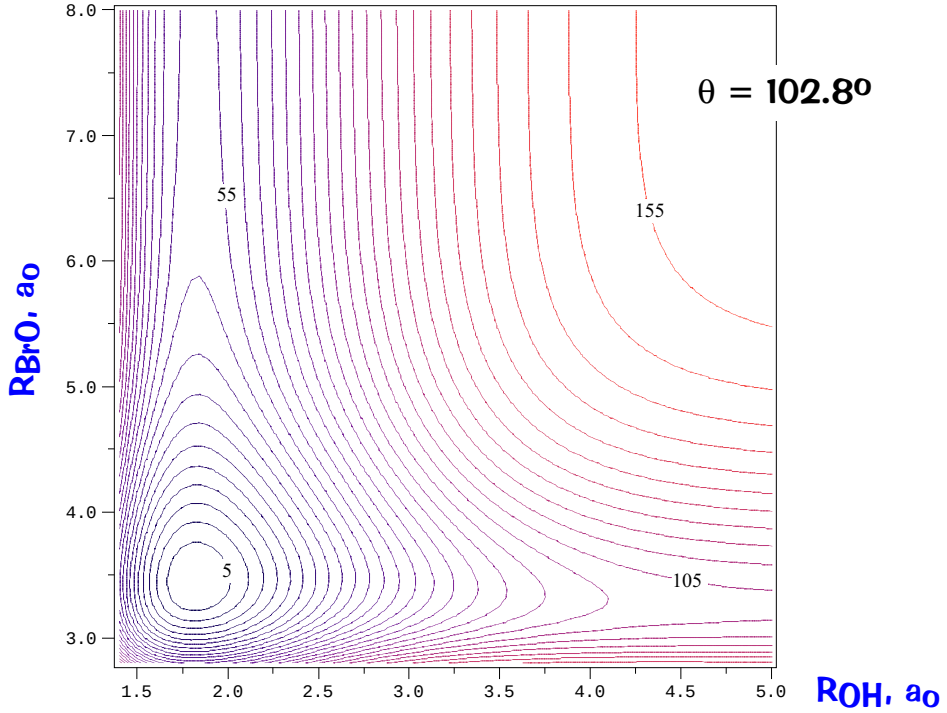
(MRCI+Q/CBS, energies in eV)

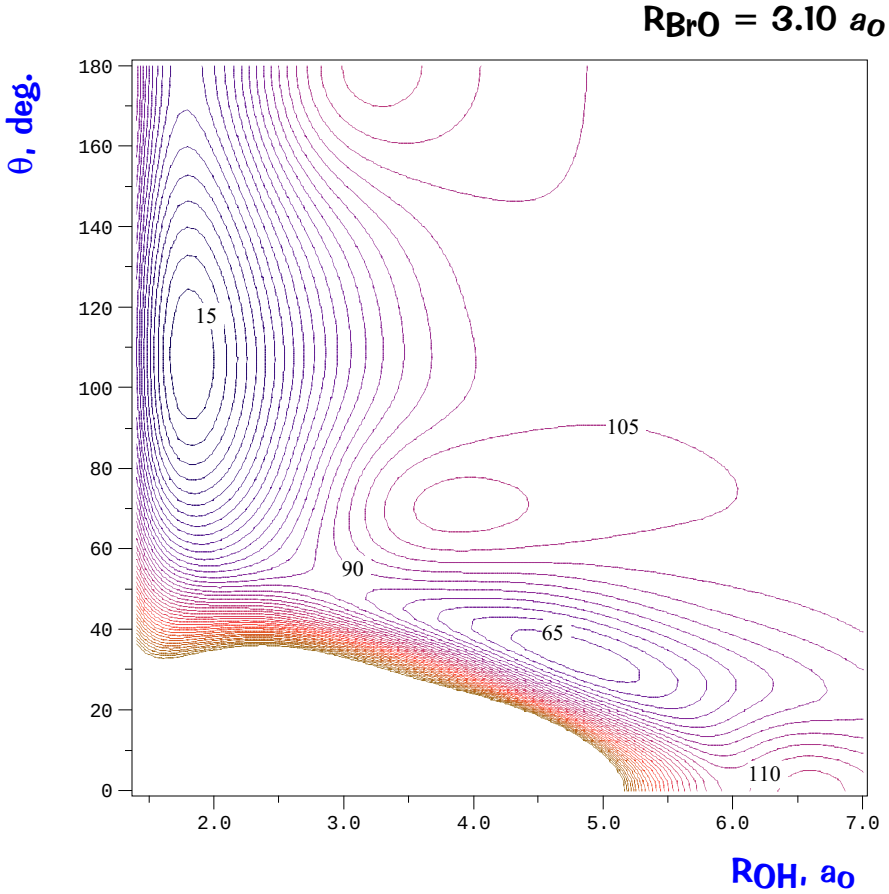


# The X¹A′ state of HOBr

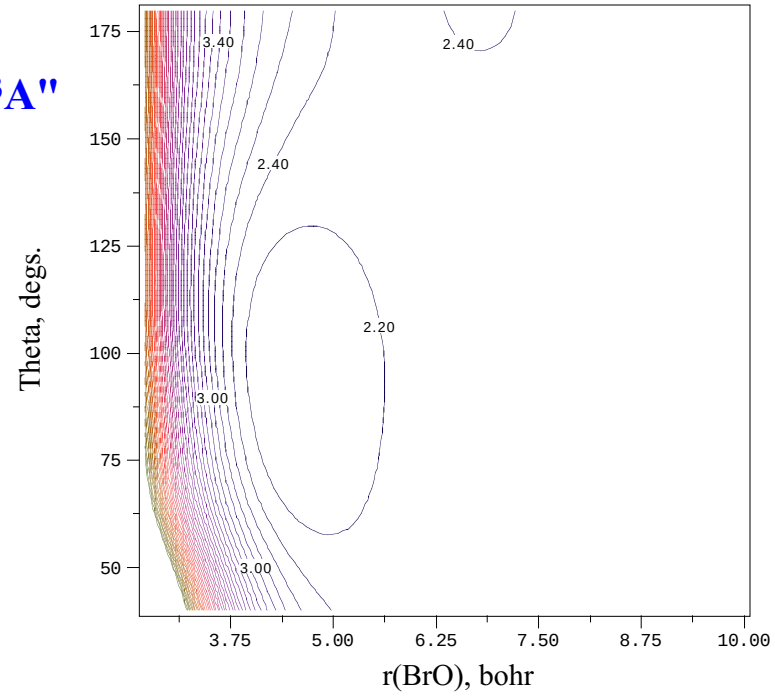


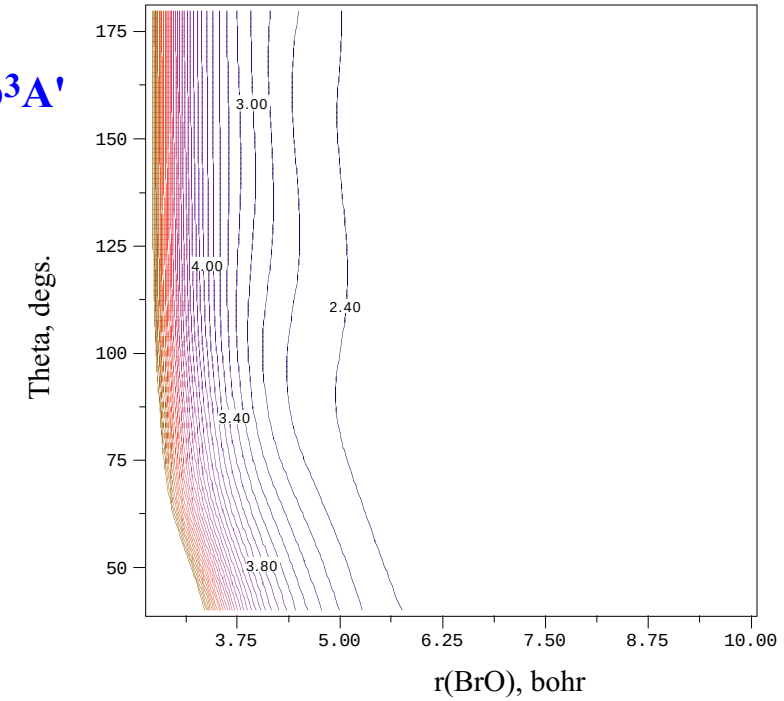




**HOBr: 708 bound states**
**HBrO: 74 localized states**

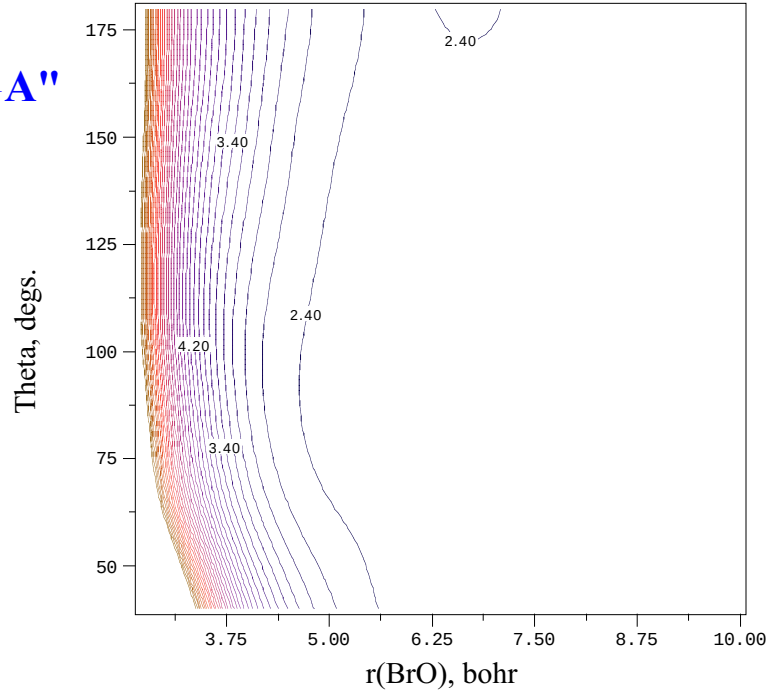
**$a^3A''$**



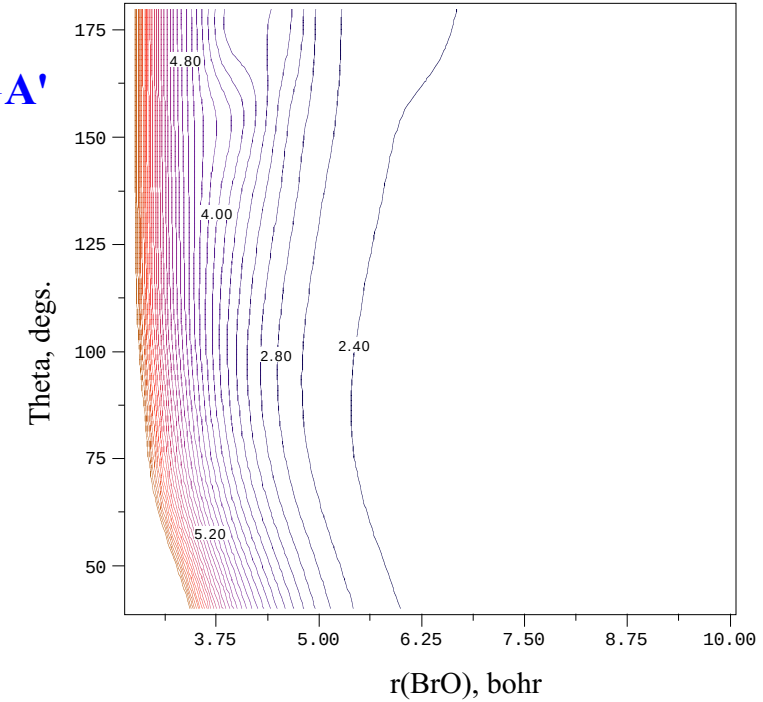

**$b^3A'$**



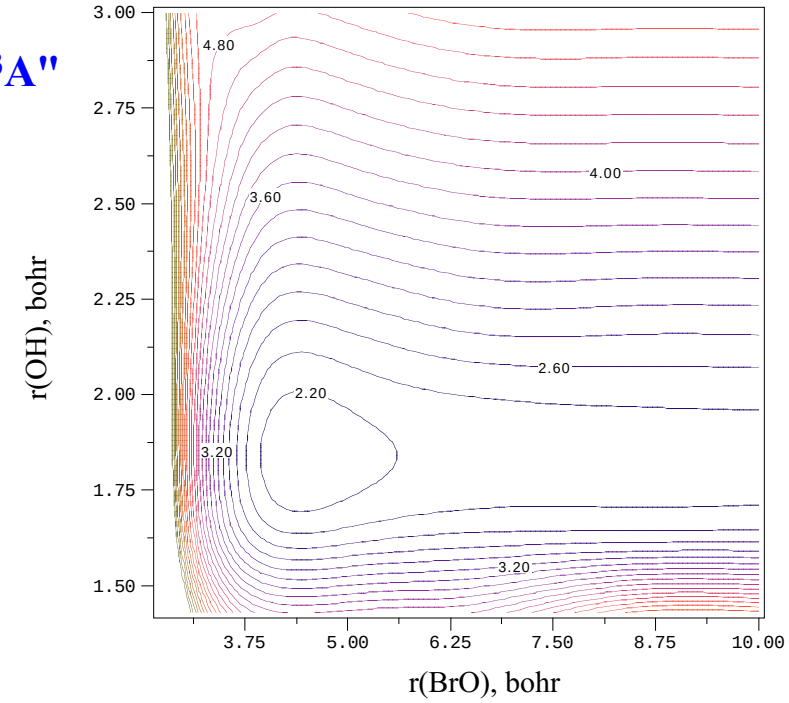

**$A^1A''$**



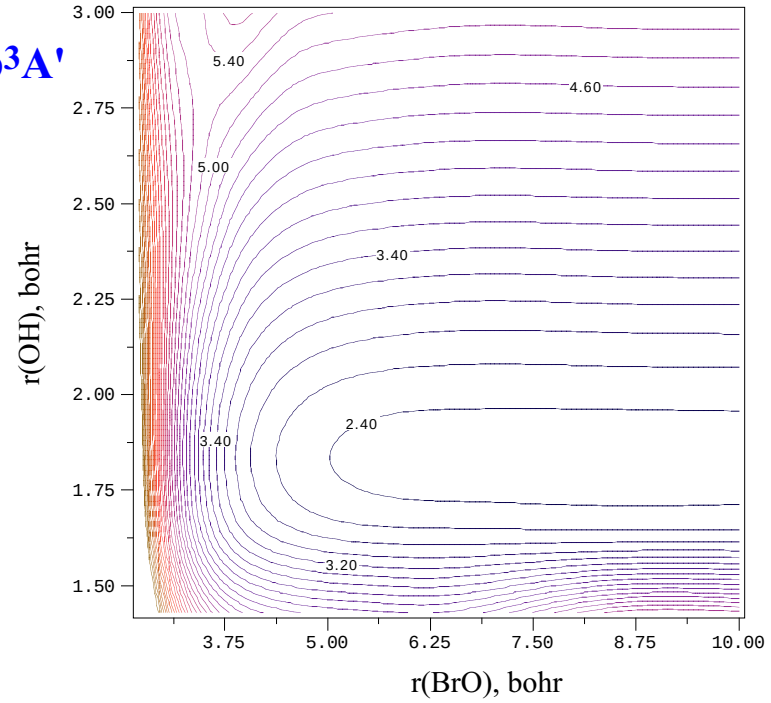

**$B^1A'$**



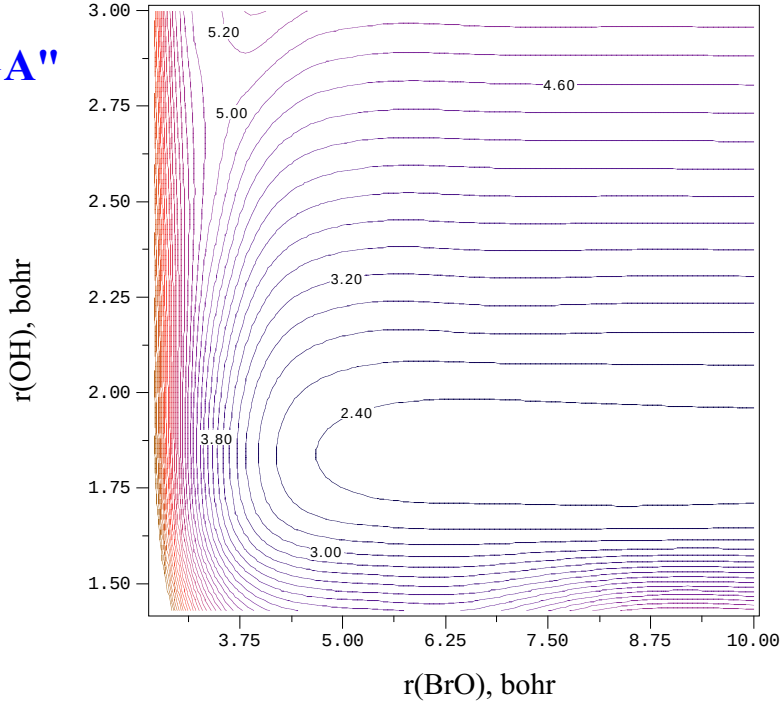
**$a^3A''$**



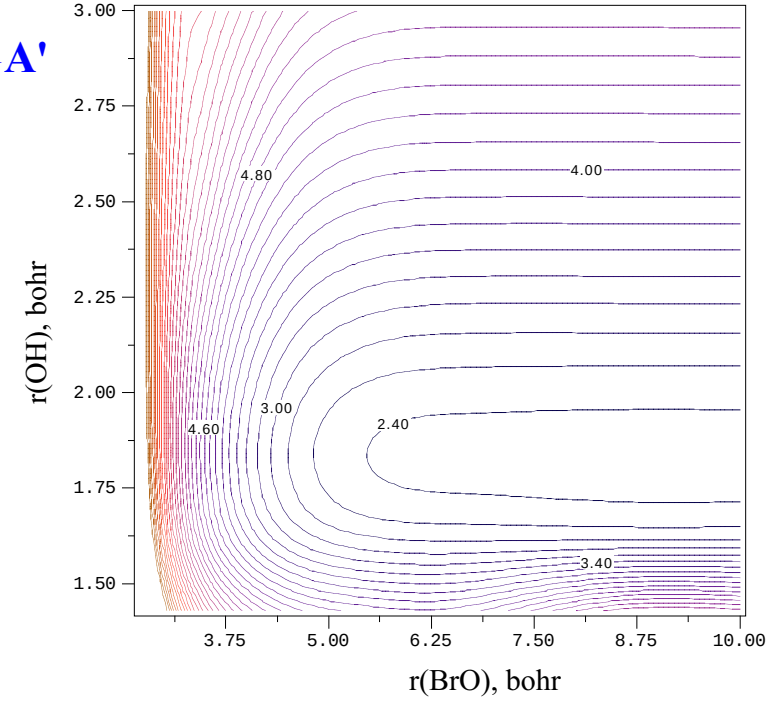

**$b^3A'$**




**$A^1A''$**



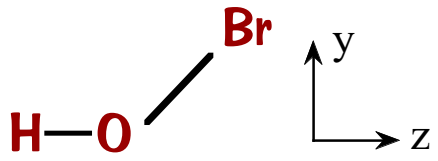

**$B^1A'$**



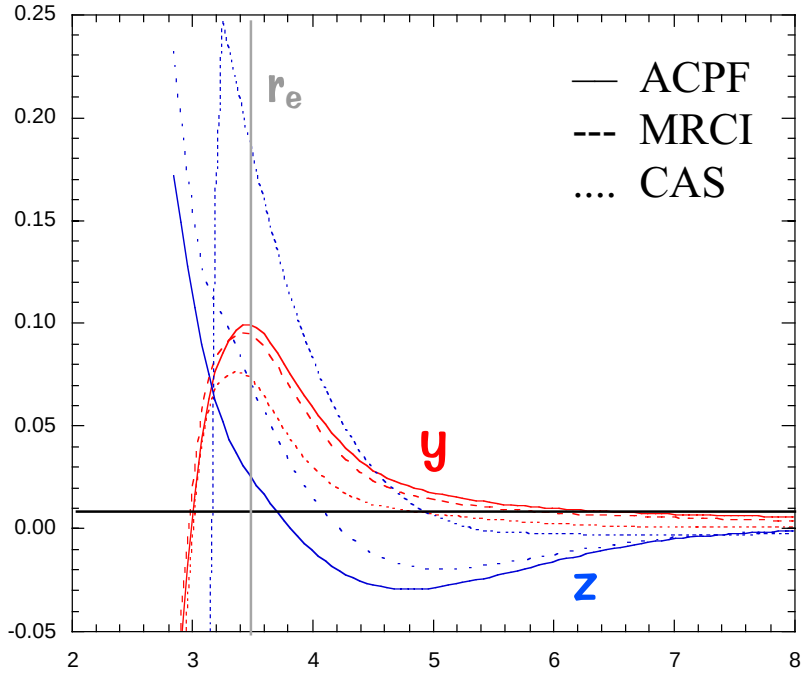
# Transition dipole moments

## The oscillator strengths for both the singlet-singlet and singlet-triplet transitions are governed at least in part by the transition dipole moment functions

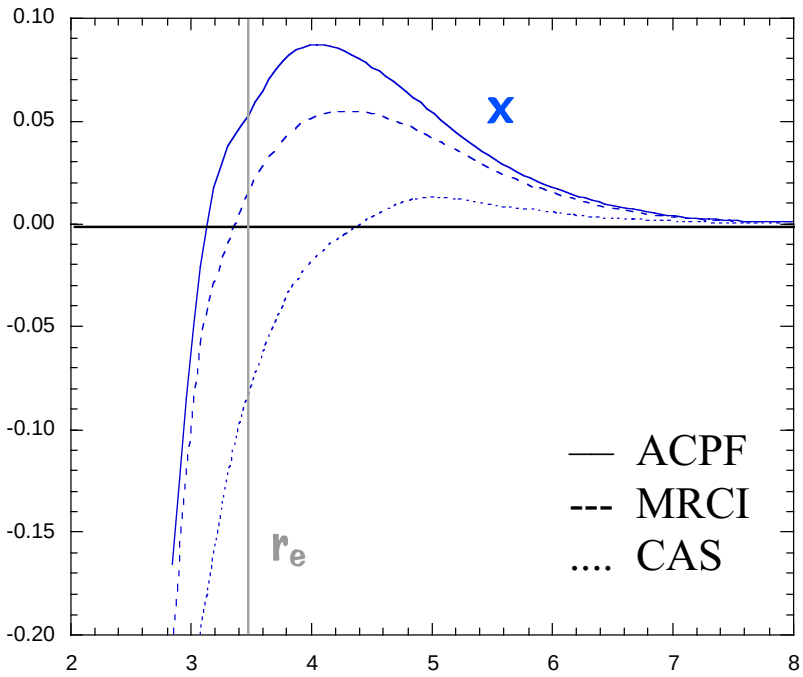
For HOBr, these turn out to be strongly dependent on the level of theory




$\langle X^1A' | \mu_{y,z} | B^1A' \rangle$




$\langle X^1A' | \mu_x | A^1A'' \rangle$

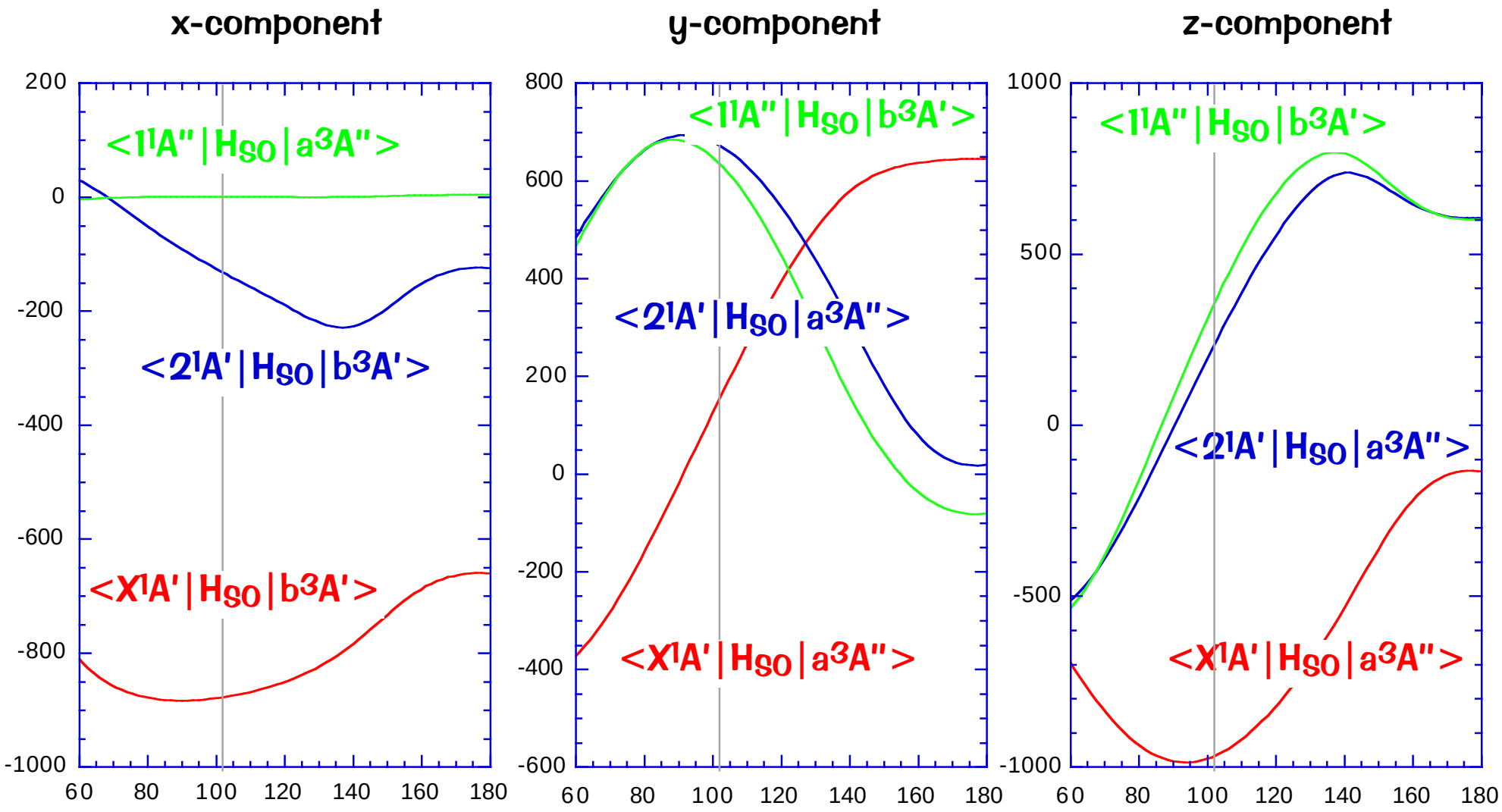



R(BrO), $a_o$

r(OH)=1.83 $a_o$

θ = 103.2°

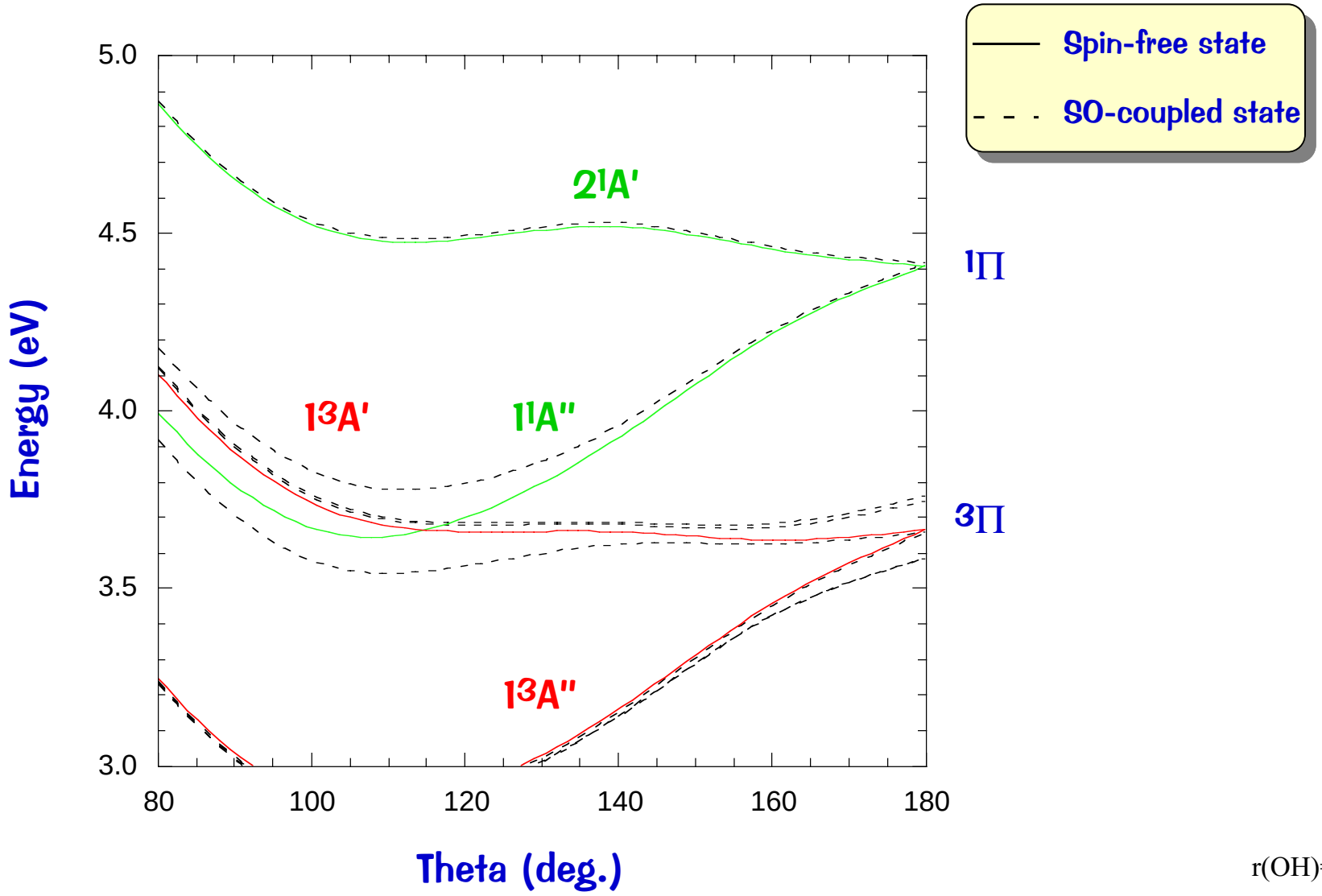
# Representative Spin-Orbit Matrix Elements ($cm^{-1}$)




r(OH)=1.83 $a_o$

r(BrO)=3.474 $a_o$

# Influence of Spin-Orbit Coupling on the Potential Energy Surfaces

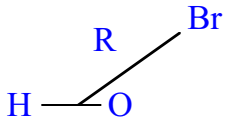



r(OH)=1.83 $a_o$

r(BrO)=3.474 $a_o$

# Approximate Spectra with and without Spin-Orbit Effects

- **CASSCF transition dipoles and SO matrix elements**
- **Effective 1-D potentials:**

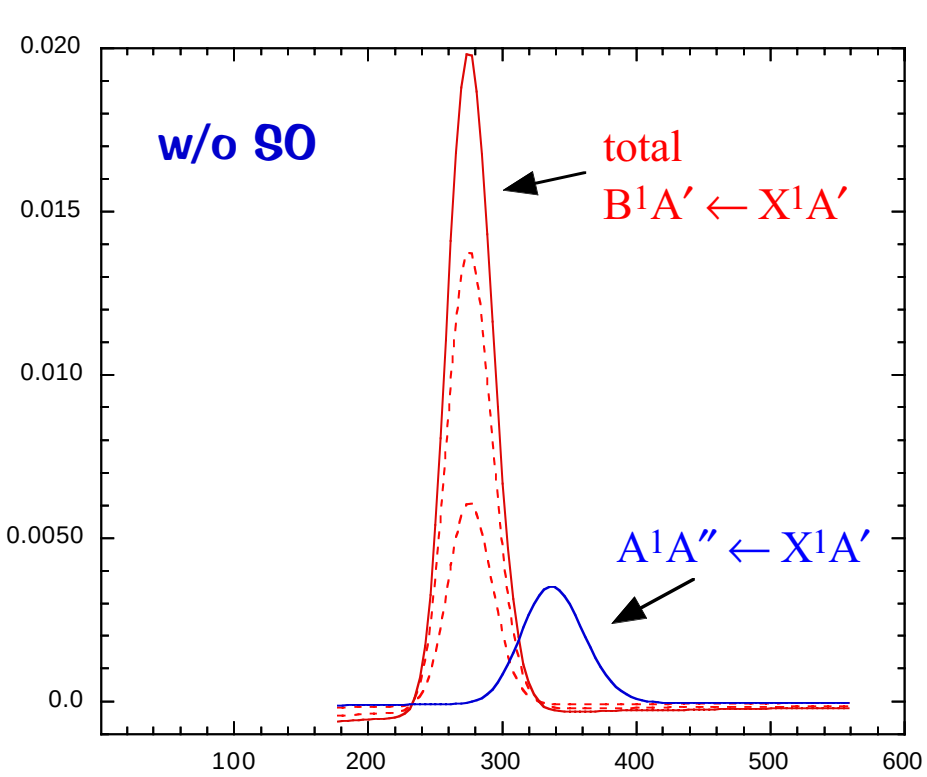


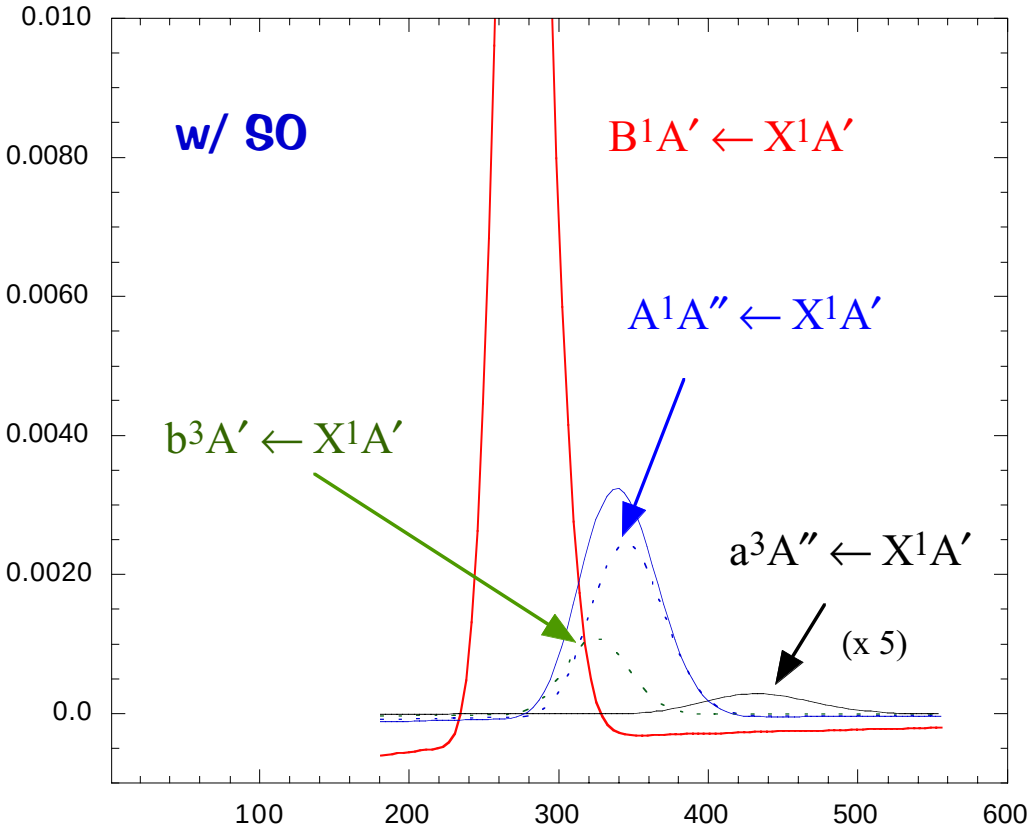

$$\sigma_{\mathrm{tot}}(\omega) \propto \int_{-\infty}^{+\infty} dt\, S(t)\, e^{i\omega t}$$

$$S(t) = \left\langle \Psi_f(0) \middle| \Psi_f(t) \right\rangle$$

$$\Psi_f(0) = \mu_{fi} \Psi_i(E_i)$$

Cross sections obtained from 1-d wavepacket propagations (Å2)



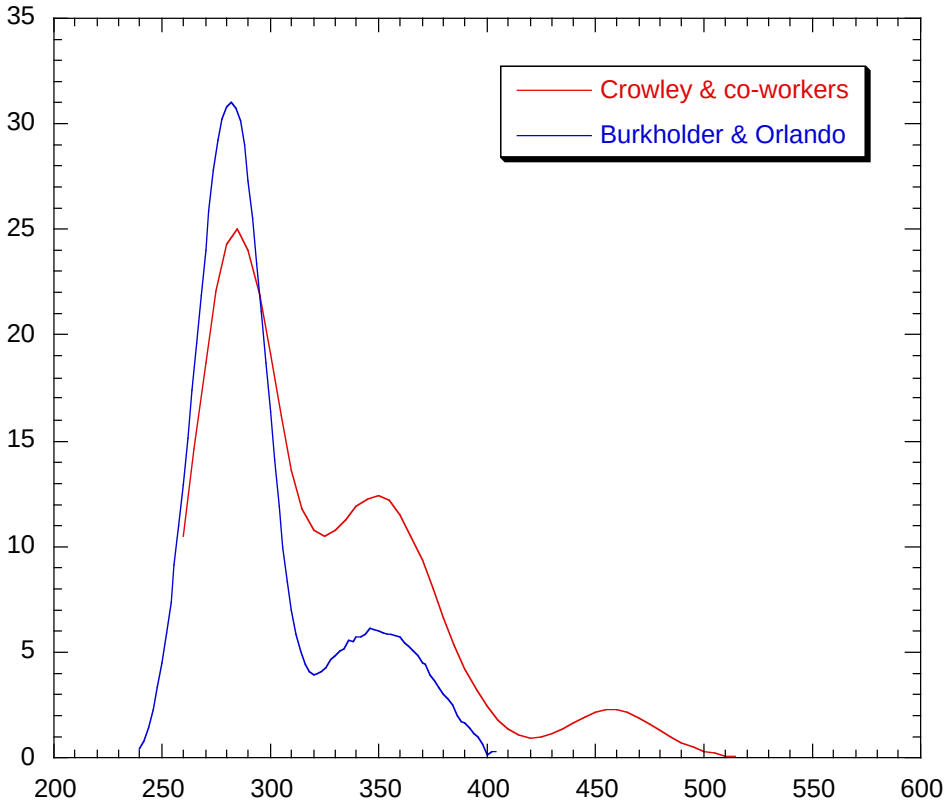




wavelength (nm)

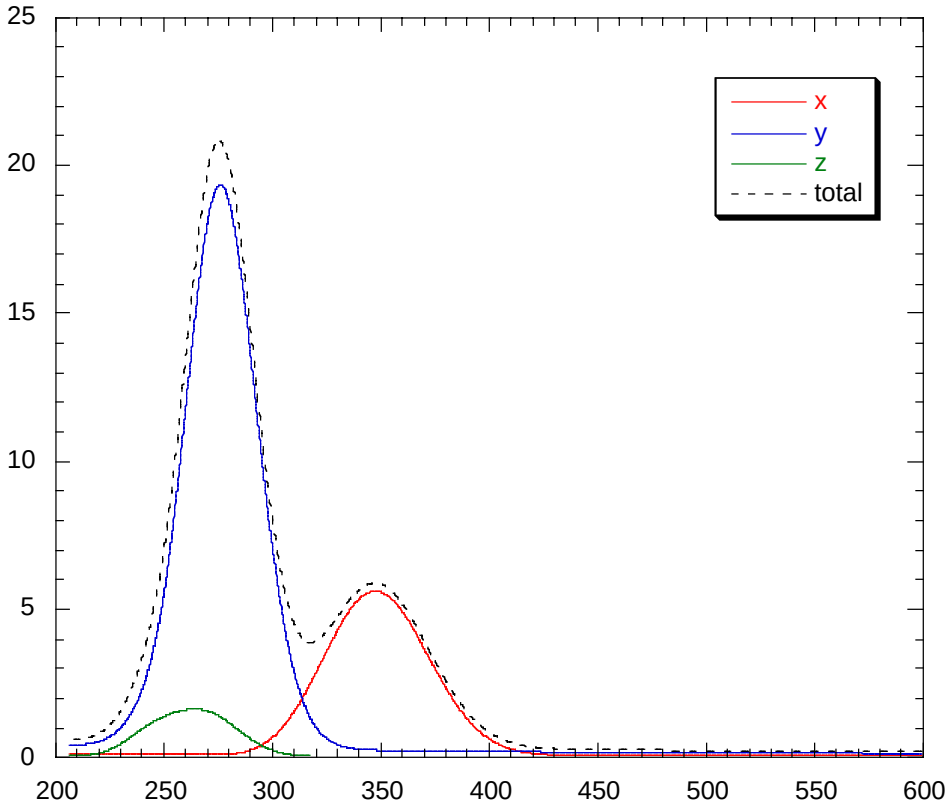
# Preliminary absorption cross sections from 3-dimensional calculations

- in collaboration with Dr. Dimitris Skouteris and Prof. Hans-Joachim Werner at Univ. Stuttgart
- wavepacket propagations carried out on a total of 8 excited states constructed from 4 spin-free (diabatic) states with spin-orbit off-diagonal couplings (ACPF transition dipoles and MRCI SO)
- diagonalization of $H_{el} + H_{so}$ currently does not include the ground state

## Experimental spectrum

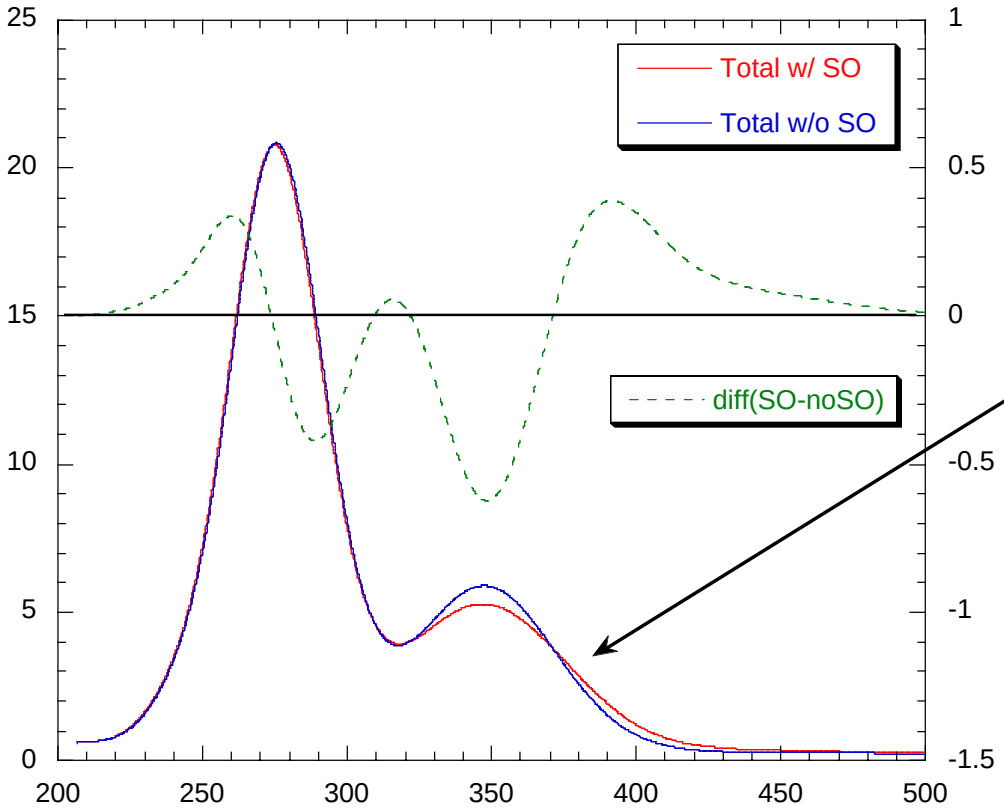



## Theory: no spin-orbit coupling



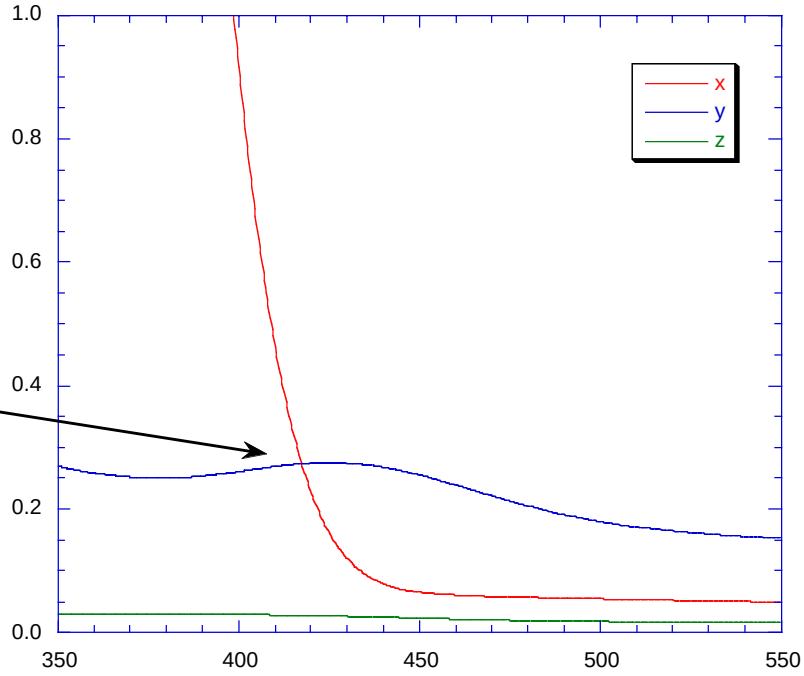

wavelength (nm)

# Inclusion of spin-orbit coupling




SO coupling between $A^1A''$ and $b^3A'$ states broaden the 2nd peak

Enlarged region near 450 nm




The intensity of the $X^1A' \rightarrow a^3A''$ transition is strongly underestimated

# Calculations in progress

- Include the $4^1A'$ state to provide a source for more intensity borrowing by the $a^3A''$ state
  - the $4^1A'$ state lies at 9 eV, but its transition moment with the ground state is ~1 a.u. (10x greater than the $2^1A'$ state)

  $a^3A''$ oscillator strength:

  w/o $4^1A'$ or $X^1A'$ : $4.3 \times 10^{-6}$

  w/ $4^1A'$ & $X^1A'$ : $1.7 \times 10^{-5}$ (factor of 4)

- Use a partially adiabatic representation, with dynamics run on the same number of states (8) as before

  (i.e., block diagonalize $X^1A'$, $2^1A'$, $4^1A'$ and $a^3A'$)

# Acknowledgments

Dr. Andreas Nicklass (halogen atoms, BrCl)

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Dr. Dimitris Skouteris and Prof. H.-J. Werner, Univ. Stuttgart (HOBr)

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