Vibronic Coupling in Radicals: Is Quantum Chemistry worth a Damn?

John F. Stanton
University of Texas at Austin

Ohio State Spectroscopy Symposium, 2009

A typical problem in this area:

Anion photoelectron spectroscopy of B_2N^-

Knut R. Asmis, Travis R. Taylor, and Daniel M. Neumark[a)]
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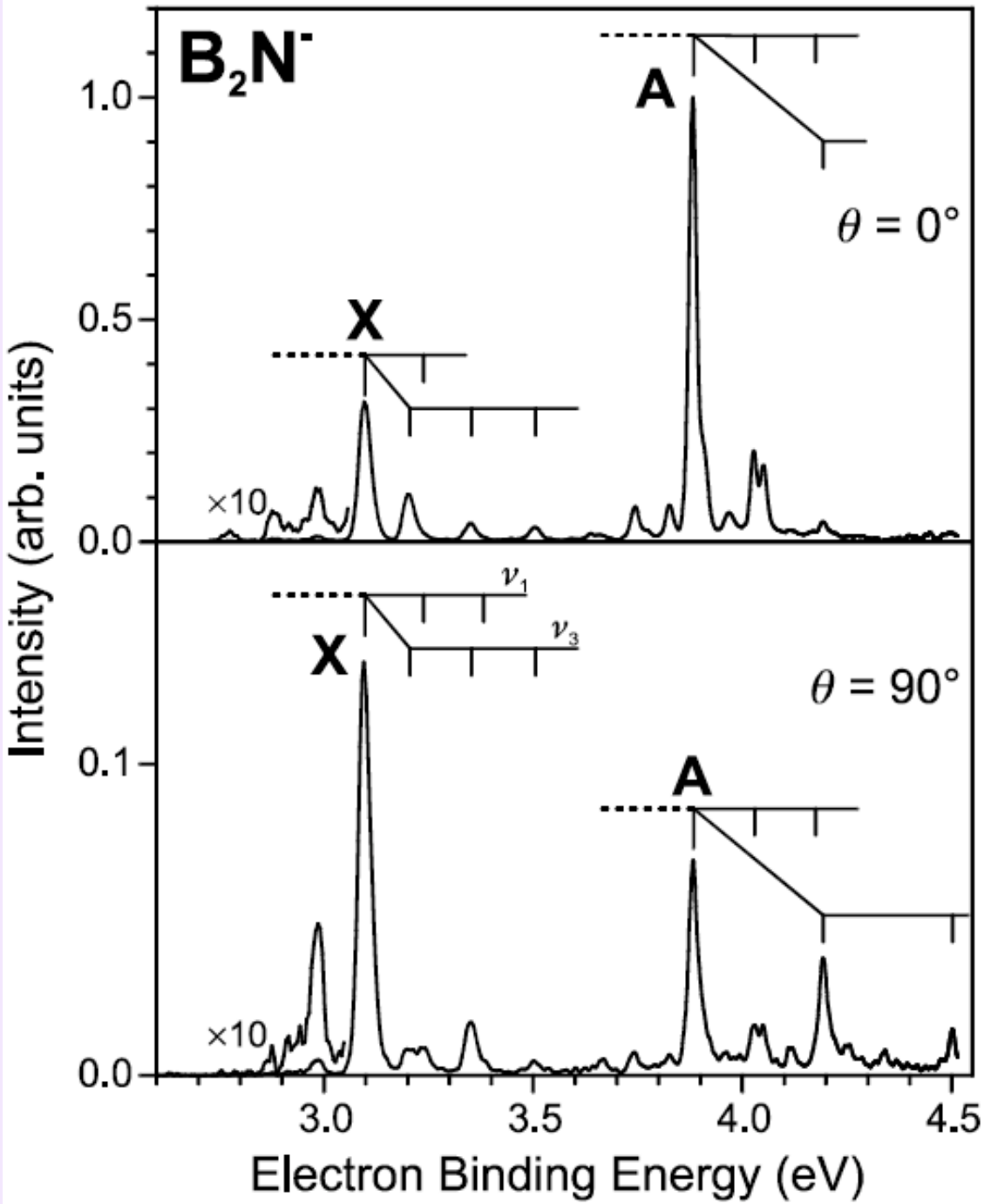
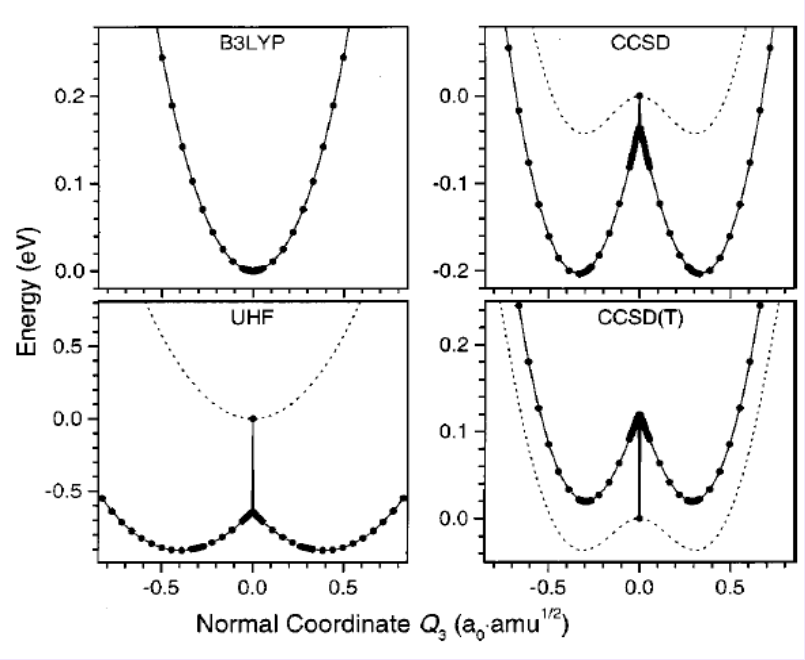
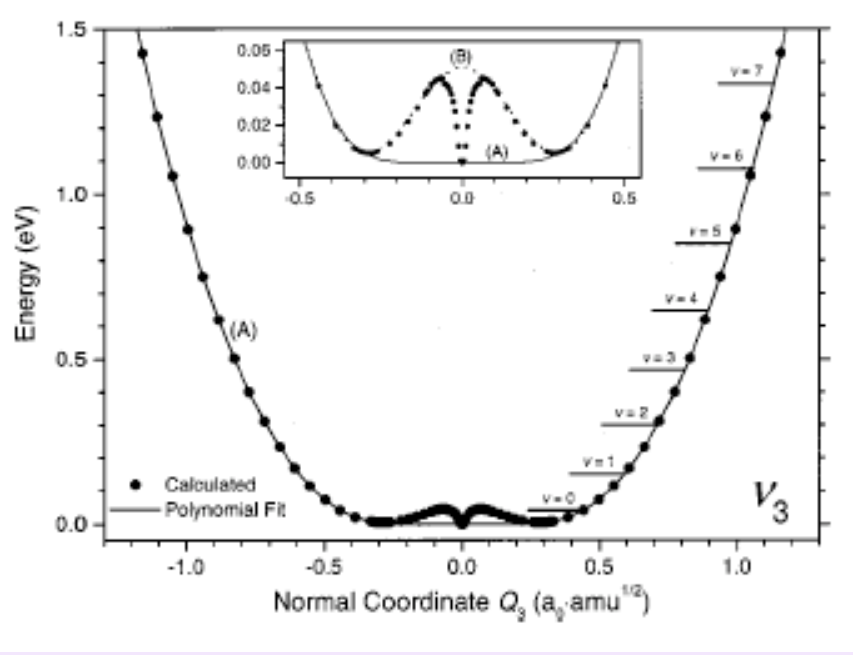
(Received 3 August 1999; accepted 20 August 1999)


B2N-
A
θ = 0°
X
×10
ν1
ν3
X
θ = 90°
A
×10
1.0
0.5
0.0
0.1
0.0
3.0
3.5
4.0
4.5
Intensity (arb. units)
Electron Binding Energy (eV)

Vibrationally resolved 355 and 266 nm anion photoelectron spectra of B_2N are presented. Photodetachment to two electronic states of linear B–N–B is observed and, aided by electronic structure calculations, assigned to the $\tilde{X}\,^1\Sigma_g^+ \rightarrow \tilde{X}\,^2\Sigma_u^+ + e^-$ and $\tilde{X}\,^1\Sigma_g^+ \rightarrow \tilde{A}\,^2\Sigma_g^+ + e^-$ transitions. The electron affinity of B_2N is 3.098 ± 0.005 eV and the $\tilde{A}\,^2\Sigma_g^+$ term energy T_0 is 0.785 ± 0.005 eV. Observation of excitations involving uneven quanta of the antisymmetric stretching mode (ν_3) indicates a breakdown of the Franck–Condon (FC) approximation and results from Herzberg–Teller vibronic coupling between the $\tilde{X}\,^2\Sigma_u^+$ and $\tilde{A}\,^2\Sigma_g^+$ states involving the ν_3 mode. Measurement of the angular dependence of the photodetached electrons serves as a sensitive probe for the identification of these FC forbidden transitions. A linear vibronic coupling model qualitatively reproduces the perturbed ν_3 potentials of the $\tilde{X}$ and $\tilde{A}$ states. Artifactual symmetry breaking along the ν_3 coordinate is observed in the *ab initio* wave functions for the neutral ground state up to the coupled-cluster level of theory, even when Brueckner orbitals are used. No evidence is found for an energetically low-lying cyclic state of B_2N, which has been invoked in the assignment of the matrix infrared spectrum of B_2N. However, the matrix infrared data agrees well with the peak spacing observed in the photoelectron spectra and reassigned to the linear $\tilde{X}\,^2\Sigma_u^+$ ground state. © *1999 American Institute of Physics*. [S0021-9606(99)00743-6]



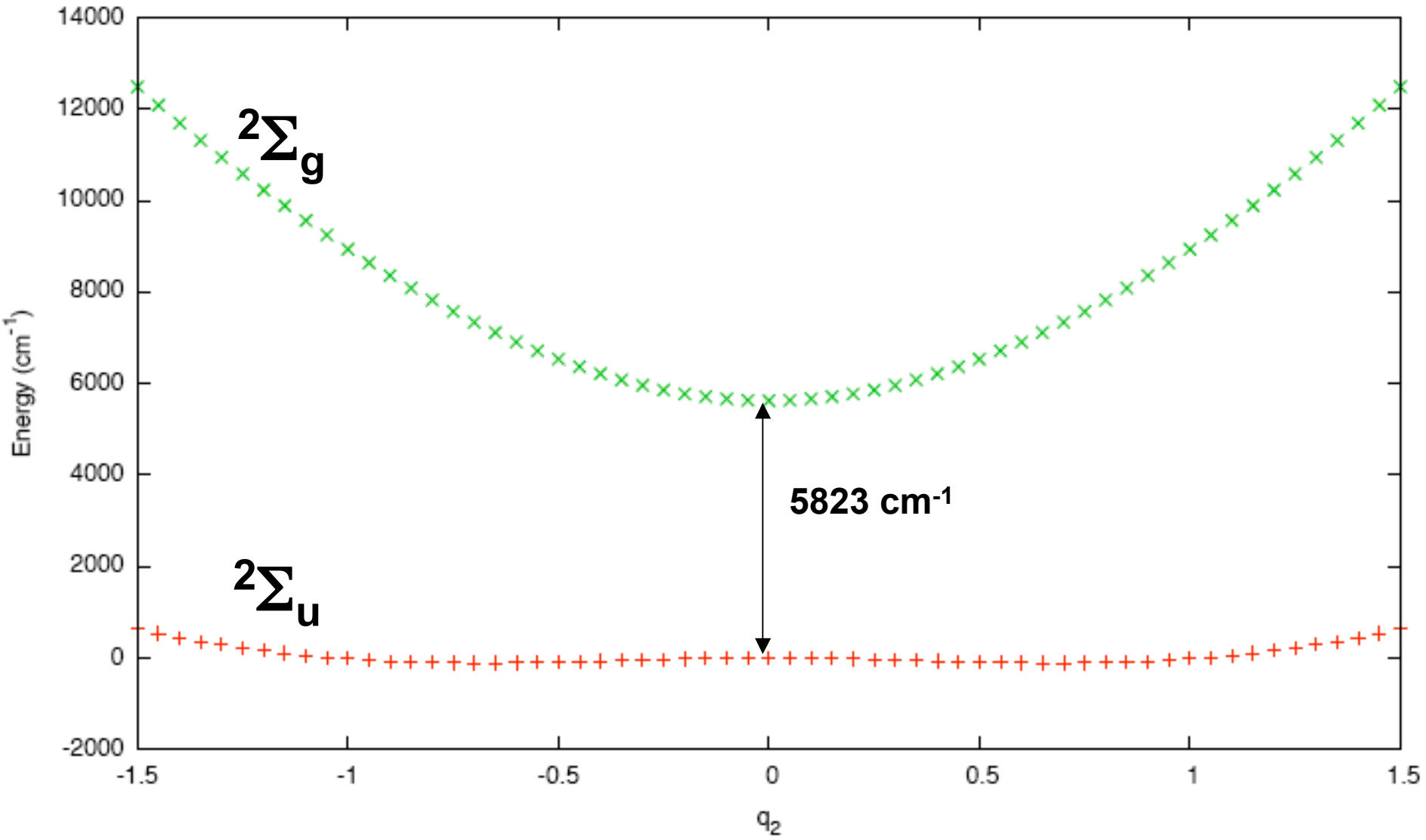


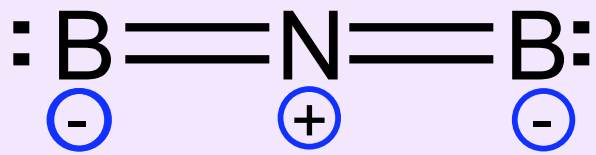
Experimentally determined levels of the asymmetric stretch

	Experiment	
v	IR matrix [c]	PES[d] (± 40 cm^{-1})
0		
1	882.3	855
2		2052
3	3330	3291
4		
5	5882	5888
6		
0		
1		2492
2		
3		

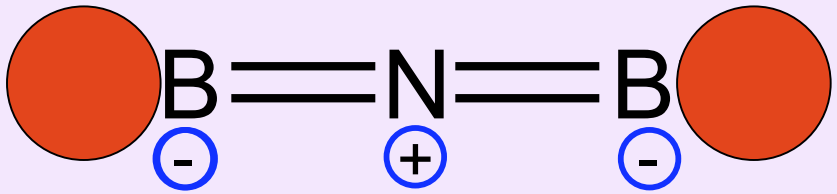
Large **positive** anharmonicity !!!!!!!!

Not consistent with otherwise reasonable-looking DFT curve.

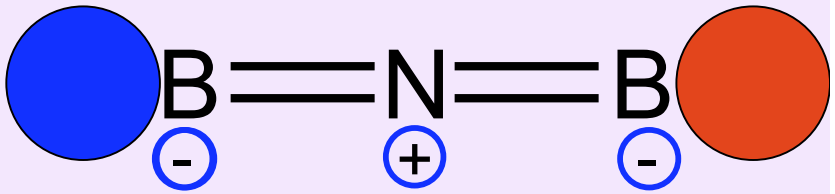

14000
12000
10000
8000
6000
4000
2000
0
-2000
Energy (cm-1)
-1.5
-1
-0.5
0
0.5
1
1.5
q2
2Σg
2Σu
5823 cm-1



anion

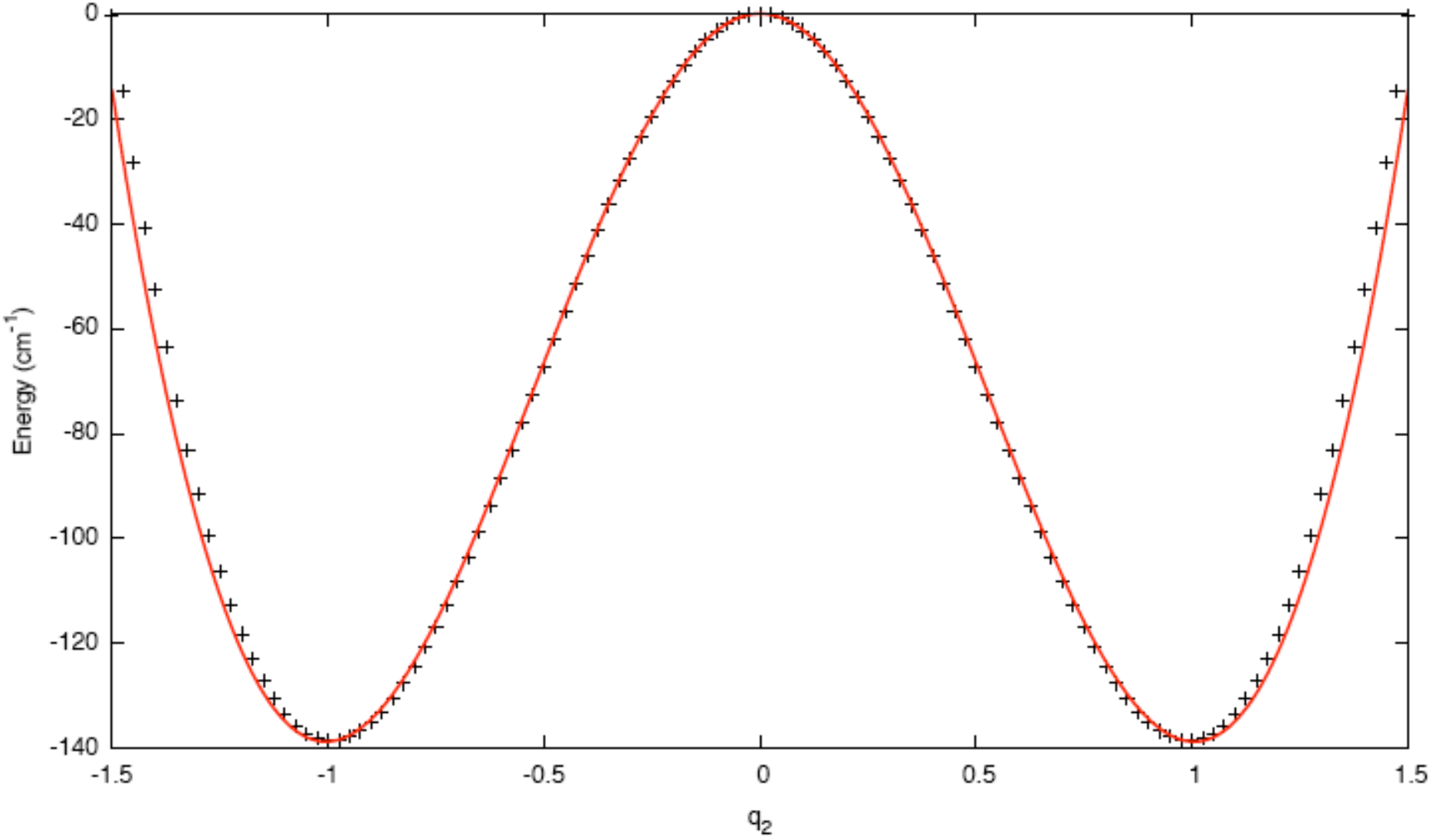


HOMO-1 (σ_g)

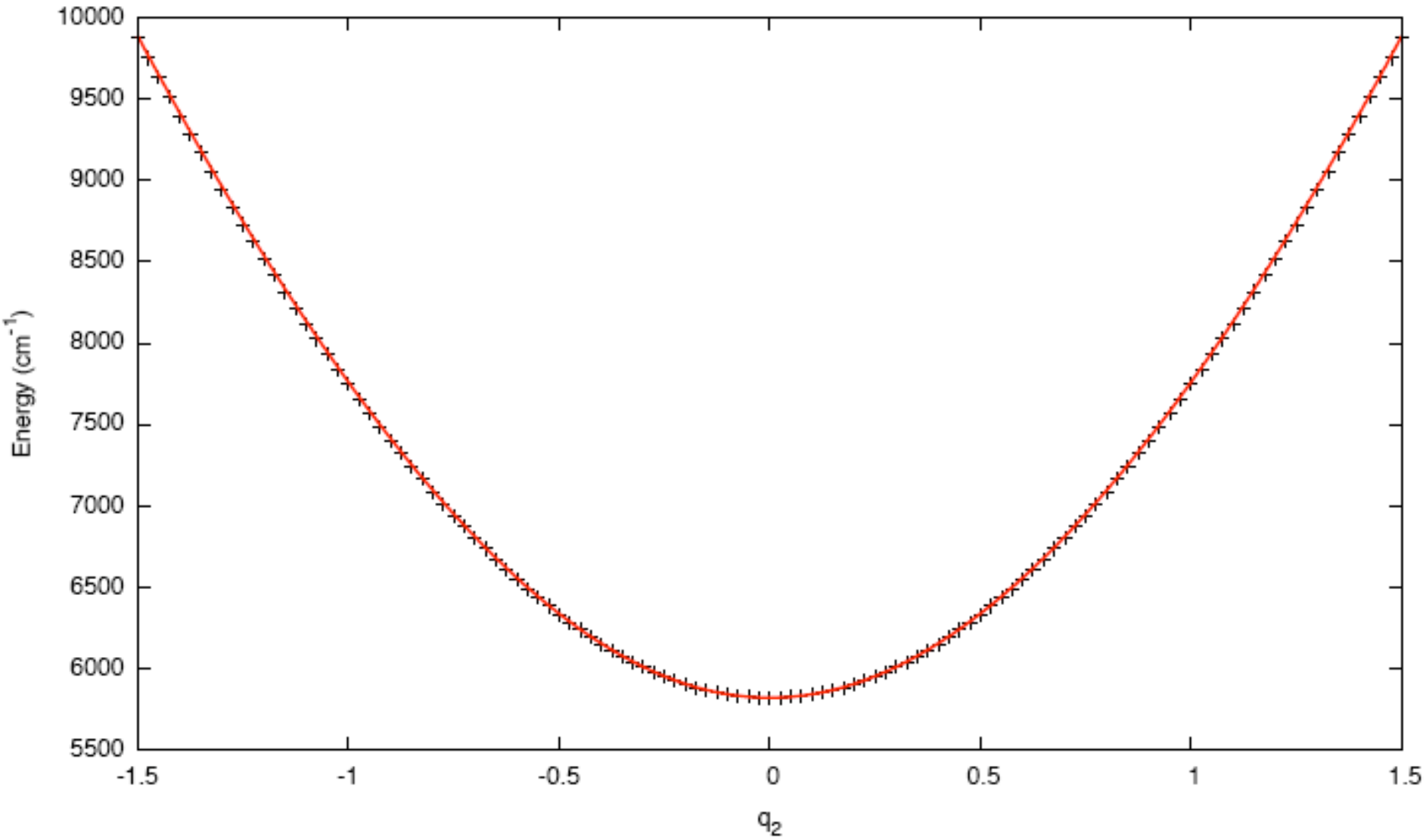


HOMO (σ_u)

$^2\Sigma_u$ adiabatic surface



$^2\Sigma_g$ adiabatic surface



How should a theoretical chemist think about this subject?

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The molecular wavefunction:

$$\Psi = \psi_{\mathbf{A}} \sum_{\mathbf{k}} \mathbf{c}_{\mathbf{k}}^{\mathbf{A}} \chi_{\mathbf{k}}(\mathbf{q}) + \psi_{\mathbf{B}} \sum_{\mathbf{k}} \mathbf{c}_{\mathbf{k}}^{\mathbf{B}} \chi_{\mathbf{k}}(\mathbf{q}) + \cdots$$

Born-Huang expansion

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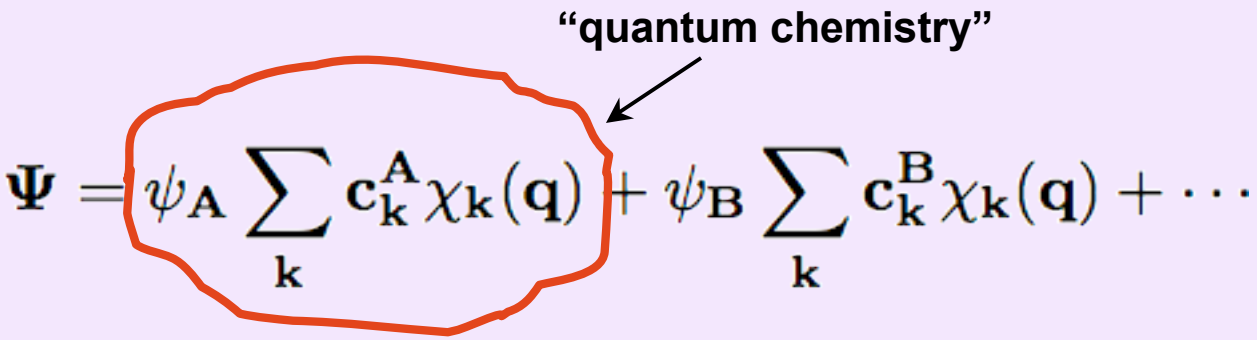

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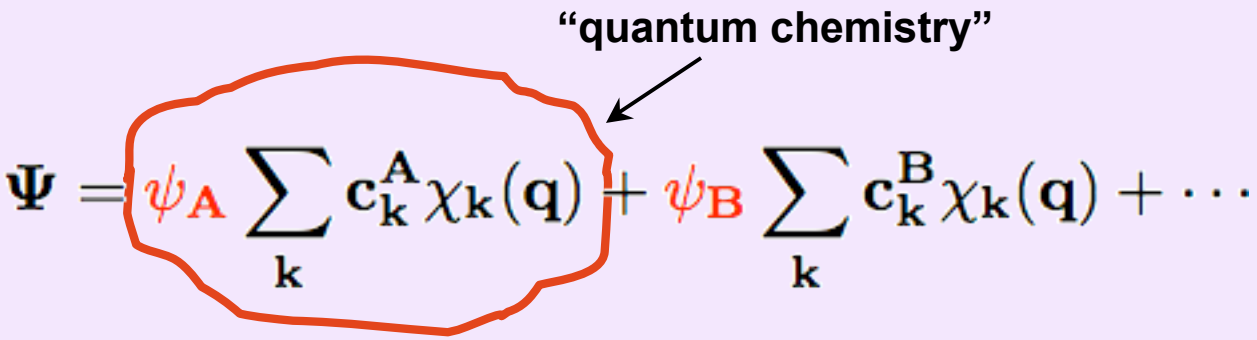


Born-Huang expansion

The usual choice is the adiabatic basis

$$\{\psi_1(r;R), \psi_2(r;R) \cdots\}$$

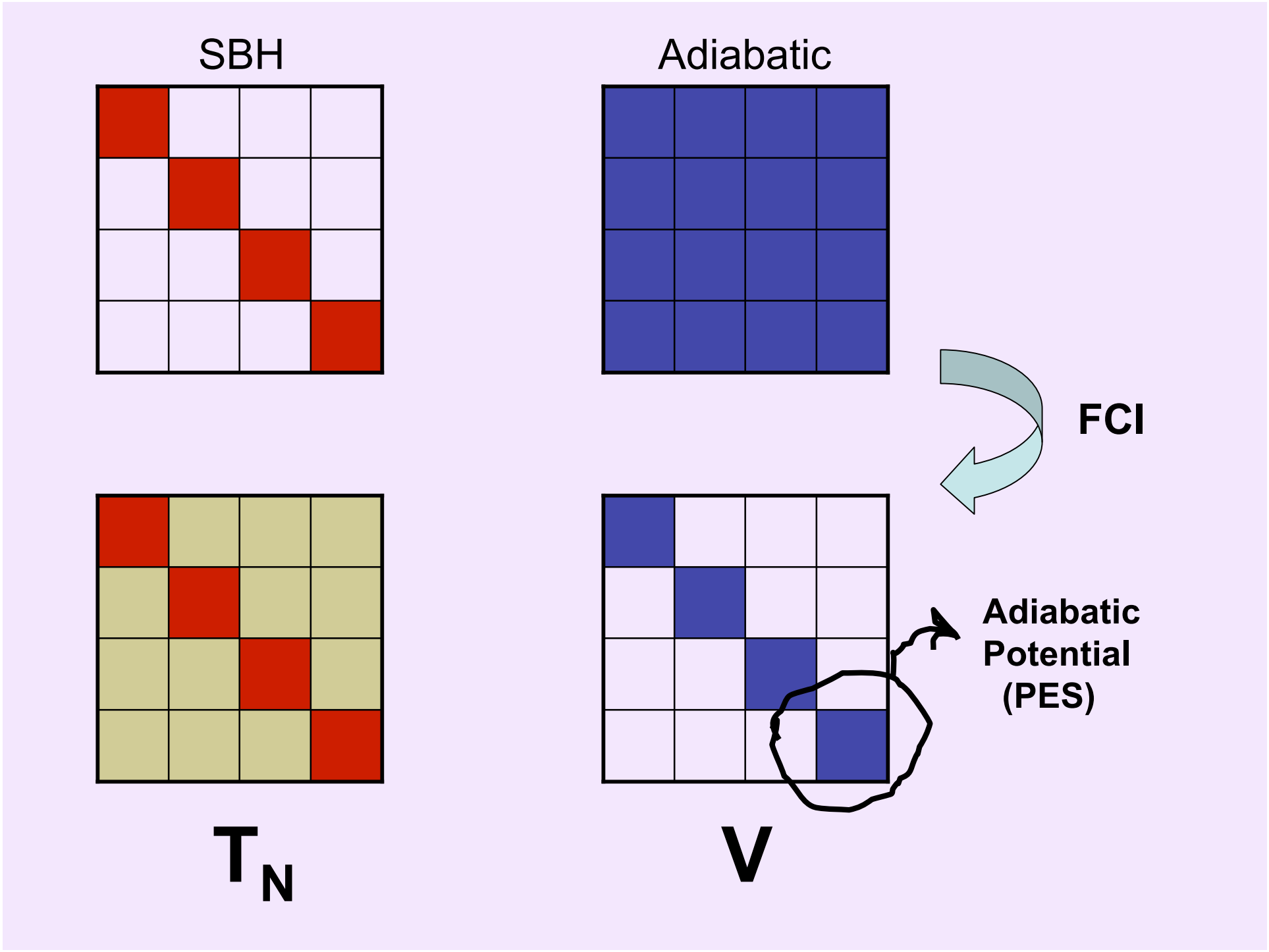
Electronic Hamiltonian is diagonal in this basis for all possible nuclear coordinates R.

A pedagogically (but not computationally) useful choice is the static Born-Huang basis

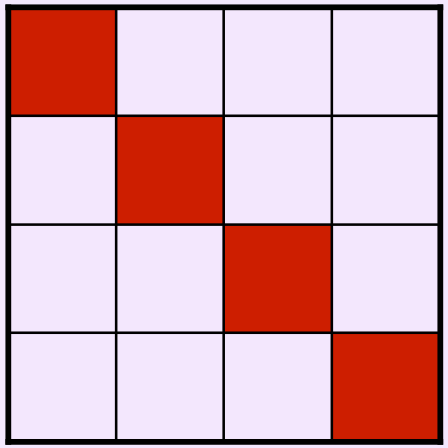
$$\{\psi_1(r;R_0), \psi_2(r;R_0) \cdots\}$$

Nuclear kinetic energy operator is diagonal in this basis. (Rigorous diabatic basis).

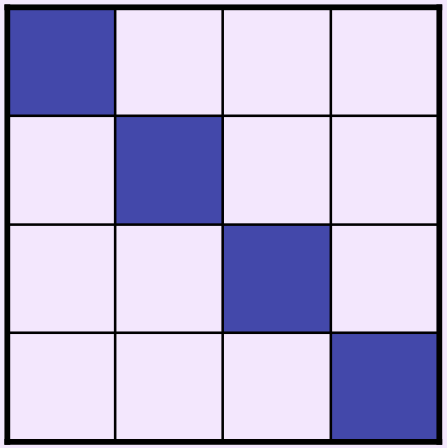
How best to think about these choices?


SBH
Adiabatic
FCI
Adiabatic
Potential
(PES)
T_N
V

The usual assumption



T_N

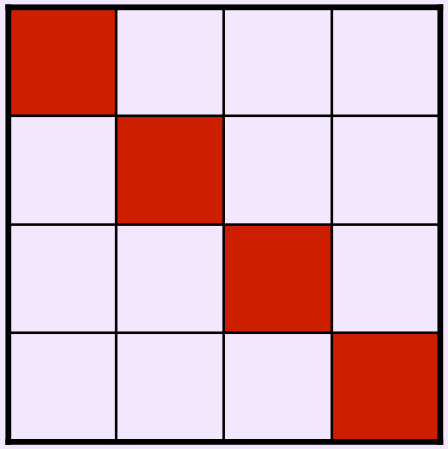


V

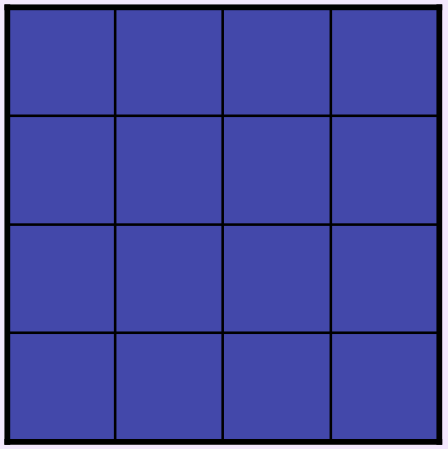
$$(T_{ii} + V_{PES,i})\,\Omega = E_{vib}\,\Omega$$

But sometimes…

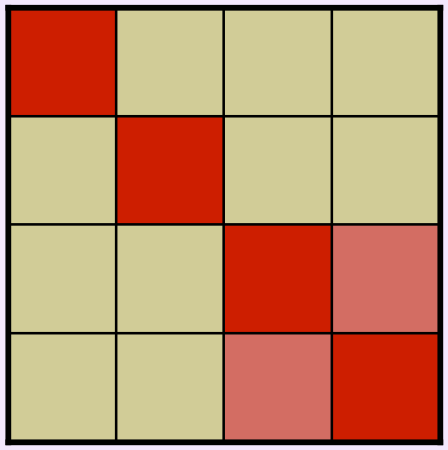
SBH



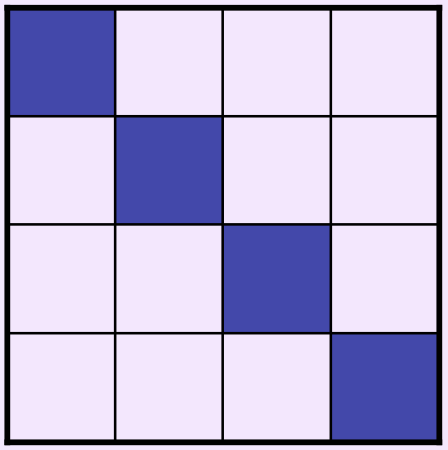
Adiabatic



FCI

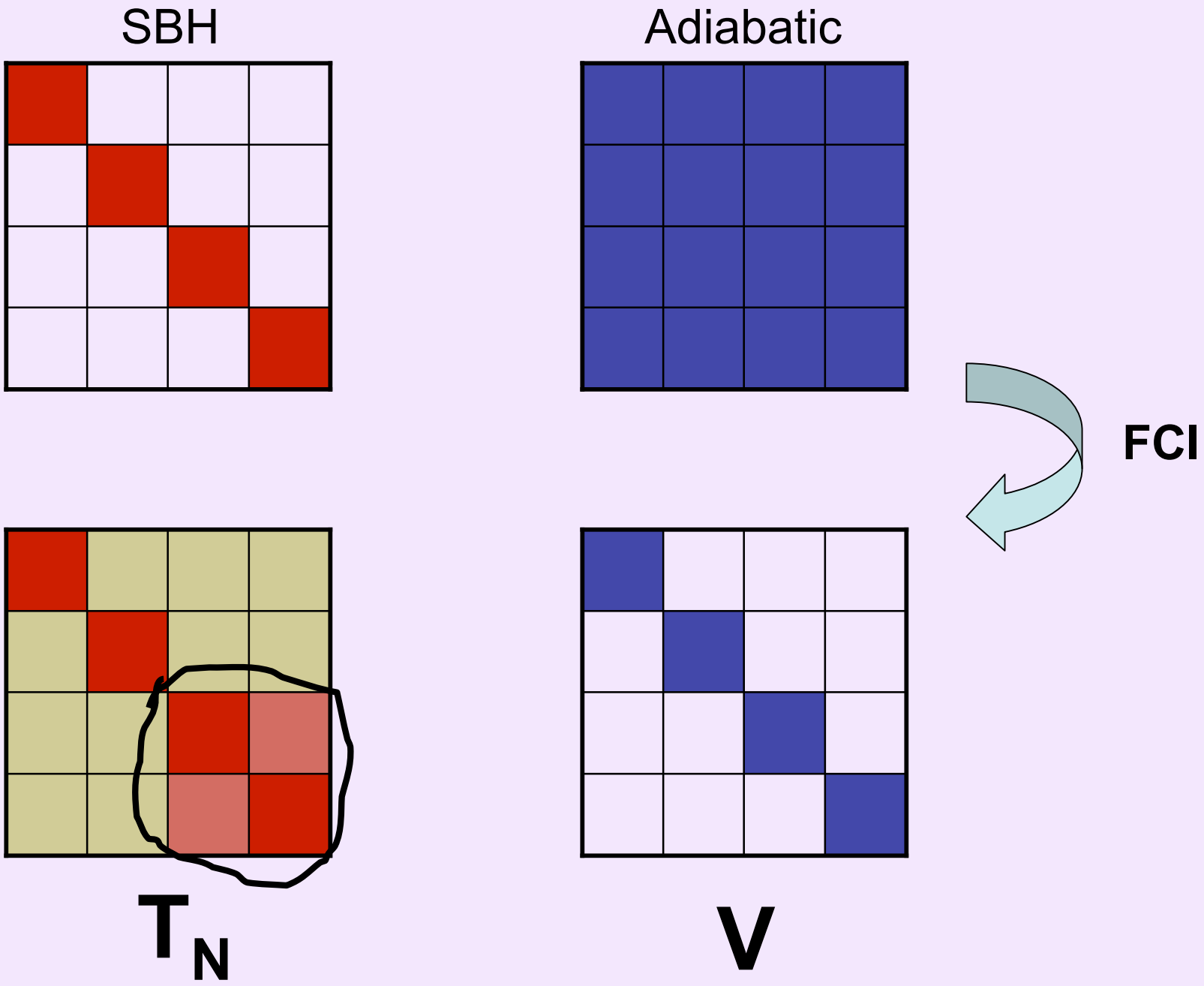


T_N

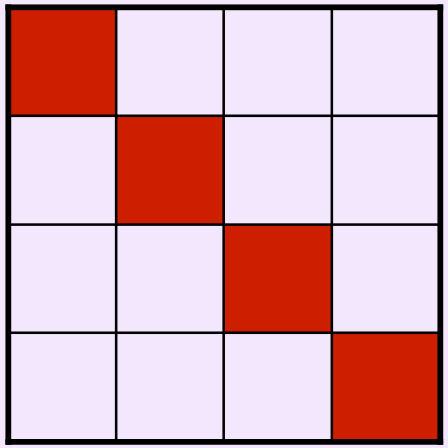


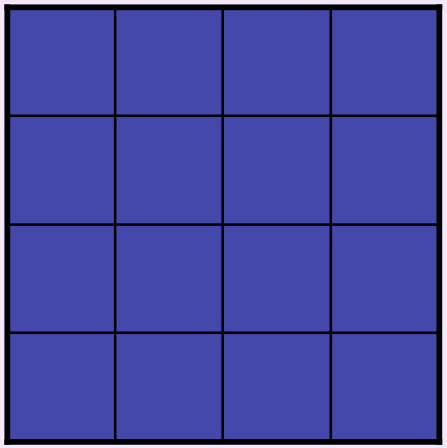
V

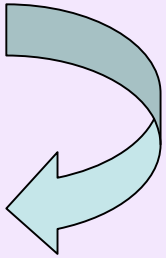
But sometimes…



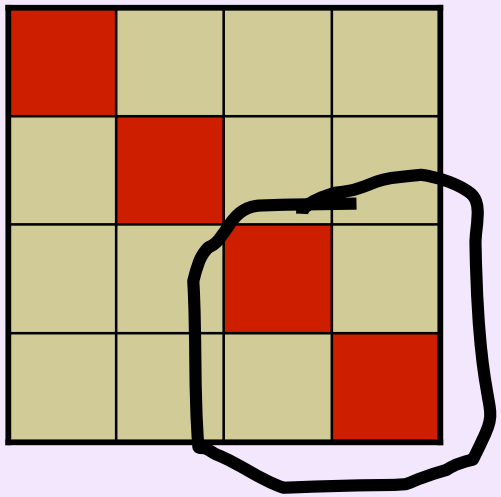
Alternative approach



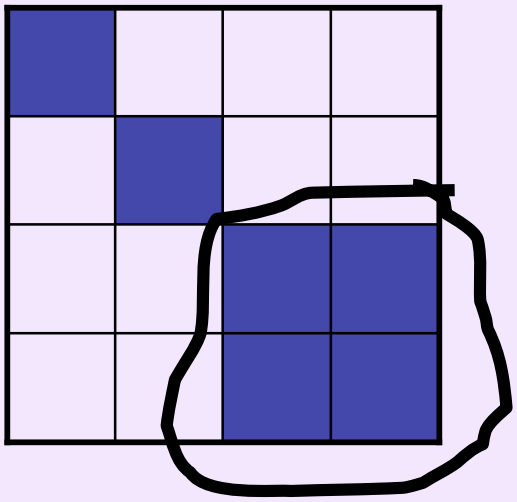




Block diagonalize



T_N



V

Eigenvectors define "quasidiabatic" electronic wavefunctions

KDC “quasidiabatic” Hamiltonian

$$\left[\begin{pmatrix} T_{AA} & 0 \\ 0 & T_{BB} \end{pmatrix} + \begin{pmatrix} V_{AA} & V_{AB} \\ V_{AB} & V_{BB} \end{pmatrix} \right] \begin{pmatrix} \Omega_A \\ \Omega_B \end{pmatrix} = E_{vibronic} \begin{pmatrix} \Omega_A \\ \Omega_B \end{pmatrix}$$

H. Köppel, W. Domcke and L.S. Cederbaum *Adv. Chem. Phys.* 57, 59 (1984)
W. Domcke, H. Köppel and L.S. Cederbaum *Mol. Phys.* 43, 851 (1981)

See also:
R.L. Fulton and M. Gouterman *J. Chem. Phys.* 35, 1059 (1961).

Recent developments: M. Nooijen (Waterloo), D. Yarkony (Johns Hopkins), UT

Pros and Cons of the LVC model in this parametrization:

Extremely simple and outstanding qualitative model that has been used for nearly thirty years to identify vibronic coupling in molecular systems. Calculations are straightforward.

But…

Does not account for either anharmonicity or Duschinsky mixing in the symmetric modes.

Two state model approach for coupling coordinates relies on assumption that "quasidiabatic force constants" for coupling modes are similar in the two states. This is chemically reasonable (unlike similar assumptions about adiabatic force constants), but at best qualitatively accurate. And there are cases where this assumption clearly fails (wagging mode of HCO_2).

There are potential problems when the number of states involved in the coupling is greater than two (cyclopentadienyl radical)

How can we make this quantitative? How "good" can it be?

Totally symmetric modes can be treated by a higher-order Taylor series. quadratic has been done sometimes (the so-called QVC) model, but we have gone up to quartic terms.

Typical parametrizations are such that the adiabatic and *ab initio* potentials are identical at the origin of the coordinate system (vertical parametrization). We have developed* a parametrization method such that the adiabatic model potentials agree exactly with the *ab initio* potentials at the minima of the final states (adiabatic parametrization).

By making an *ansatz* for the quasidiabatic states, we have recently come up with an analytic method for calculating the coupling constants. This allows us to extend the coupling to nonlinear terms.**

* T. Ichino, A.J. Gianola, W.C. Lineberger and J.F. Stanton, JCP 125, 084312 (2006).
**T. Ichino, J. Gauss and J.F. Stanton, JCP, in press.

	Diabatic Model H (LVC)	Diabatic Model H (elaborate)	Expt.*
$3_0^1(^2\Sigma_u)$	797		855
$3_0^2(^2\Sigma_u)$	1961		2052
$3_0^3(^2\Sigma_u)$	3153		3291
$3_0^4(^2\Sigma_u)$	4443		
$3_0^5(^2\Sigma_u)$	5186		5888
$3_0^1(^2\Sigma_g)$	2582		2479

*K.R. Asmis, T.R. Taylor and D.M. Neumark JCP 111, 8838 (1999)

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$3_0^4(^2\Sigma_u)$	4443	4545	
$3_0^5(^2\Sigma_u)$	5186	5866	5888
$3_0^1(^2\Sigma_g)$	2582	2492	2479

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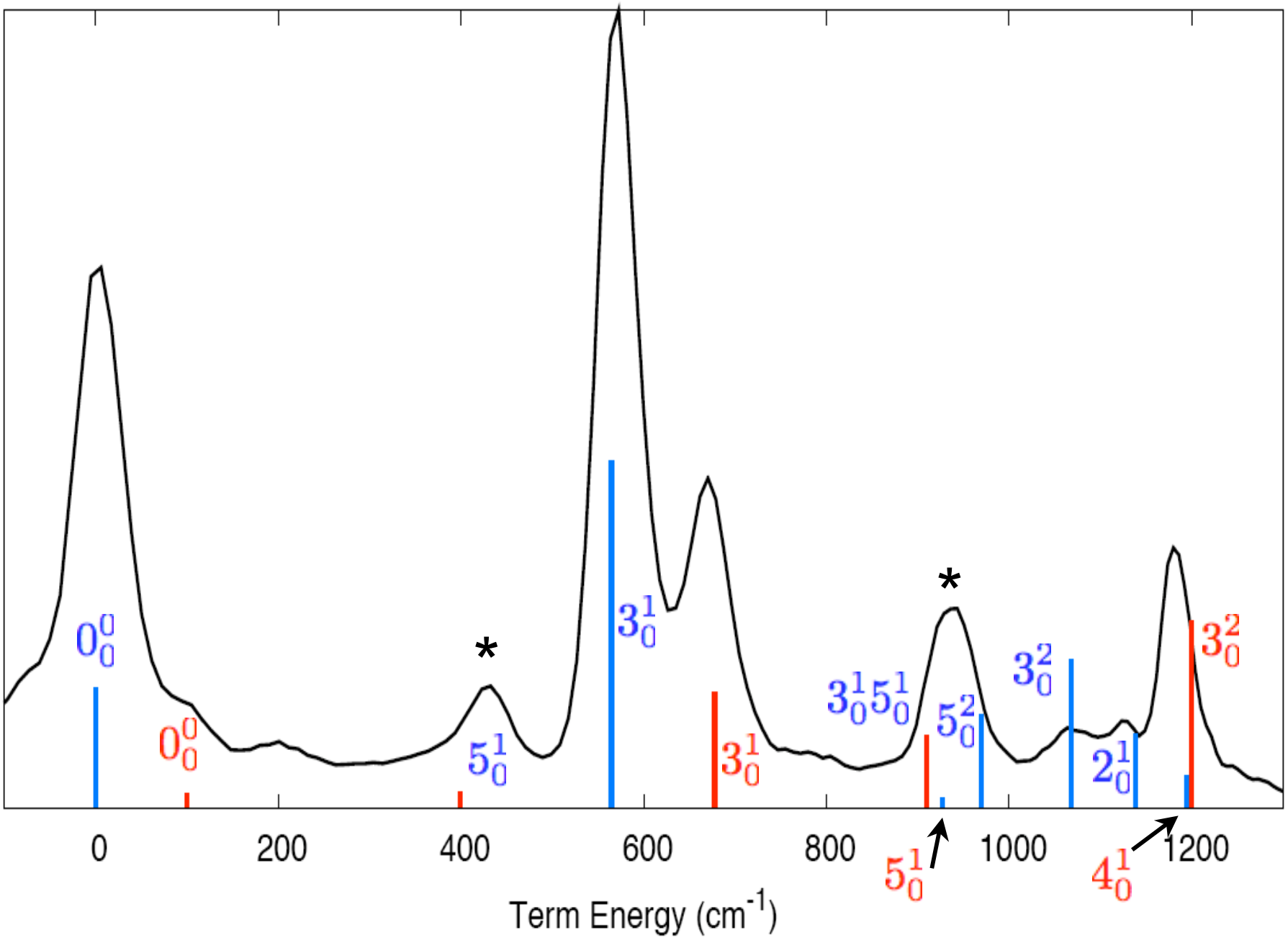

0_0^0
0_0^0
5_0^1
*
3_0^1
3_0^1
$3_0^1 5_0^1$
5_0^2
*
3_0^2
2_0^1
3_0^2
5_0^1
4_0^1
0
200
400
600
800
1000
1200
Term Energy (cm^{-1})

Table II. DCO_2^- SEVI spectra peak positions, shifts from origin and PAD as well as the calculated frequencies and assignments.

Peak	eBE (cm^{-1})	Shift from origin (cm^{-1})	PAD[a]	Calculated position (cm^{-1})	Assignment[b]
A	28362	0	*p*	0.0	$0_0^0(^2A_1)$
B	28449	87	*s*	100.5	$0_0^0(^2B_2)$
C	28792	430	*s*	399.8	$5_0^1(^2A_1)$
D	28925	563	*p*	564.8	$3_0^1(^2A_1)$
E	29028	666	*s*	677.8	$3_0^1(^2B_2)$
F	29310	948	*s*	910.0 970.2	$3_0^2 5_0^1(^2A_1)$ $5_0^1(^2B_2)$
G	29446	1084	*p*	1068.3	$3_0^2(^2A_1)$
H	29498	1136	*p*	1138.6	$2_0^1(^2A_1)$
I	29555	1193	*s*	1199.7	$3_0^2(^2B_2)$
J	29882	1520	*p*	1478.1 1492.6	$1_0^1(^2A_1)$ $3_0^1 5_0^2(^2A_1)$
K	30105	1743	*s*	1770.0	highly mixed
L	30153	1791	*s*	1835.9	highly mixed
M	30385	2023	*p*	1997.4	highly mixed
N	30780	2418			
O	30945	2583	*p*		

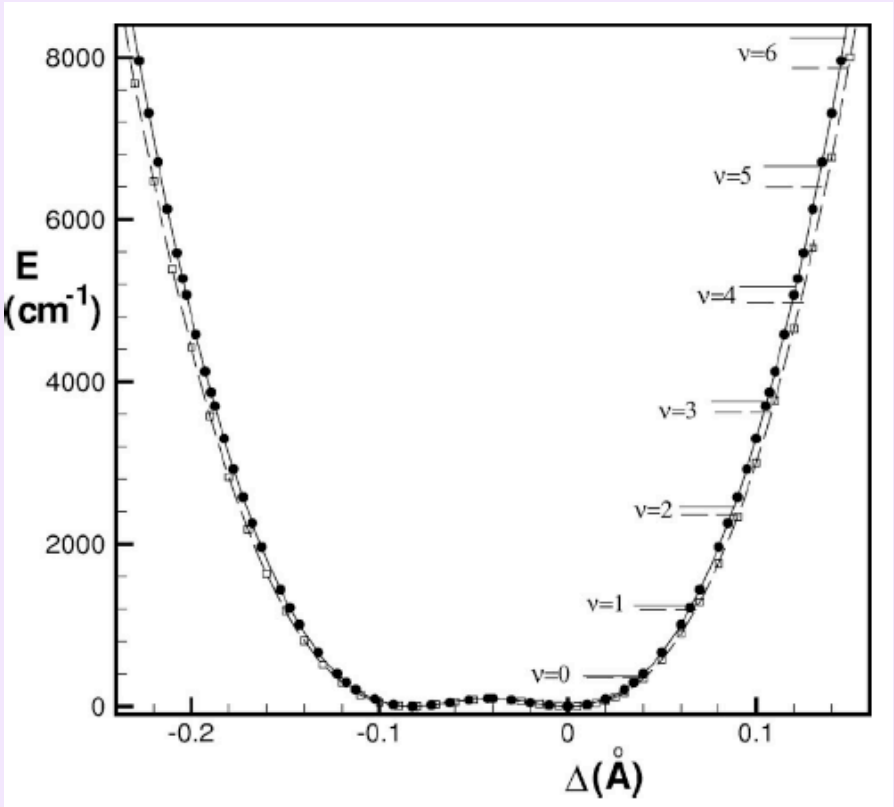
E. Garand *et al.* JPC, in preparation.

THE JOURNAL OF CHEMICAL PHYSICS **126**, 224304 (2007)

Real or artifactual symmetry breaking in the BNB radical: A multireference coupled cluster viewpoint

Xiangzhu Li and Josef Paldus[a)]
Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

(Received 17 April 2007; accepted 9 May 2007; published online 12 June 2007)



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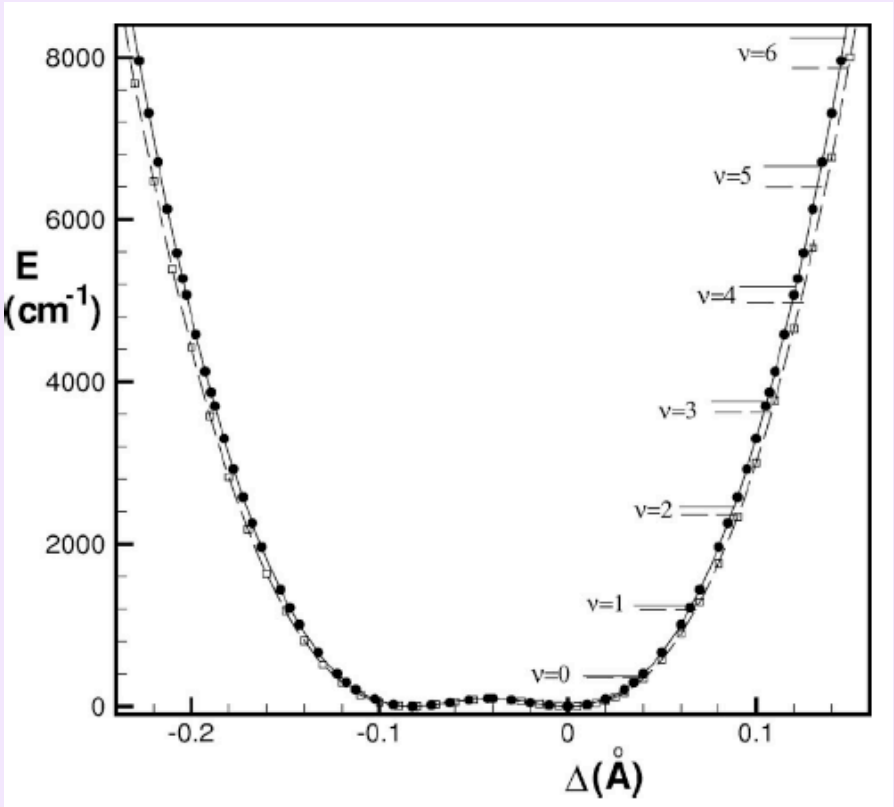


Calculated fundamental for "asymmetric stretch" was *ca.* 930 cm^{-1}, about 50 cm^{-1} above experiment.

Just how accurate are adiabatic vibrational levels?

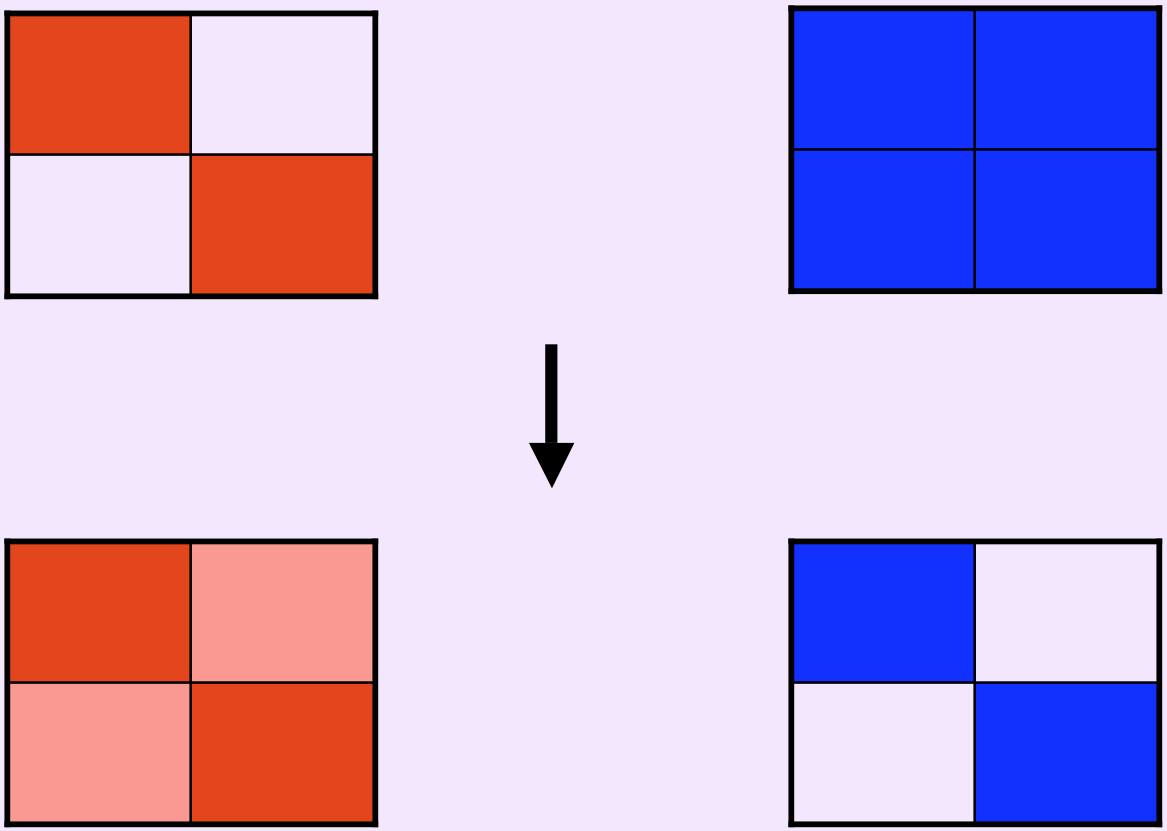
In other words:

"If I were to do a full CI calculation in a complete basis, and solve the vibrational problem exactly, would the results agree with experiment?"

Partial answer (and unsatisfying) answer:

"For water, it has been amply demonstrated that one can get accuracies of *ca.* 1 cm^{-1} by such an approach. But for NO_3 and other strongly coupled systems, who knows?"

Agree with me that H_{KDC} “works”



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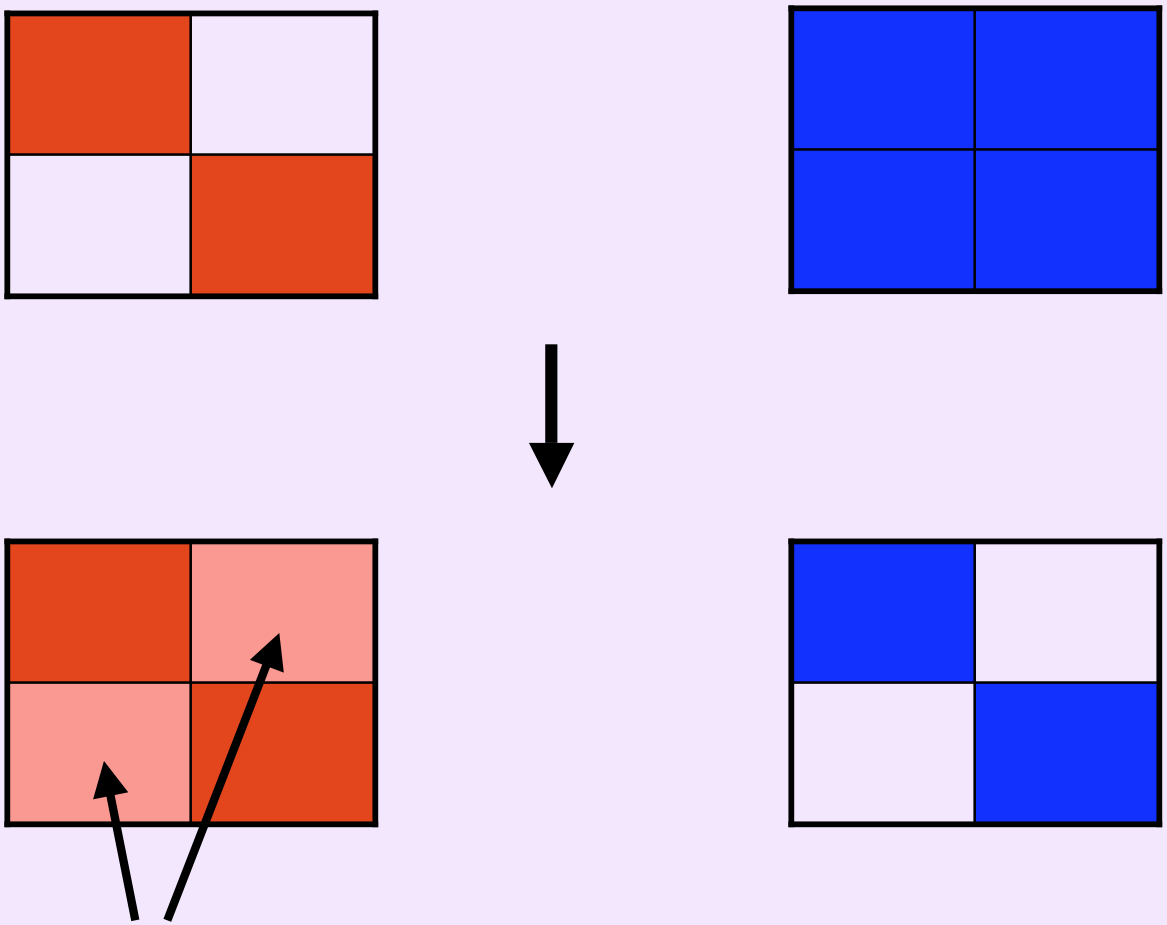

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$3_0^4(^2\Sigma_u)$	4545		
$3_0^5(^2\Sigma_u)$	5846		5888
$3_0^1(^2\Sigma_g)$	2502		2479

WOW

All done…

Thanks to:
NSF, DOE and the Welch Foundation
Many members of the audience

Polynomial expansion

$$\frac{V_-}{hc} = \frac{1}{2}[-656]q^2 + \frac{1}{24}[6260]q^4 + \frac{1}{720}[-74950]q^6 + \cdots$$

Very anharmonic!

Levels from one-dimensional Sch. Eqn. (DVR)

	Level	Diff.	Expt*
2_1	781.2	781.2	855
2_2	1914.3	1133.1	2052
2_3	3106.6	1192.3	3291
2_4	4378.4	1271.8	

*K.R. Asmis, T.R. Taylor and D.M. Neumark JCP 111, 8838 (1999)

Postdocs
Michael Harding
Takatoshi Ichino
Juana Vazquez
Graduate Students
Harshal Gupta
David Price
Chris Simmons
Mychel Varner
Undergrads
Eric Buchanan
Devin Matthews
Ben McKown

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Eric Buchanan
Devin Matthews
Ben McKown
DOE-BES, NSF, Welch Foundation

Towards more quantitative accuracy…

A more elaborate Hamiltonian

$$= \begin{pmatrix} \kappa_1^A q_1 + \frac{1}{2}\omega_1^A q_1^2 + \frac{1}{2}\omega_2 q_2^2 + \frac{1}{6}\Phi_{111} q_1^3 \\ + \frac{1}{2}\Phi_{122} q_1 q_2^2 + \frac{1}{24}\Phi_{1111} q_1^4 + \frac{1}{4}\Phi_{1122} q_1^2 q_2^2 & \lambda_2 q_2 + \lambda_{12} q_1 q_2 + \lambda_{112} q_1^2 q_2 \\ \lambda q_2 + \lambda_{12} q_1 q_2 + \lambda_{112} q_1^2 q_2 & \kappa_1^B q_1 + \frac{1}{2}\omega_1^B q_1^2 + \frac{1}{2}\omega_2 q_2^2 + \frac{1}{6}\Phi_{111} q_1^3 \\ & + \frac{1}{2}\Phi_{122} q_1 q_2^2 + \frac{1}{24}\Phi_{1111} q_1^4 + \frac{1}{4}\Phi_{1122} q_1^2 q_2^2 - \Delta_0 \end{pmatrix}$$

Towards more quantitative accuracy…

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Outline

I. Vibronic Coupling in the Context of Negative Ion Photoelectron Spectroscopy.

II. Problems Encountered in Theoretical Descriptions Of Vibronic Effects: “Real v. Artifactual”.

III. Diabatic v. Adiabatic Pictures: The BNB Model System.

IV. Accurate Energy Level Positions for a Strongly Coupled System: Which Approach is Intrinsically More Accurate?

V. Application to Spectra of HCO_2^- and DCO_2^-.

Selection rules in photodetachment spectroscopy

$$I \propto |\langle \Psi_- | \mu | \Psi_0 \Psi_{e^-} \rangle|^2$$

Born-Oppenheimer

$$\propto |\langle \psi_- | \mu | \psi_0 \psi_{e^-} \rangle|^2 \; |\langle \chi_- | \chi_0 \rangle|^2$$

Crude (Koopmans') MO model

$$\propto |\langle \phi_- | \mu | \phi_{e^-} \rangle|^2 \; \langle \chi_- | \chi_0 \rangle|^2$$

Photodetachment Cross-section

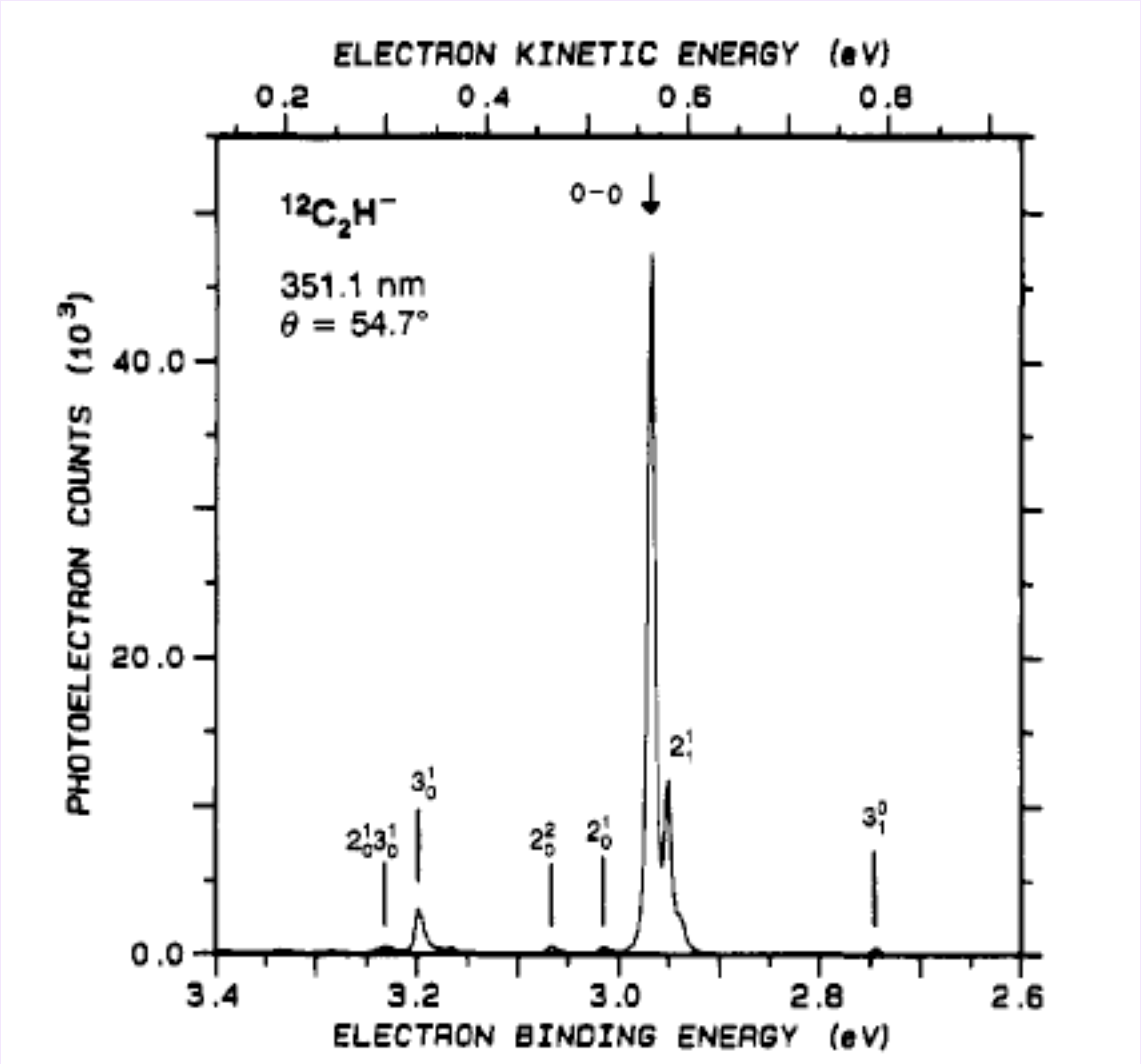
Franck-Condon Factor (FCF)

General guidelines based on approximate models

1. Electrons can be detached from any electronic state (provided sufficiently energetic photons are supplied), and angular distribution of outgoing electron can be inferred.

2. If electron is detached from the ground state of the anion, only totally symmetric vibrations of the neutral should be seen in spectrum. Those which are most prominent are those associated with large changes in geometry between the anion and the neutral.

A tool that gives structural, symmetry and thermodynamic information about reactive molecular species.



K.M. Ervin and W.C. Lineberger, JPC 95, 1167 (1991).

Causes of breakdown of Franck-Condon approximation

1. Mixing of vibrational and electronic wavefunctions

   (VIBRONIC COUPLING)

2. In this case, the molecular wavefunction of the bending level is “mixed” with that of the excited $\tilde{A}^2\Pi$ electronic state.

$$\Psi \approx \psi_{\tilde{X}}\chi_{010} + \lambda\, \psi_{\tilde{A}}\chi_{0000}$$

Vibronic coupling constant

A tool that gives structural, symmetry and thermodynamic information about reactive molecular species.

What causes “artifactual” symmetry breaking?

The Hartree-Fock Hamiltonian, unlike the exact Born-Oppenheimer Electronic Hamiltonian does **not** commute with the symmetry operations associated with the point group of the nuclear framework

The Hartree-Fock wavefunction, again unlike the exact electronic (Born-Oppenheimer clamped-nucleus) wavefunction, does **not** have to transform as a pure irreducible representation of the point group, even for a non-degenerate state. The density will then not have the symmetry of the molecule, with various weird consequences.

HF is an energy-minimization variational approach, so it can “cheat” on symmetry and find lower-energy solutions. Notorious problem found often in radicals (allyl, mixed-oxidation states of bimetallic systems, many others). “Spin contamination” is a related phenomenon which we won’t discuss today.

What can we do about it?

Use density-functional theory, which usually avoids it, but often has the "opposite" problem. This is precisely what is seen for BNB.

Use "multireference" methods. Often said, but this is not a panacea, and exactly the same sort of problems can occur there. A useful path to go down, but one that needs to be walked with care. Many alligators and perils to be found.

Completely avoid starting out with a zeroth-order description of the state of in the first place. Sounds peculiar, but such methods (Greens' functions and propagator methods) are well-known in many-body physics.

Coupled Cluster Theory

The wavefunction:

$$\psi_{\mathbf{CC}} = \exp(\hat{\mathbf{T}})\psi_{\mathbf{HF}}$$

Schrödinger equation:

$$\hat{\mathbf{H}}\exp(\hat{\mathbf{T}})\psi_{\mathbf{HF}} = \mathbf{E}\exp(\hat{\mathbf{T}})\psi_{\mathbf{HF}}$$

$$\exp(-\hat{\mathbf{T}})\hat{\mathbf{H}}\exp(\hat{\mathbf{T}})\psi_{\mathbf{HF}} = \mathbf{E}\psi_{\mathbf{HF}}$$

Transformed Hamiltonian:

$$\bar{\mathbf{H}}\psi_{\mathbf{HF}} = \mathbf{E}\psi_{\mathbf{HF}}$$

Coupled-cluster equations:

$$\langle\psi_{\mathbf{HF}}|\bar{\mathbf{H}}|\psi_{\mathbf{HF}}\rangle = \mathbf{E}$$

$$\langle\psi_{\mathbf{S}}|\bar{\mathbf{H}}|\psi_{\mathbf{HF}}\rangle = \mathbf{0}$$

$$\langle\psi_{\mathbf{D}}|\bar{\mathbf{H}}|\psi_{\mathbf{HF}}\rangle = \mathbf{0}$$

Coupled Cluster Theory

THIS is the problem!

The wavefunction:

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$$\langle\psi_{\mathrm{D}}|\bar{\mathbf{H}}|\psi_{\mathrm{HF}}\rangle = \mathbf{0}$$

Equation-of-motion coupled-cluster theory

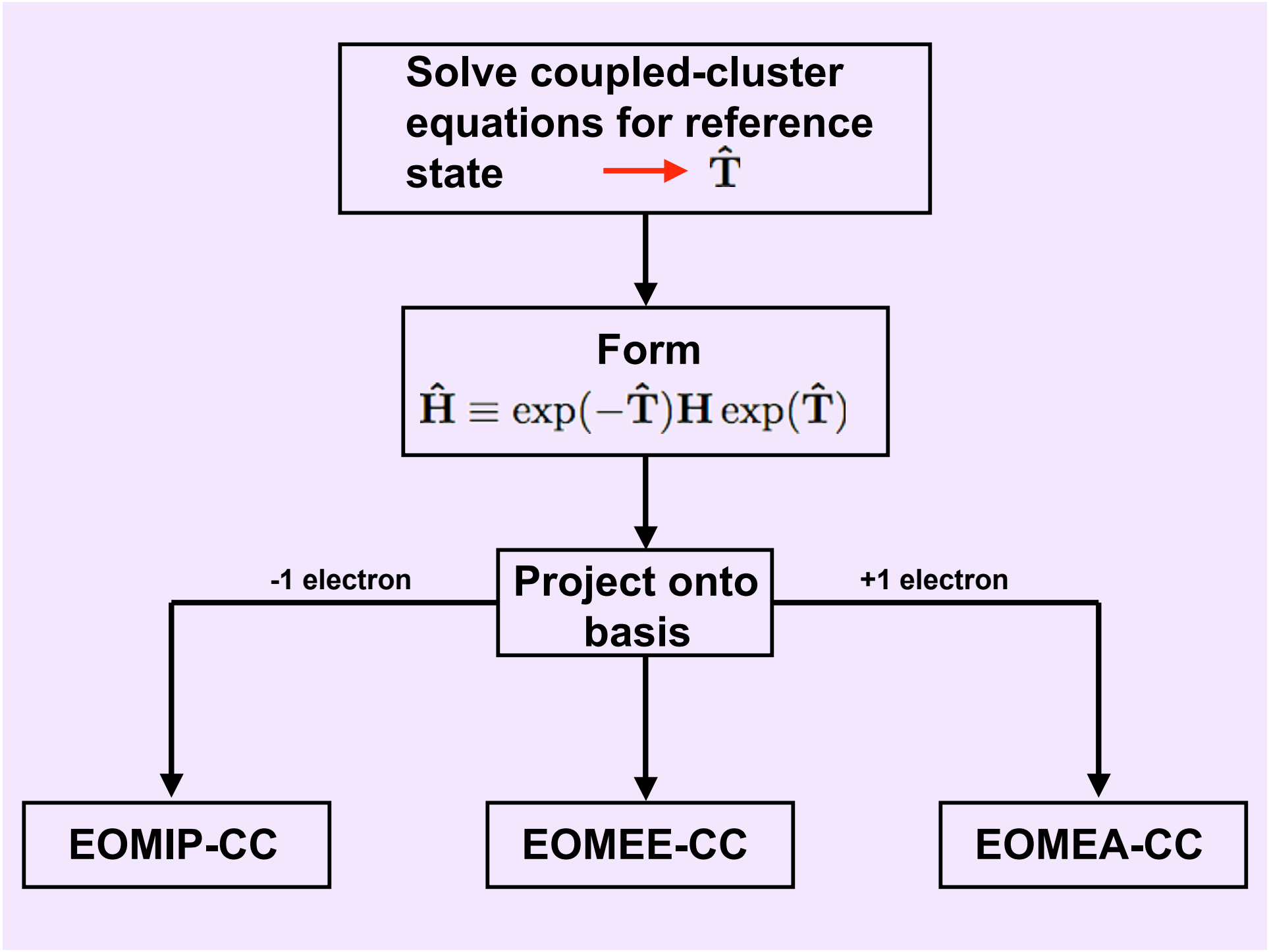
I hear that term all the time. What is it, exactly?

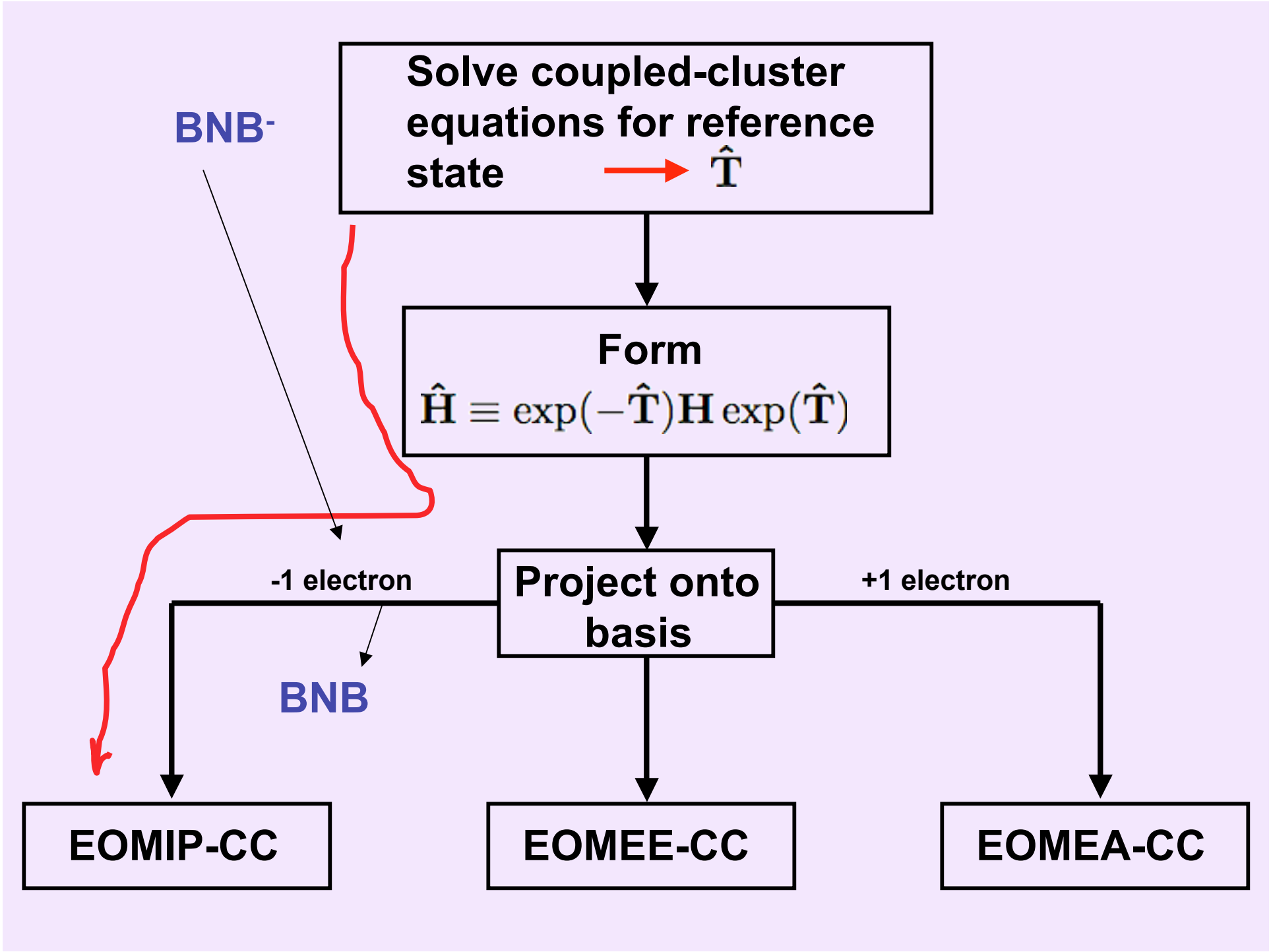
Coupled-cluster theory suffers from symmetry breaking issues, so why would adding three words at the front make any difference?

EOM-CC is parametrized with coupled-cluster calculations, but is not coupled-cluster theory in a strict sense. It is, rather, a form of configuration interaction that use a "dressed" Hamiltonian, scales properly with the size of the system (usually) and can be improved systematically.

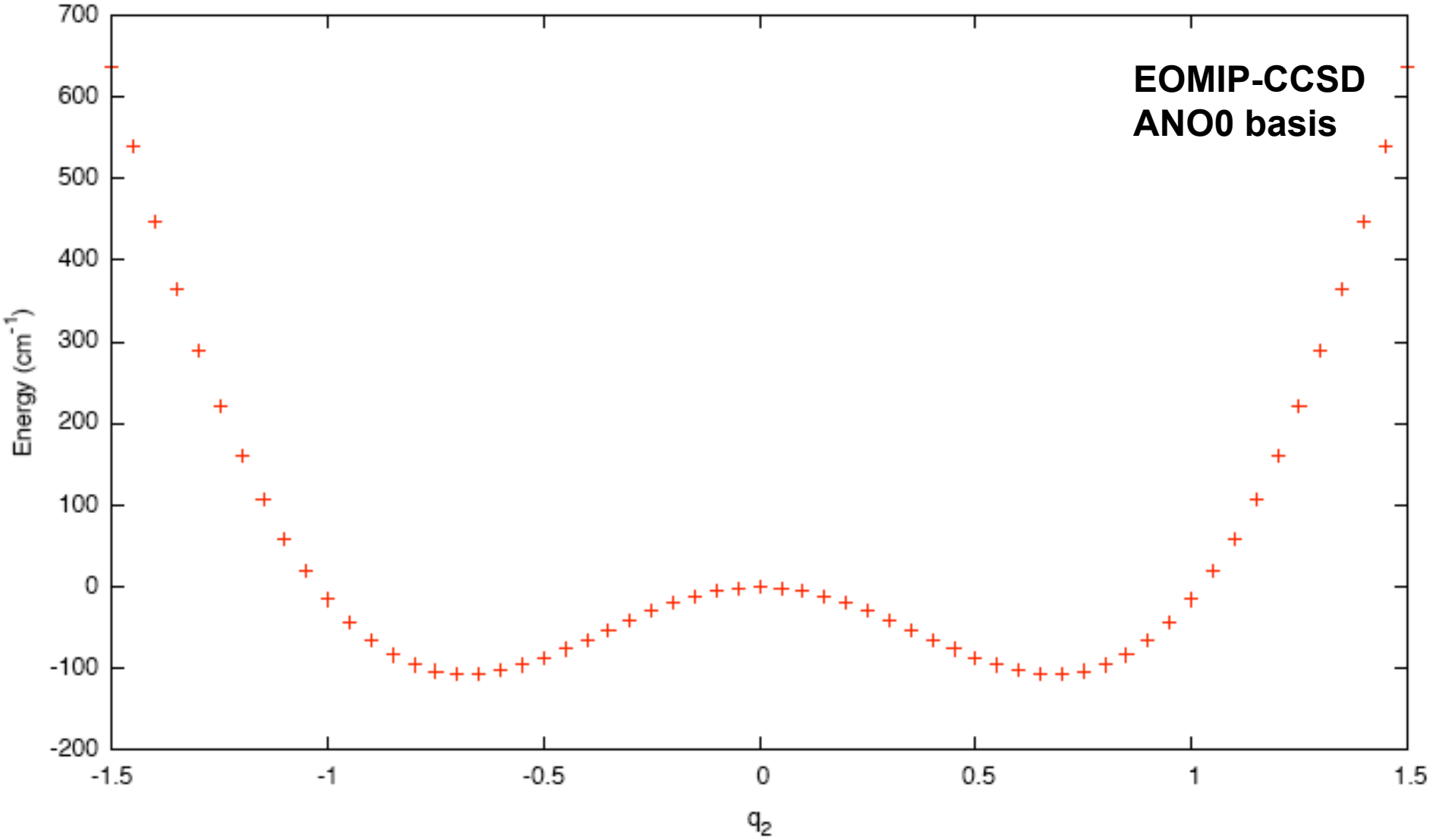
Similar conceptually to Green's function methods.

Completely avoids the symmetry breaking issue.


Solve coupled-cluster equations for reference state
$\hat{\mathbf{T}}$
Form
$\hat{\mathbf{H}} \equiv \exp(-\hat{\mathbf{T}})\mathbf{H}\exp(\hat{\mathbf{T}})$
-1 electron
Project onto basis
+1 electron
EOMIP-CC
EOMEE-CC
EOMEA-CC

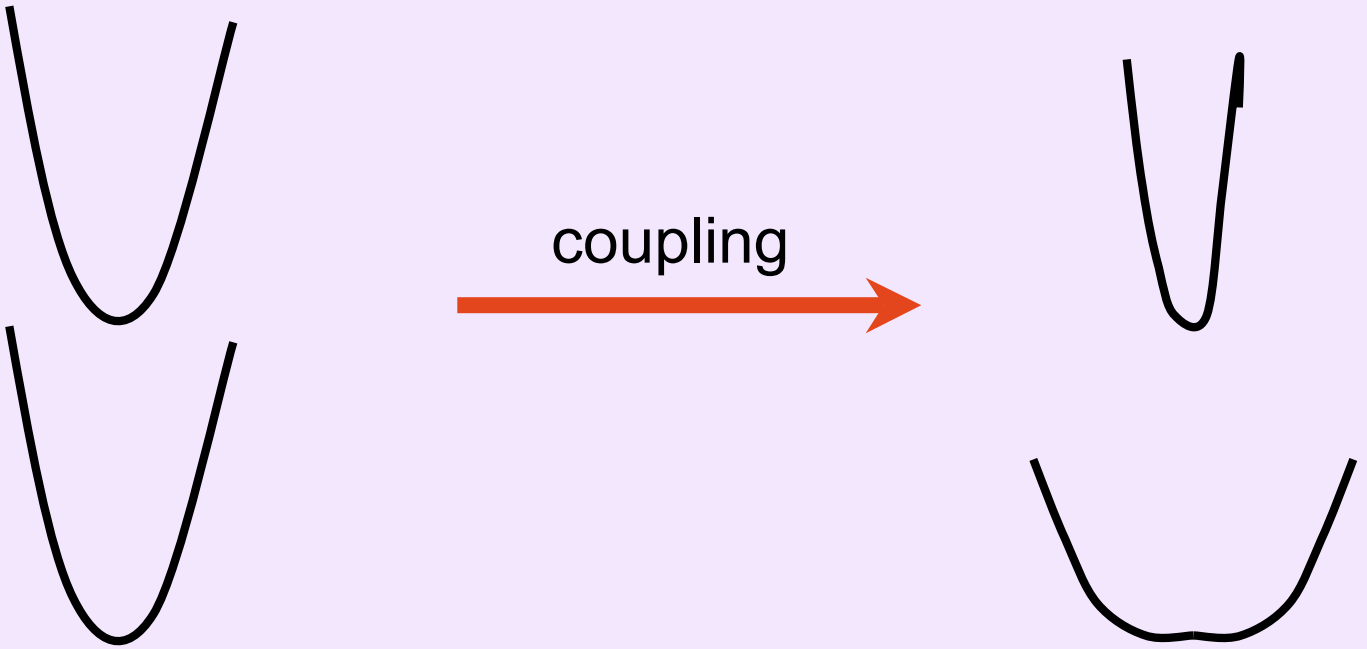

BNB-
Solve coupled-cluster equations for reference state
$\hat{T}$
Form
$\hat{H} \equiv \exp(-\hat{T})H\exp(\hat{T})$
Project onto basis
-1 electron
+1 electron
BNB
EOMIP-CC
EOMEE-CC
EOMEA-CC

$^2\Sigma_u$ state of BNB



But what are the physics underlying all of this?

Potential energy surface distortion is the Born-Oppenheimer manifestation of "vibronic coupling"



Where is the perturber? Can we seriously expect to describe this situation without explicitly considering it?

$$\frac{V_-}{hc} = \frac{1}{2}[-656]q^2 + \frac{1}{24}[6260]q^4 + \frac{1}{720}[-74950]q^6 + \cdots$$

$$\frac{V_+}{hc} = \frac{1}{2}[4212]q^2 + \frac{1}{24}[-6030]q^4 + \frac{1}{720}[74940]q^6 + \cdots$$

Two-by-two matrix review

$$M \equiv \begin{pmatrix} a & c \\ c & b \end{pmatrix}$$

$$\lambda_{\pm} = \frac{1}{2}\left\{ a + b \pm (a-b)\left[1 + \frac{4c^2}{(a-b)^2}\right]^{\frac{1}{2}} \right\}$$

$$(1+x)^{1/2} = 1 + \frac{x}{2} - \frac{x^2}{8} + \frac{x^3}{16} - \frac{5x^4}{128} + \cdots$$

$$\lambda_- = b - \frac{c^2}{a-b} + \frac{c^4}{(a-b)^3} - \frac{2c^6}{(a-b)^5} - \cdots$$

$$\lambda_+ = a + \frac{c^2}{a-b} - \frac{c^4}{(a-b)^3} + \frac{2c^6}{(a-b)^5} - \cdots$$

The adiabatic potential energy surfaces are very nearly equal to eigenvalues of the matrix:

$$\begin{pmatrix} \frac{1}{2}\omega_2 q_2^2 & \lambda q_2 \\ \lambda q_2 & \Delta_0 + \frac{1}{2}\omega_2 q_2^2 \end{pmatrix}$$

with

Only two parameters for the “complicated” coordinate

Strongly suggests that whatever electronic basis admits to this representation might be a very useful qualitative and interpretive tool for studying the spectroscopy.

What is this basis?

Simplest representation of V:
The "linear vibronic coupling" model

For BNB:

$$V_{LVC} = \begin{pmatrix} \kappa^A q_1 + \frac{1}{2}\omega_1^A q_1^2 + \frac{1}{2}\omega_2^A q_2^2 & \lambda^{AB} q_2 \\ \lambda^{AB} q_2 & \Delta_0 + \kappa^B q_1 + \frac{1}{2}\omega_1^B q_1^2 + \frac{1}{2}\omega_2^B q_2^2 \end{pmatrix}$$

Parametrization (major topic):

1. Quasidiabatic states coincide with adiabatic states along coordinates that do not have the coupling symmetry; plain old analytic gradient theory and plain old coupled-cluster theory work just fine.

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Parametrization (major topic):

1. Quasidiabatic states coincide with adiabatic states along coordinates that do not have the coupling symmetry; plain old analytic gradient theory and plain old coupled-cluster theory work just fine.

2. Coupling constants are usually approximated by

$$\lambda = \frac{1}{2}\left(\left[\frac{\partial^2 E^{upper}_{adiabatic}}{\partial q_c^2} - \frac{\partial^2 E^{lower}_{adiabatic}}{\partial q_c^2}\right]\Delta_0\right)^{\frac{1}{2}}$$

Simplest representation of V:
The "linear vibronic coupling" model

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$$V_{LVC} = \begin{pmatrix} \kappa^A q_1 + \frac{1}{2}\omega_1^A q_1^2 + \frac{1}{2}\omega_2^A q_2^2 & \lambda^{AB} q_2 \\ \lambda^{AB} q_2 & \Delta_0 + \kappa^B q_1 + \frac{1}{2}\omega_1^B q_1^2 + \frac{1}{2}\omega_2^B q_2^2 \end{pmatrix}$$

Parametrization (major topic):

…and the diabatic force constants for the coupling mode are assumed equal

$$\omega_2^A = \omega_2^B = \frac{1}{2}\left[\frac{\partial^2 E_{adiabatic}^{upper}}{\partial q_2^2} + \frac{\partial^2 E_{adiabatic}^{lower}}{\partial q_2^2}\right]$$

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Lower state adiabatic force field becomes:

$$
\begin{aligned}
\phi^{-}_{22} &= \omega^{B}_{2} - \frac{2\lambda_2^2}{\Delta_0} \\
\phi^{-}_{122} &= \Phi^{B}_{122} + \frac{2\lambda_2^2(\kappa_1^A - \kappa_1^B)}{\Delta_0^2} - \frac{4\lambda_2\lambda_{12}}{\Delta_0} \\
\phi^{-}_{2222} &= \Phi^{B}_{2222} + \frac{24\lambda_2^4}{\Delta_0^3} + \frac{12\lambda_2^2(\omega_2^A - \omega_2^B)}{\Delta_0} \\
\phi^{-}_{1122} &= \Phi^{B}_{1122} - \frac{4\lambda_2^2\left(\kappa_1^A - \kappa_1^B\right)^2}{\Delta_0^3} + \frac{2\lambda_2^2(\omega_1^A - \omega_1^B)}{\Delta_0} \\
&\quad + \frac{8\lambda_2\lambda_{12}(\kappa_1^A - \kappa_1^B)}{\Delta_0^2} - \frac{4\lambda_{12}^2}{\Delta_0} - \frac{4\lambda_2\lambda_{112}}{\Delta_0}
\end{aligned}
$$

EOMIP-CCSDT/ANO1 basis

		Diabatic		Ab initio		Model Hamiltonian	
	Anion	$^2\Sigma_u$	$^2\Sigma_g$	$^2\Sigma_u$	$^2\Sigma_g$	$^2\Sigma_u$	$^2\Sigma_u$
ϕ_{11}	1130	1110	1140	1110	1140	1110	1140
ϕ_{22}	1784	1778	1778	-341	3897	-341	3897
ϕ_{111}	261	255	255	253	257	255	255
ϕ_{122}	388	391	391	170	617	172	610
ϕ_{1111}	45	45	45	45	45	45	45
ϕ_{1122}	70	71	71	55	88	54	88
ϕ_{2222}	112	114	114	4931	-4701	4890	-4662

Some results for BNB (Telluride, 2008)

1. Solve for eigenvalues of diabatic model Hamiltonian

2. Diagonalize diabatic potential

3. Solve variational problem on adiabatic potential

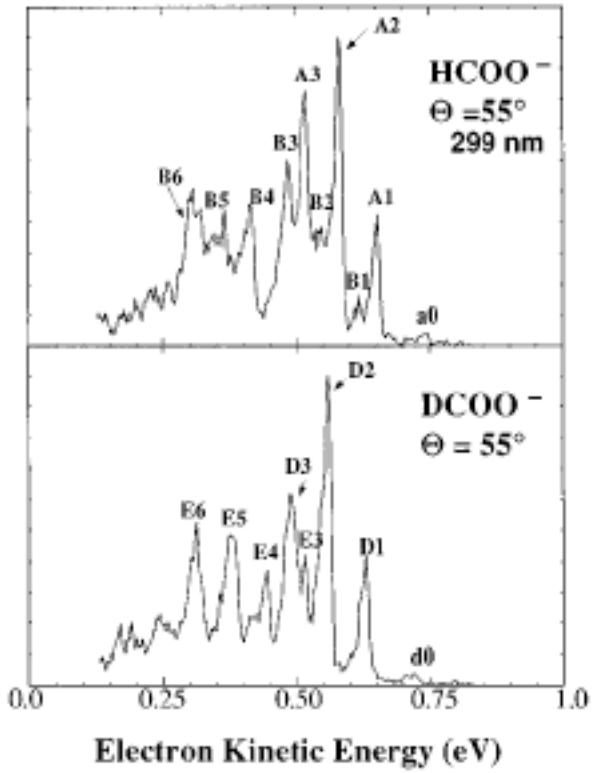
4. Compare

Study of HCO_2 and DCO_2 by negative ion photoelectron spectroscopy

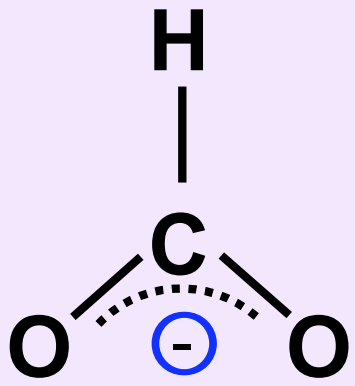
E. H. Kim, S. E. Bradforth,[a] D. W. Arnold,[b] R. B. Metz,[c] and D. M. Neumark[d]
Department of Chemistry, University of California, Berkeley, California 94720

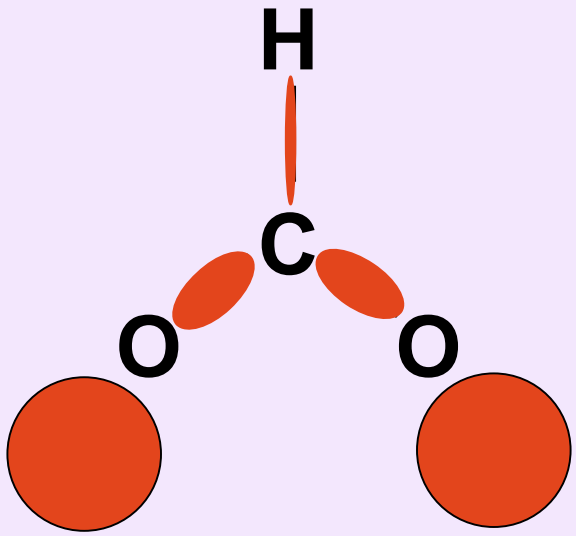
(Received 26 June 1995; accepted 1 August 1995)

Photoelectron spectra of HCO_2^- and DCO_2^- at 299 nm, 266 nm, and 213 nm are reported. Photodetachment accesses the $^2A_1$, $^2B_2$, and $^2A_2$ states of the formlyoxyl radical, HCO_2. The $^2A_1$ state is assigned as the HCO_2 ground state, although it is nearly degenerate with the $^2B_2$ state (T_0=0.027 eV), and the $^2A_2$ state lies at T_0=0.536 eV. The electron affinity of HCO_2 is 3.498±0.015 eV. The spectra show partially resolved vibrational features, primarily involving progressions in the CO_2 bending mode. The irregular appearance of the spectra in some regions suggests vibronic coupling between the $^2A_1$ and $^2B_2$ states. The possible role of the HCO_2 radical as an intermediate in the OH+CO→H+CO_2 reaction and in H+CO_2 inelastic scattering is discussed. © *1995 American Institute of Physics.*

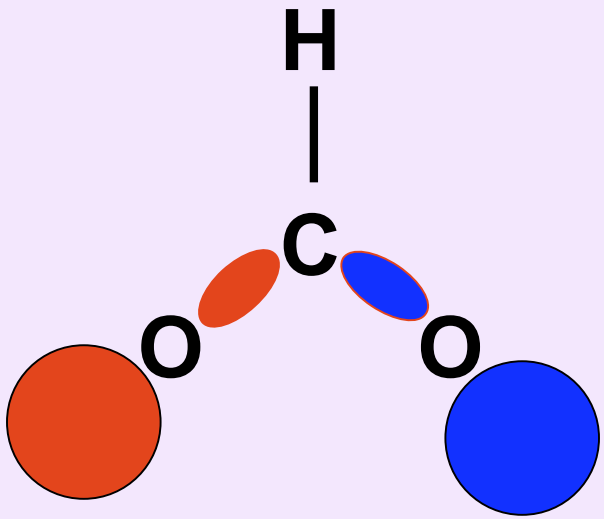


All three electronic bands show resolved vibrational structure. The observed progressions are primarily due to excitation of the CO_2 bend (the ν_3 mode) upon photodetachment of the anion. Simulations of the spectra show that the $^2A_2$ band consists of a 3_0^n progression superimposed on a $2_0^1 3_0^n$ combination band. While much of the $^2A_1$ and $^2B_2$ bands could be simulated by only permitting transitions involving totally symmetric vibrational modes, this was insufficient to reproduce many of the spectral features. It therefore appears likely that vibronic coupling between these two states via the b_2 vibrational modes is contributing to the spectra.





HOMO-1 (a_1)

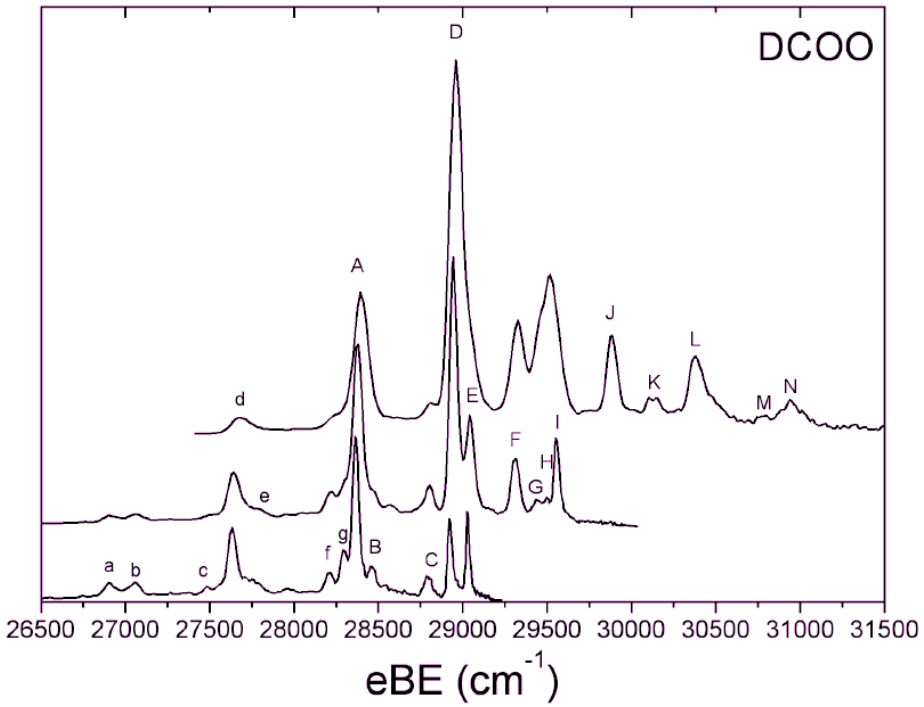


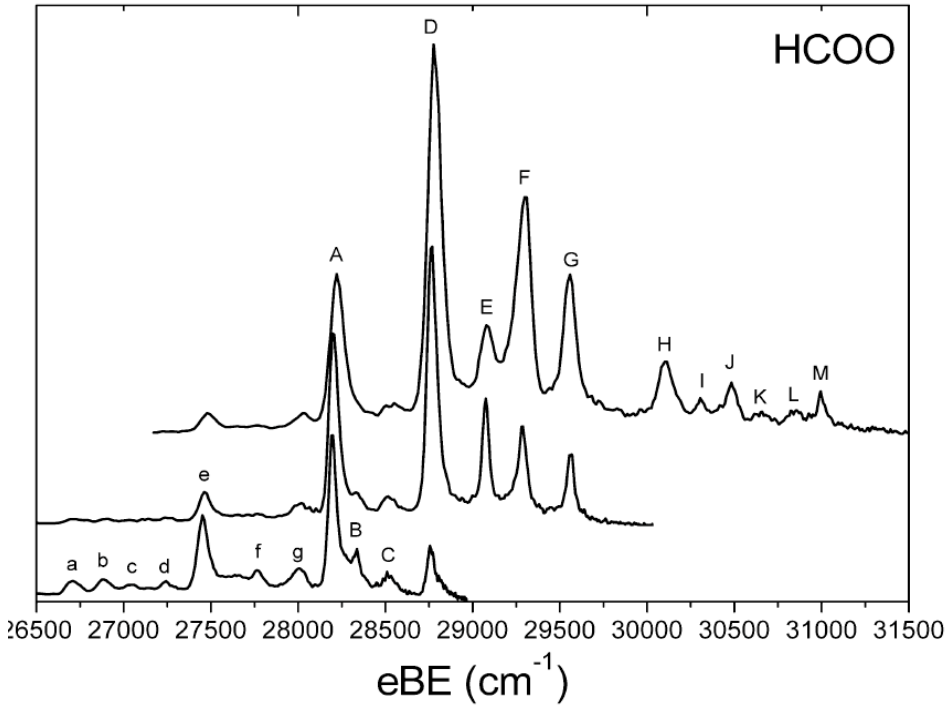
HOMO (b_2)

Expectations:

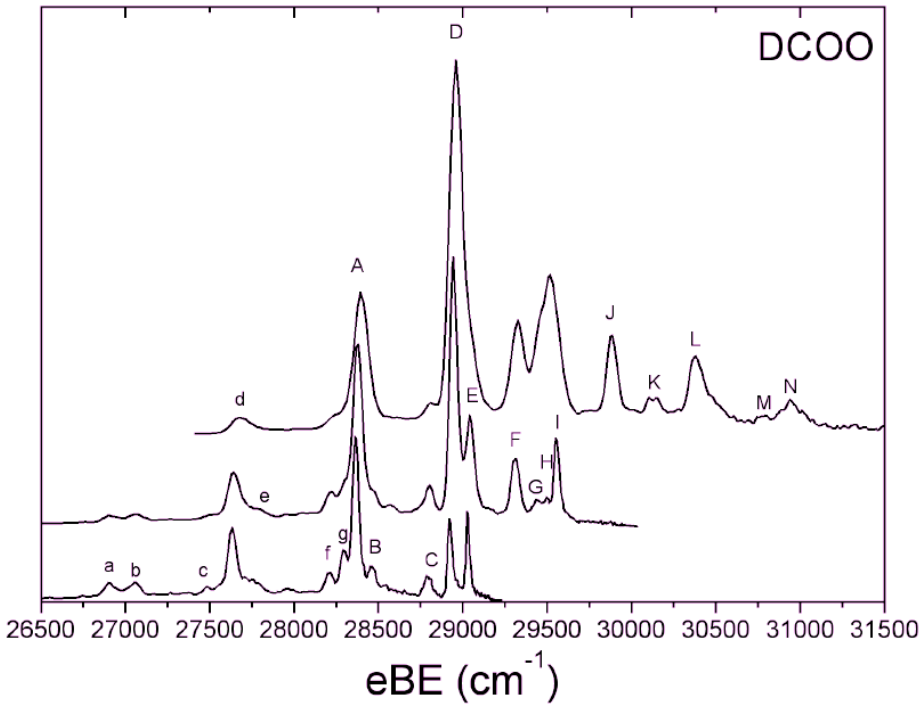
Bond angle larger in $^2A_1$ state

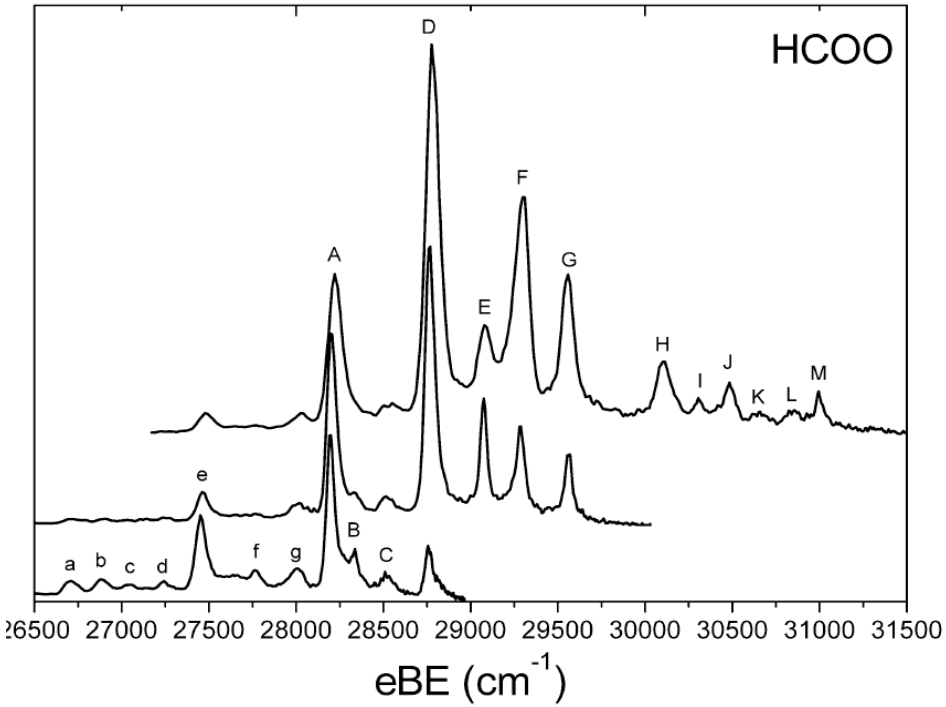
	Anion	$^2B_2$	$^2A_1$
r_{CH}	1.133	1.093	1.159
r_{CO}	1.255	1.257	1.227
θ_{OCO}	130.6	112.5	144.8





Is it possible to get reasonable assignments for these spectra?

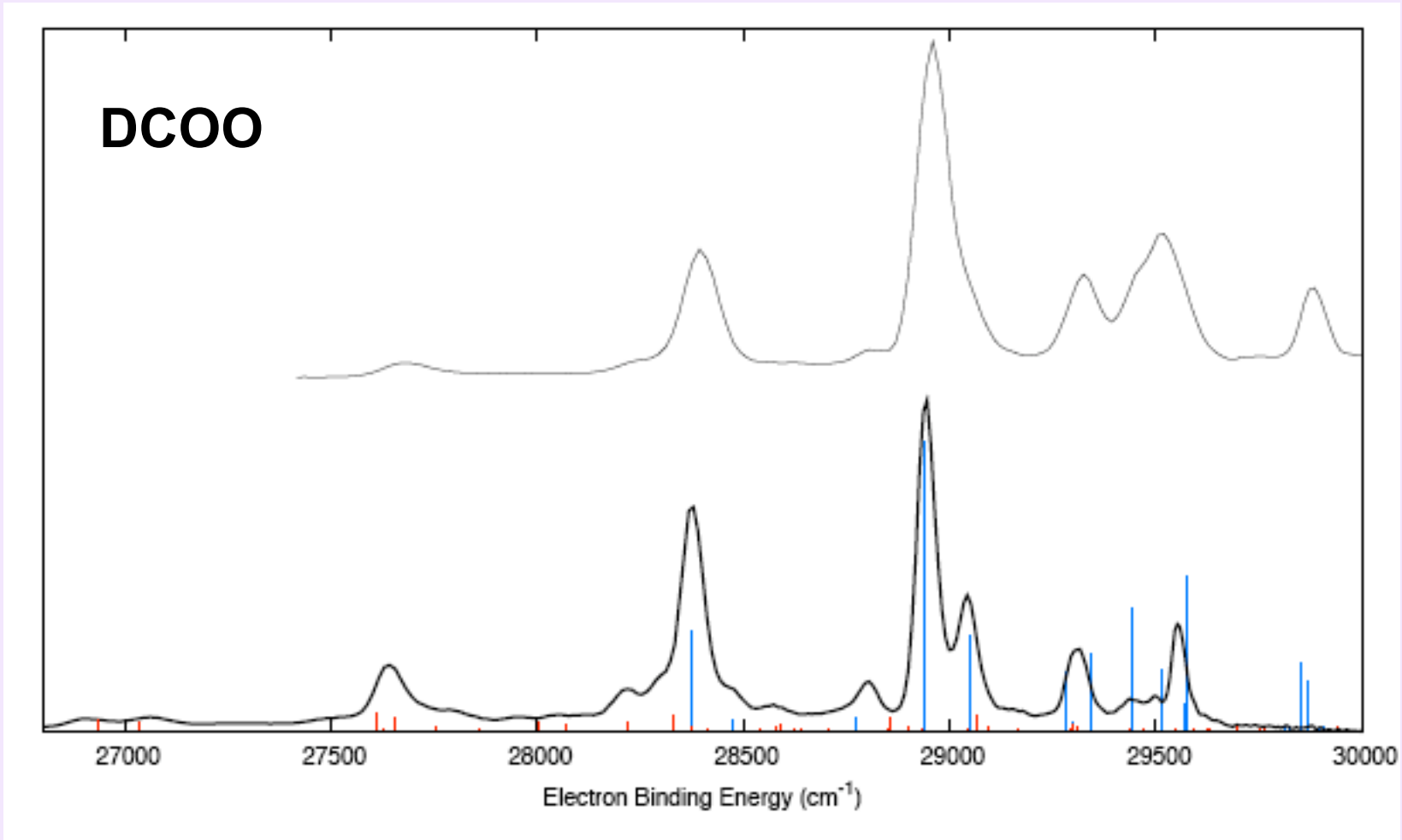




Is it possible to get reasonable assignments for these spectra?

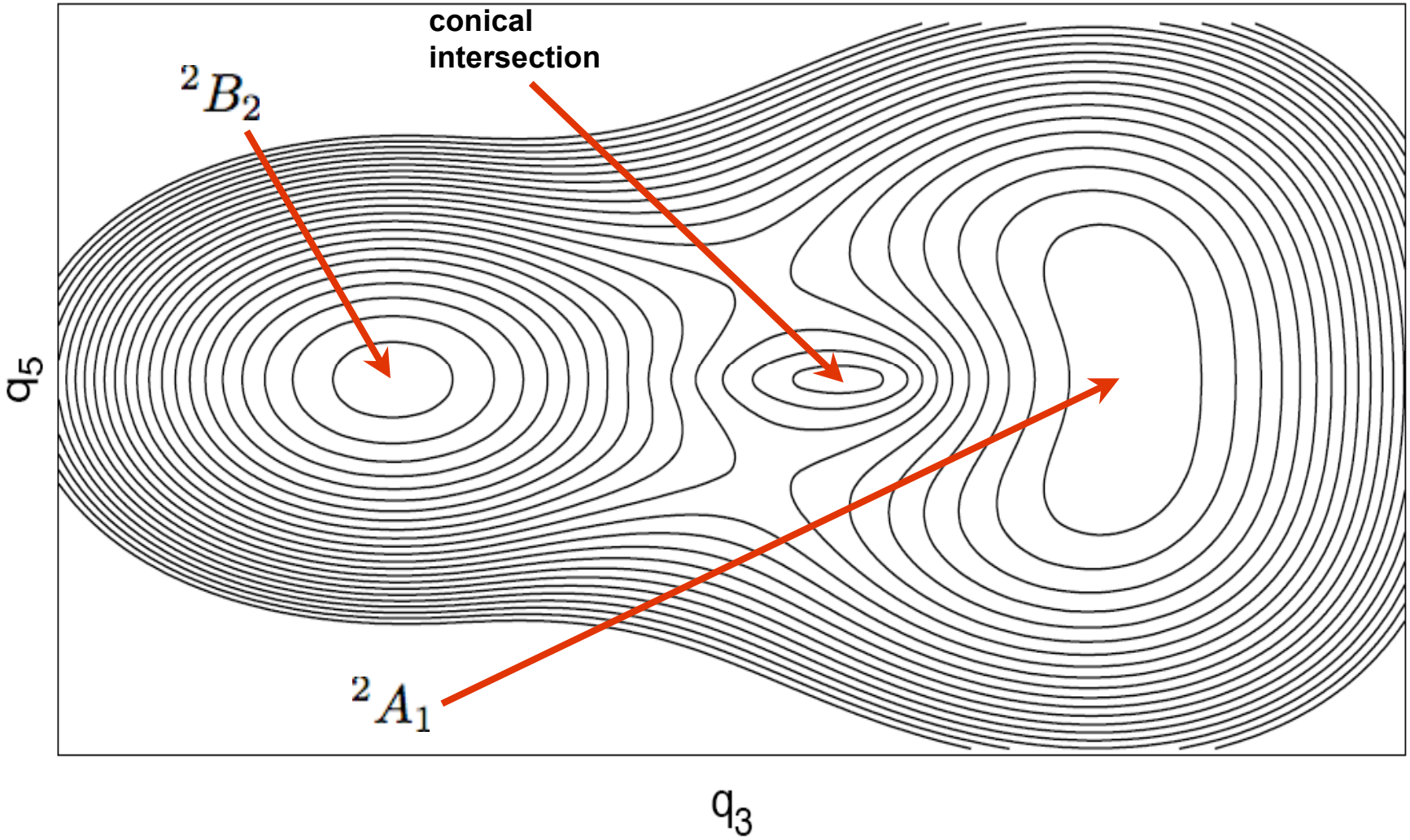
Approach:

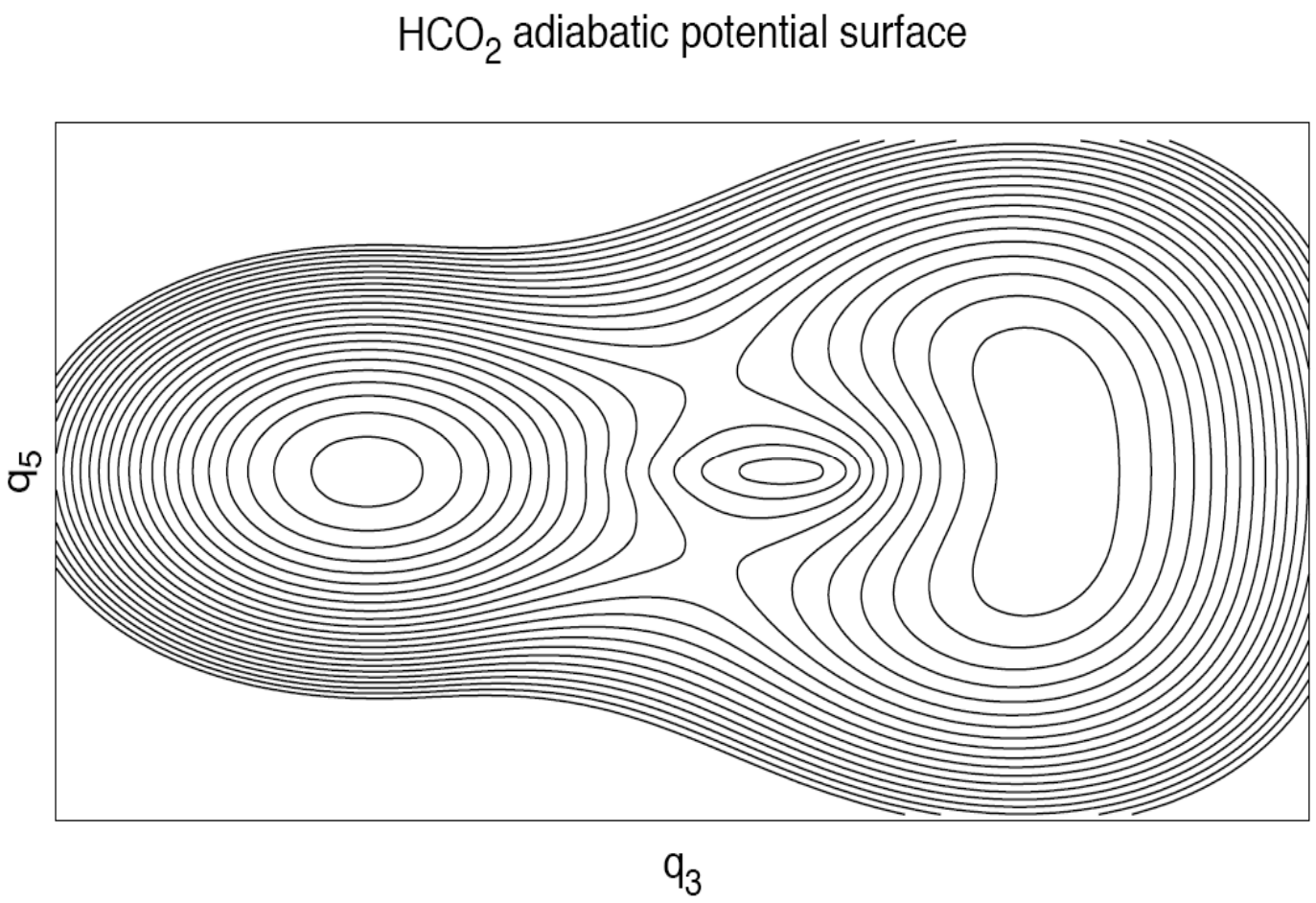
Adiabatic parametrization
Quartic expansion
Analytic coupling constants


DCOO
27000
27500
28000
28500
29000
29500
30000
Electron Binding Energy (cm-1)

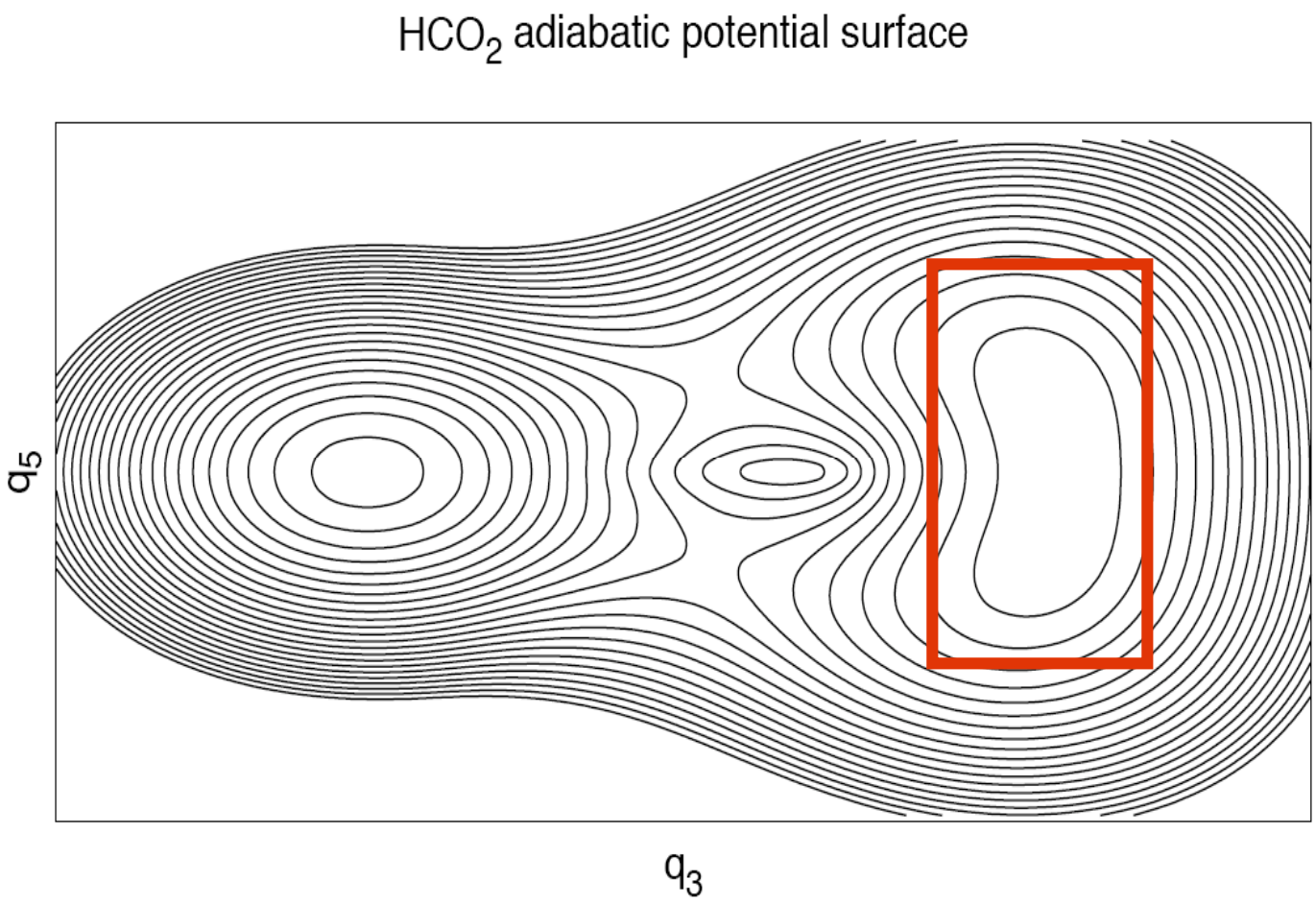
A	28362		0	0	0_0	*p*
B	28449		87	100	0_0	*s*
C	28792		430	400	5_1	*s*
D	28925		563	565	3_1	*p*
E	29028		666	678	3_1	*s*
F	29310		948	910,970	$3_1 5_1$; 5_1	*s*
G	29446		1084	1068	3_2	*p*
H	29498		1136	1138	2_1	*p*
I	29555		1193	1200	3_2	*s*
J	29882		1520	1478,1492	1_1; $3_1 5_2$	*p*

HCO_2 adiabatic potential surface





$^2A_1$ sits *ca.* 525 cm^{-1} higher than $^2B_2$ state,
and is ***not*** a minimum on the potential surface!



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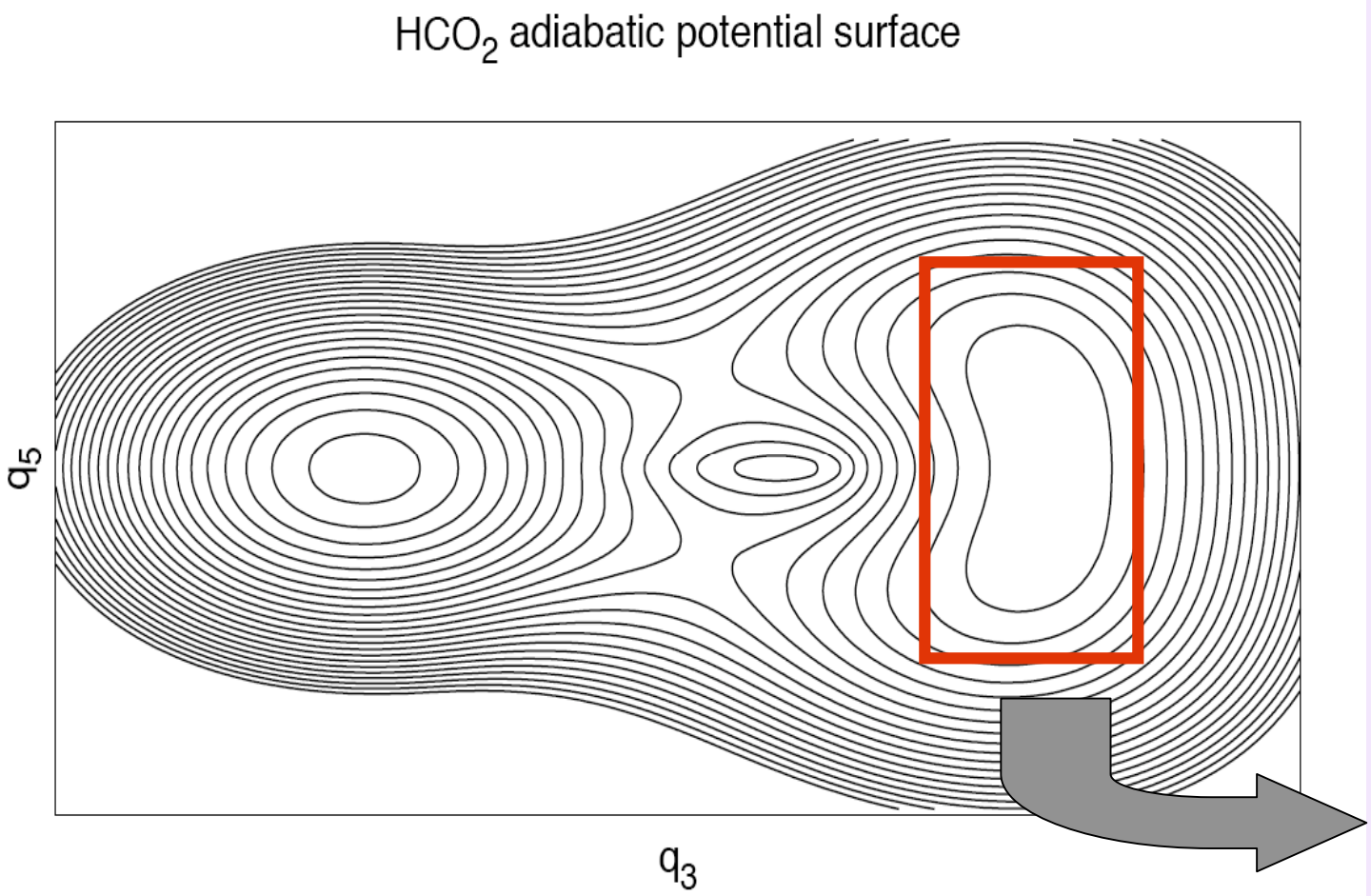

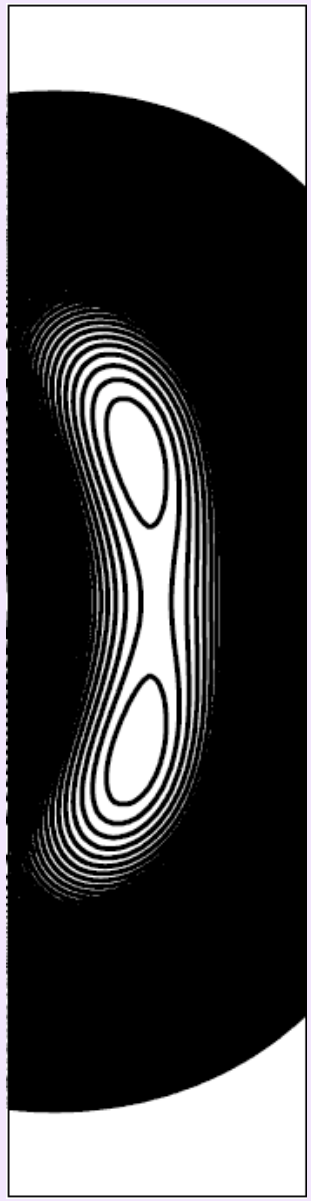

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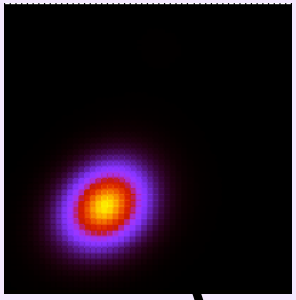
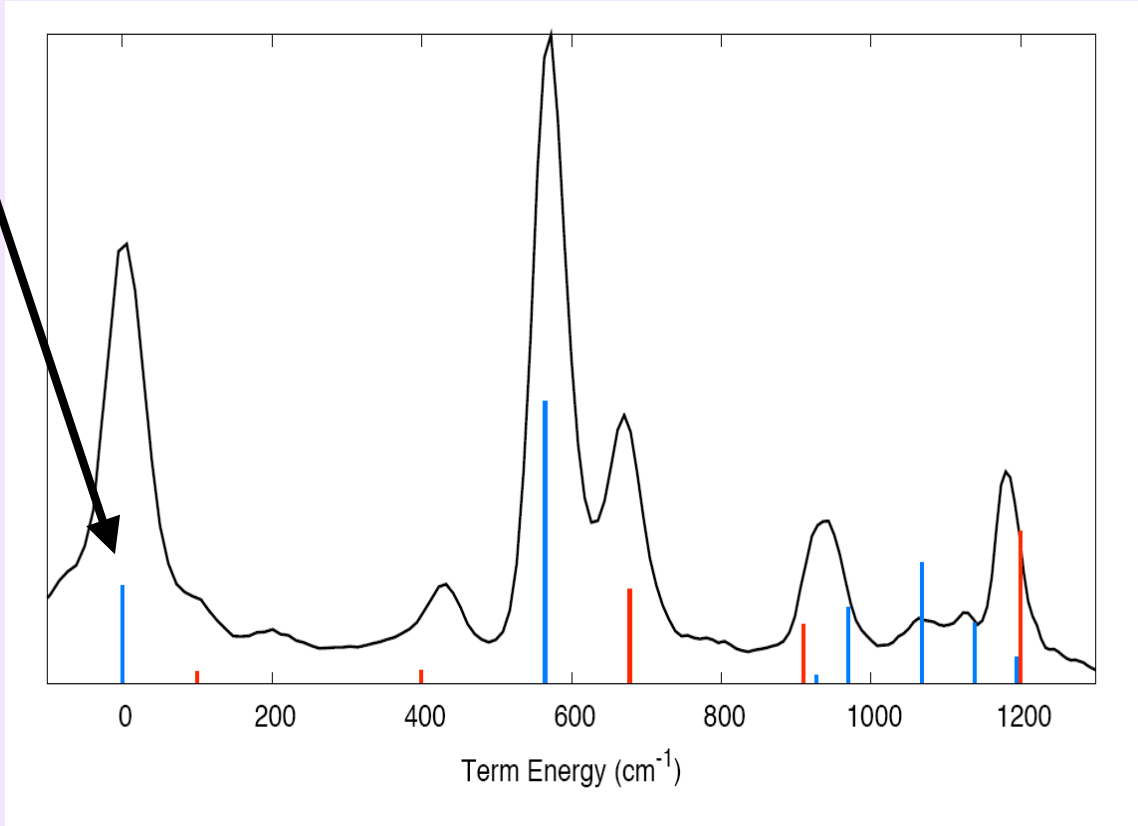
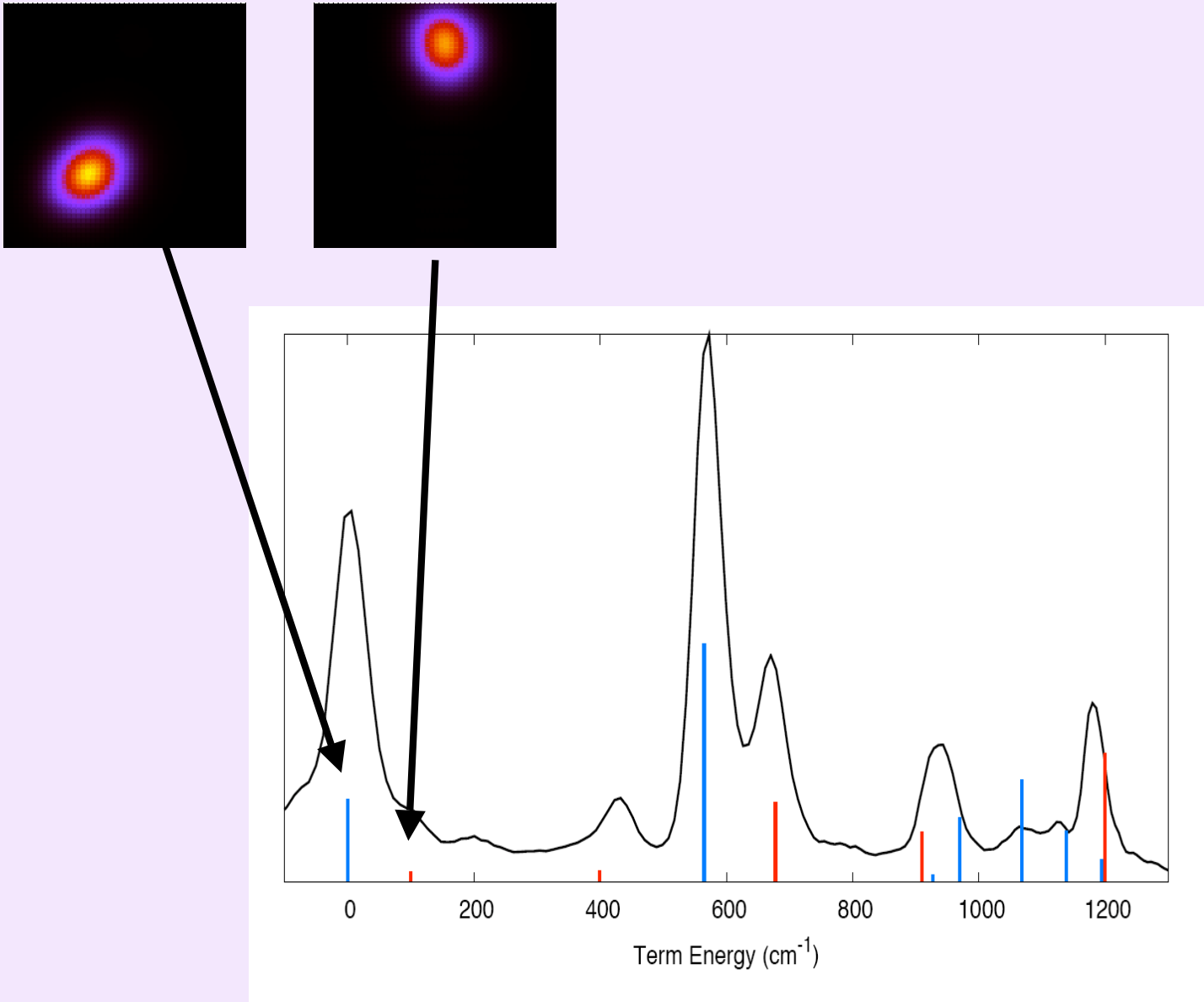
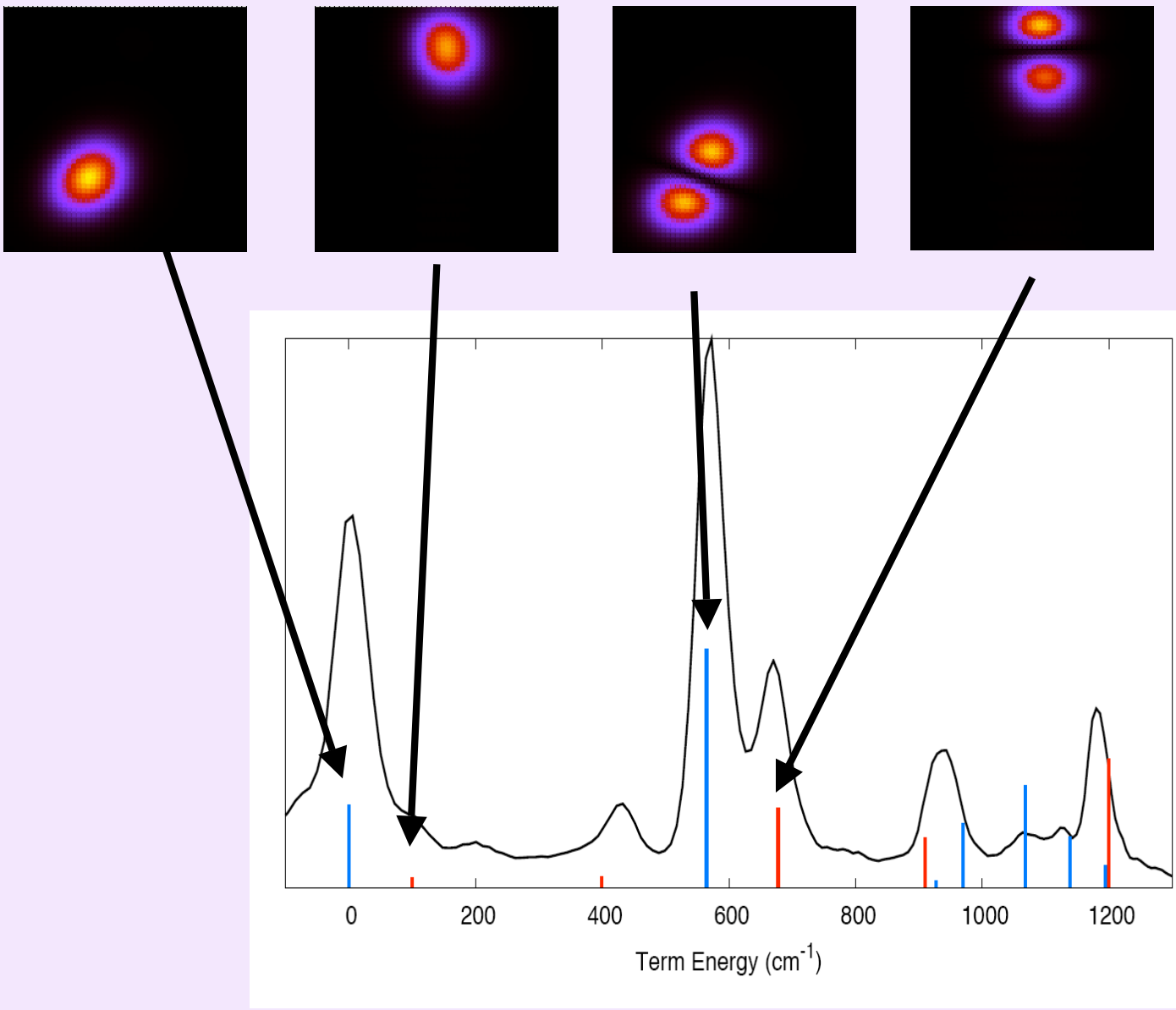



0
200
400
600
800
1000
1200
Term Energy (cm-1)


0
200
400
600
800
1000
1200
Term Energy (cm-1)


0
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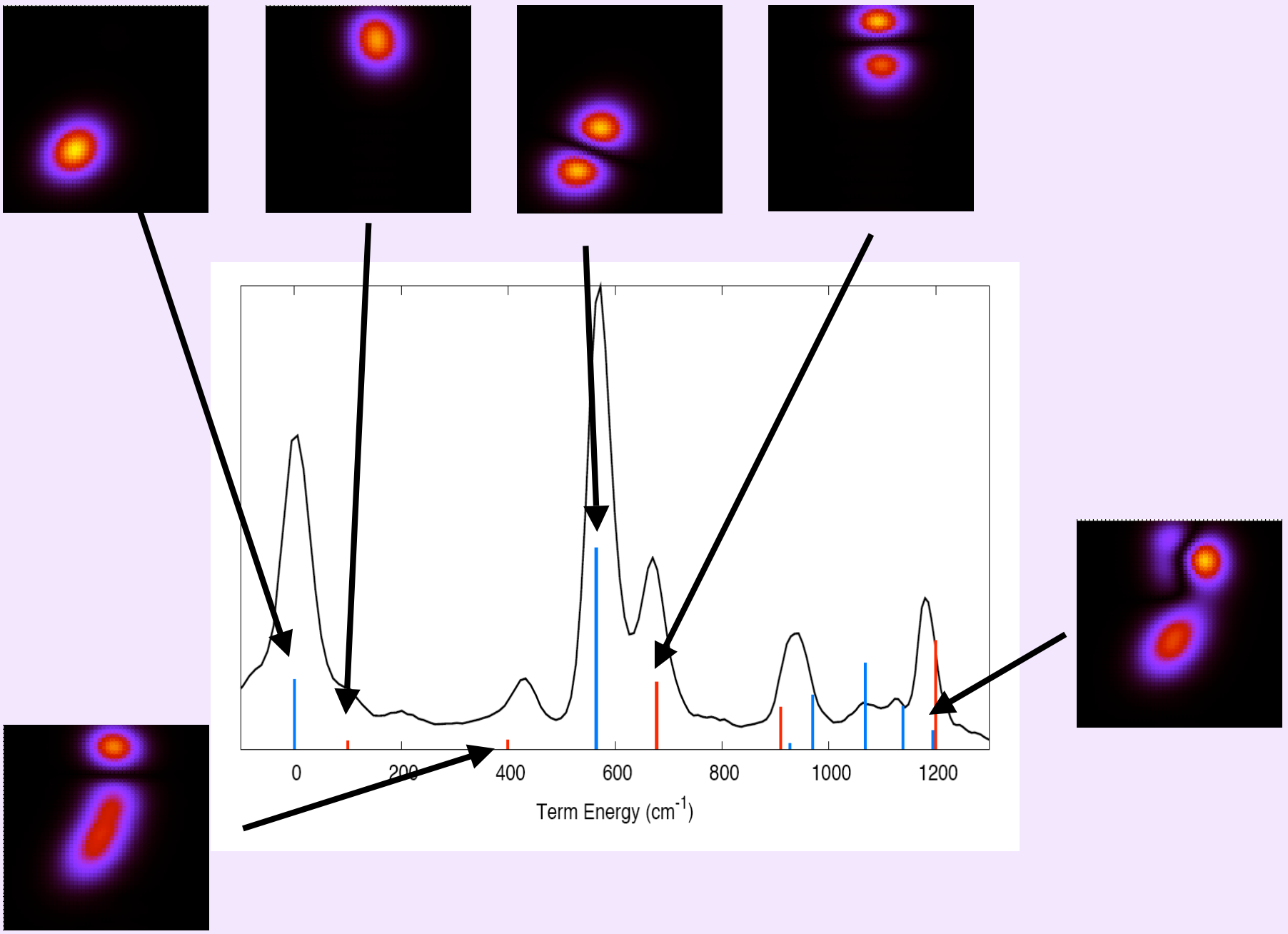
Term Energy (cm-1)


0
200
400
600
800
1000
1200
Term Energy (cm-1)

Conclusions

Vibronic coupling calculations, in addition to being useful in a qualitative sense in interpreting spectra, can be made quantitative

Calculations on BNB show that "non-adiabatic" effects on level positions can be extremely large (50-100 cm^{-1}), raising the question of whether brute-force QC is the best way to calculate these things.

Analytic calculation of diabatic couplings is enormously useful, especially for complicated multimode systems.