Influence of molecular geometry on positron binding to molecules*

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In collaboration with S. Ghosh, A. Swann, G. Gribakin, and C. Surko

*This work supported by US NSF grant PHY2010699

Summary

- Low energy positrons are observed to bind to most polyatomic molecules.
  - → Downshift of vibrational Feshbach resonances provide a direct measurement of the positron-molecule binding energy, E_B.
  - → E_B has been measured for > 90 molecules, covering a wide variety of species, symmetries, and composition.

- Ab-initio calculations of E_B are very difficult, thus we often make empirical fits to the data using global parameters (e.g., polarizability, dipole moment), but these often fail when making new predictions.

- Here, we discuss 2 studies:

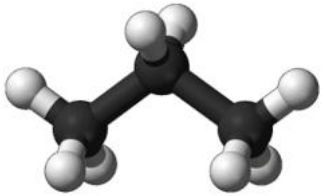
  1) Select group of isomer molecule pairs that demonstrate the strong effect that molecular geometry appears to have on the binding energy

  2) Large study of molecules with chlorine substitutions that demonstrates how effective potential model combined with the full geometry can capture these effects.

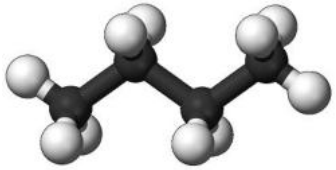
Molecule Names and Geometry

n-alkanes

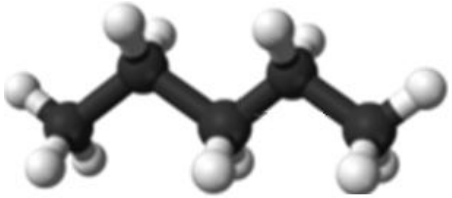
propane
C_3H_8



n-butane
C_4H_{10}

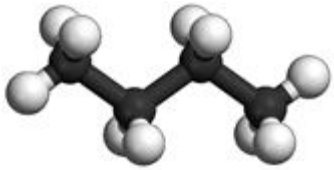


n-pentane
C_5H_{12}

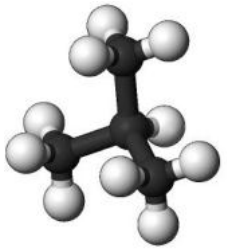


isomers

butane, C_4H_{10}

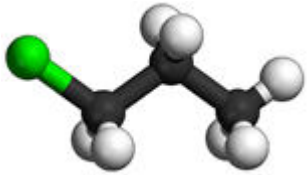


isobutane, C_4H_{10}

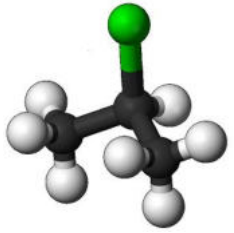


substitutions

1-chloropropane
C_3H_7Cl



2-chloropropane
C_3H_7Cl



Some History -- "Rapid" Annihilation

Phys. Rev. 83, 866 (1951)

Three-Quantum Decay of Positronium*

MARTIN DEUTSCH
Department of Physics and Laboratory for Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received June 25, 1951)

ing 8×10^{-8} sec are due to ortho-positronium. At lower pressures a second group appears which is not suppressed by NO and shows a rapid decay depending strongly on pressure. We make the hypothesis that this behavior is due to a large "positron attachment coefficient" of CCl_2F_2 which results in an anomalously large molecular annihilation cross section for free positrons. It may not be accidental that Freon is known to show extremely strong electron attachment.

J. Chem. Phys. 39, 3160 (1963)

Annihilation Rates and Collision Complex of Positrons in Freon-12

J. H. GREEN AND S. J. TAO
Department of Nuclear and Radiation Chemistry, University of New South Wales, Sydney, Australia
(Received 5 August 1963)

It is tempting to conclude that these observations are consistent with the formation of a collision complex ("compound"), $CCl_2F_2e^+$, between Freon and positrons of low kinetic energy.

Phys. Rev. Lett. 11, 493 (1963)

RAPID ANNIHILATIONS OF POSITRONS IN POLYATOMIC GASES*

D. A. L. Paul and L. Saint-Pierre†
Royal Military College of Canada, Kingston, Ontario, Canada
(Received 23 October 1963)

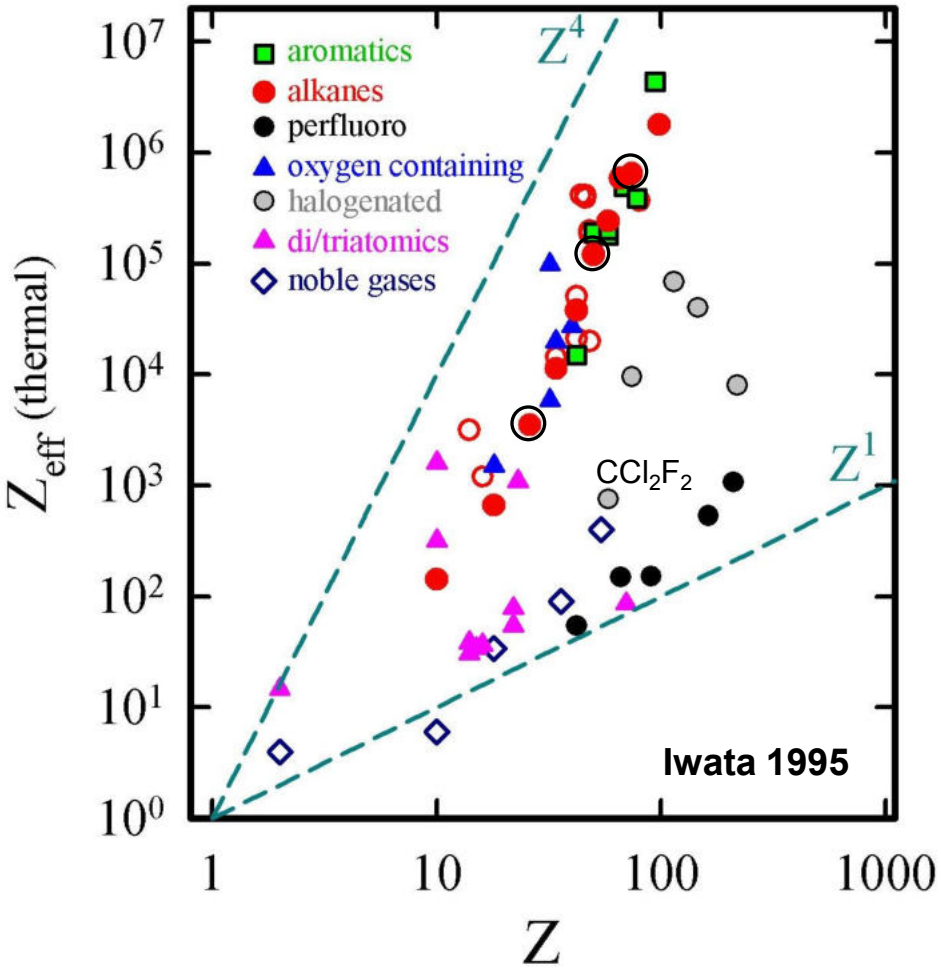
This report presents experimental values of the annihilation rates in gases of slow positrons which have failed to form positronium. The observed values for argon, methane, ethane, propane, *n*-butane, isobutane, and carbon tetrachloride are found to exceed the values derived from Eq. (1) below by factors ranging from 3 to 700.

λ_{Dirac}

In view of the findings of Khare,[6] we cannot ignore the possibility of the formation of positron-molecular ions in polyatomic gases. For polyatomic molecules where the polarizability is high, it would seem likely that bound states should exist. The formation of such a state will generally result in annihilation taking place within a few times 10^{-9} sec. An observed value of λ in the gas would then represent the rate of capture of the positron to form a bound state plus the direct annihilation rate. The probability of

"Rapid" Annihilation (thermal e+)

Z = number of electrons



Dirac annihilation rate:

$$\lambda_{Dirac} = n_e \pi r_0^2 c$$

for atoms and molecules:

$$n_e \approx Z n_m$$

→ for simple collisions:

$$\lambda_{meas} \sim Z \lambda_{Dirac}$$

Normalized annihilation rate:

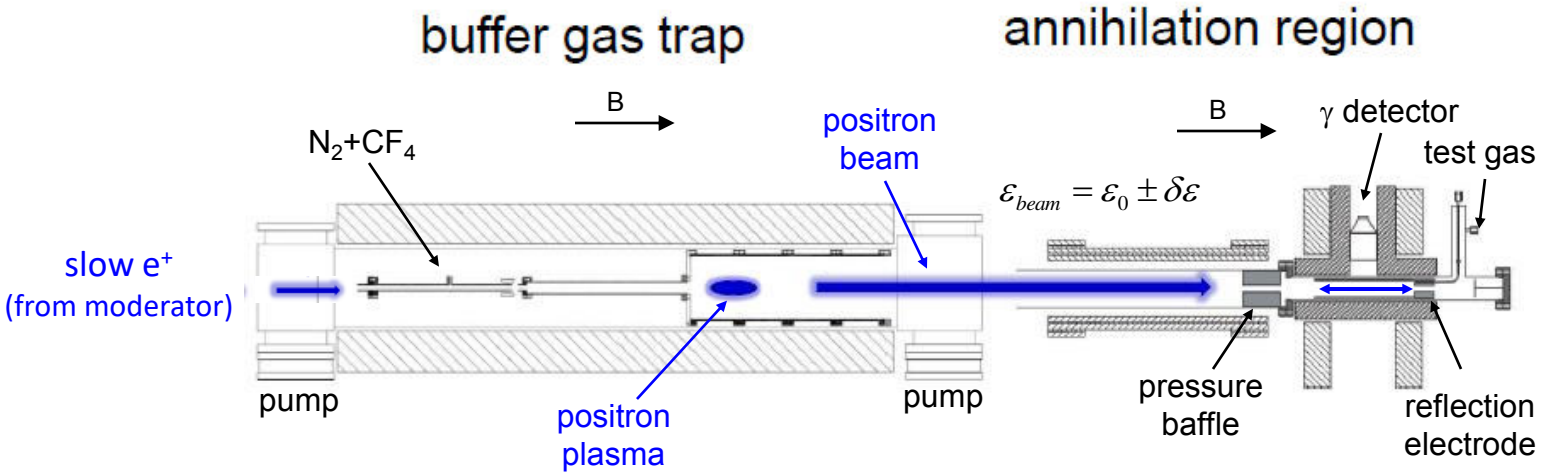
$$Z_{eff} = \frac{\lambda_{meas}}{\lambda_{Dirac}}$$

for most molecules:

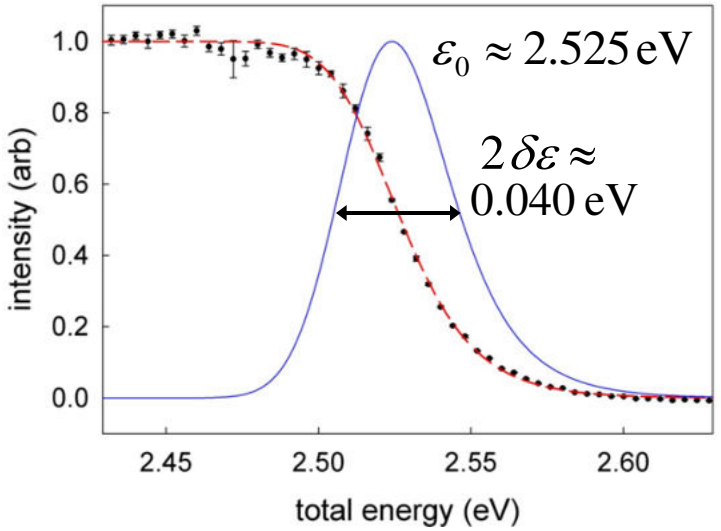
$$Z_{eff} >> Z$$

Resonances and bound states?

UCSD Positron Beam Experiment



RPA measurement of total energy spread of beam



High resolution positron beam*

Parallel Energy FWHM ~ 25 meV

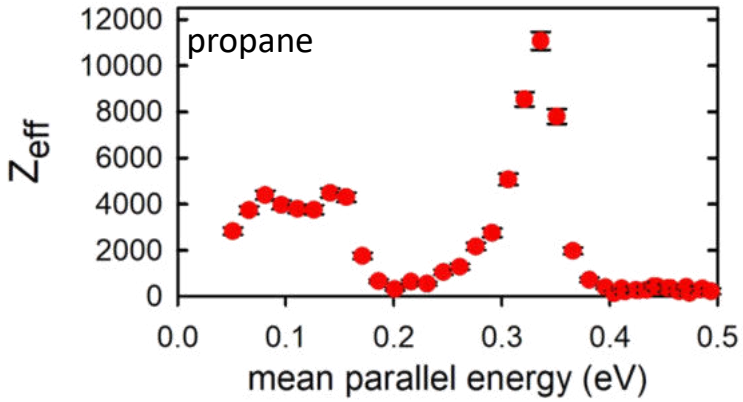
Perpendicular Energy ~ 20 meV

Total Energy Spread ~ 40 meV

Tunable from 50 meV < ε_0 < 100 eV

*Barnes (2003), Natisin (2015)

Propane Spectra Fitting



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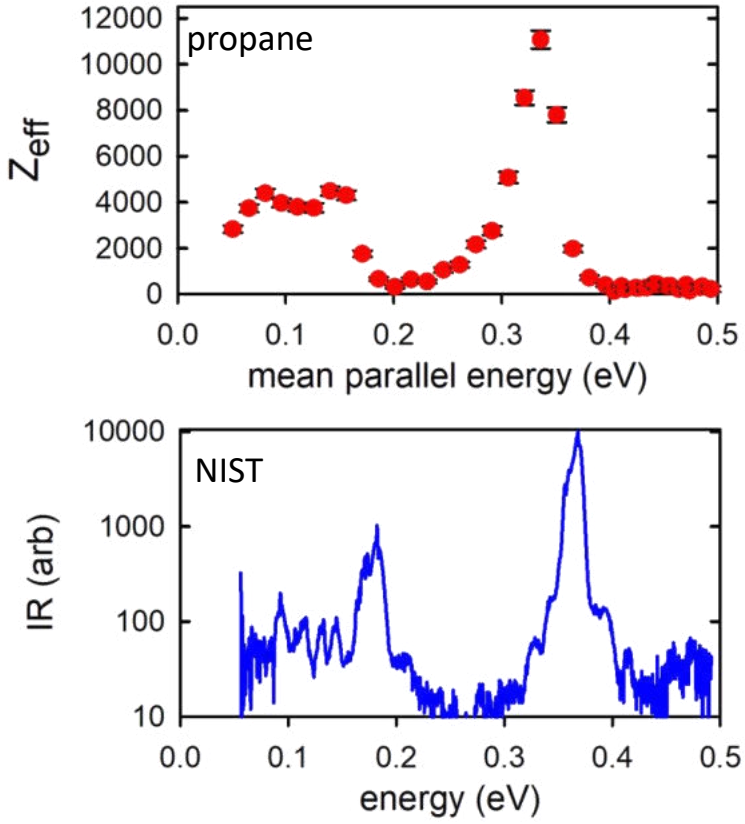

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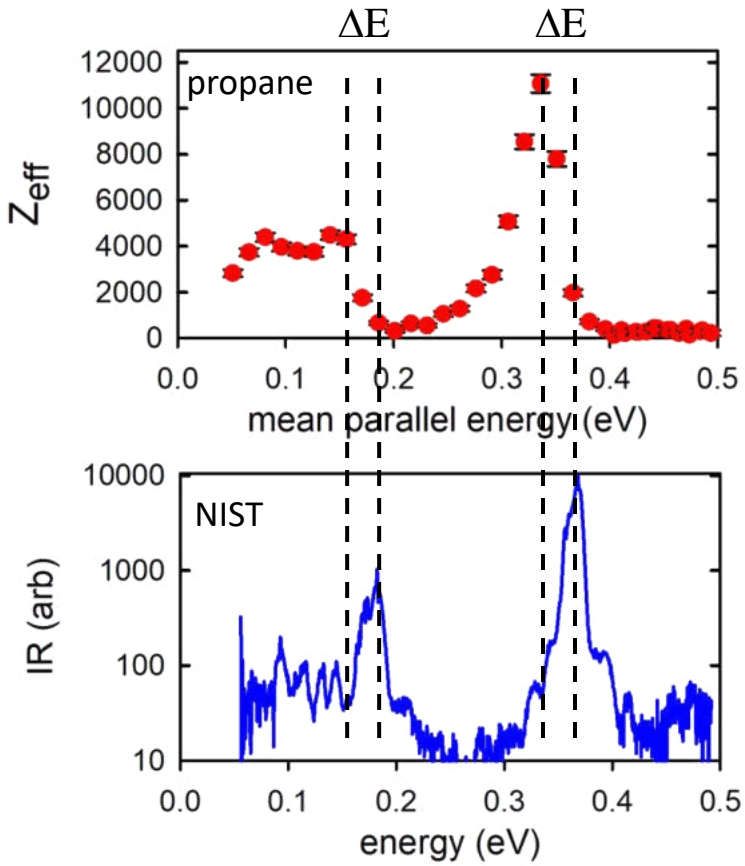

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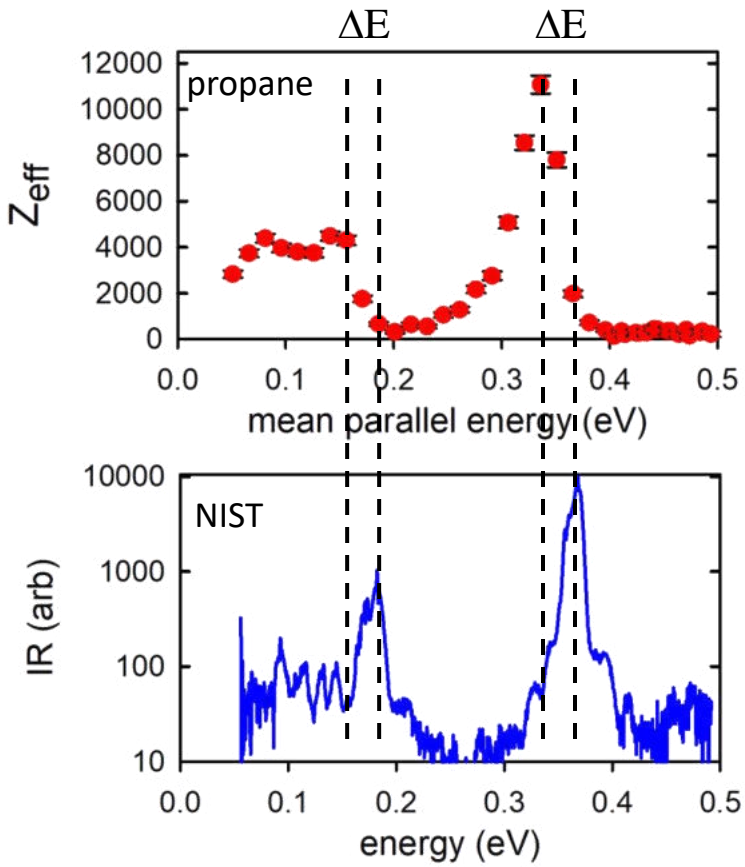
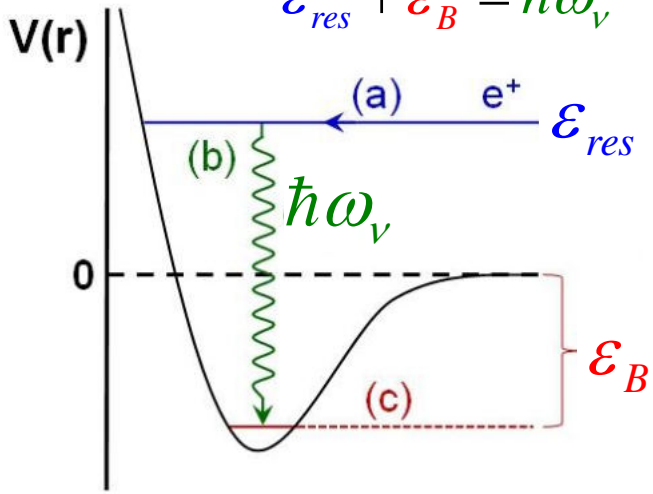


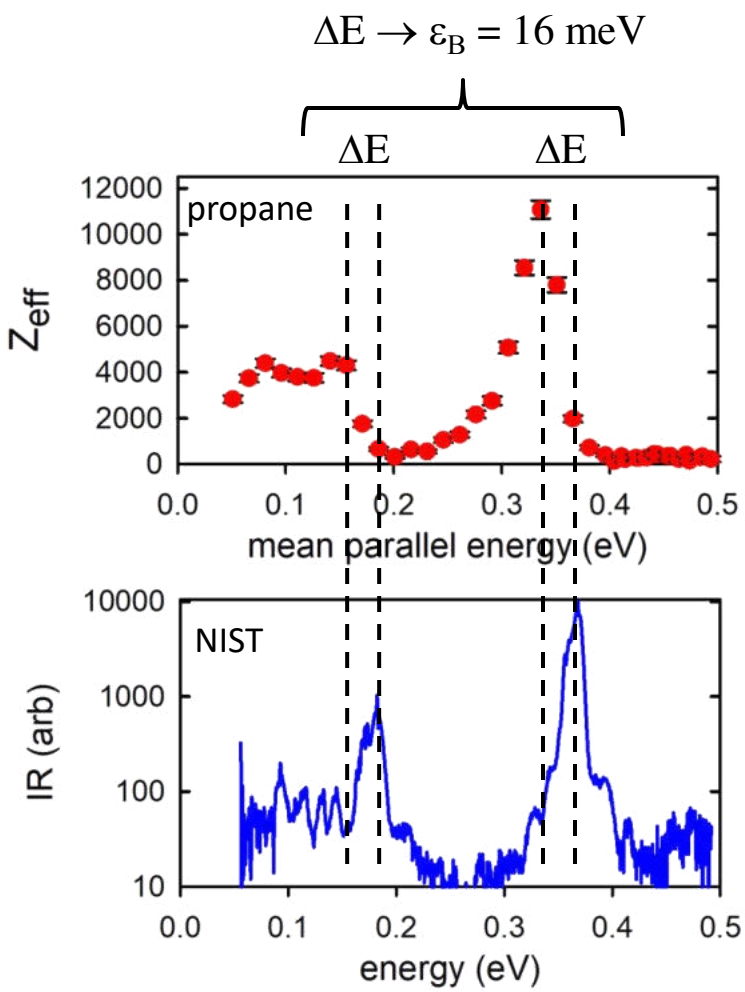
Vibrational Feshbach Resonance (VFR)*

$$\varepsilon_{res} + \varepsilon_B = \hbar\omega_v$$



*Gribakin 2002 and Gribakin and Lee 2006

Propane Spectra Fitting



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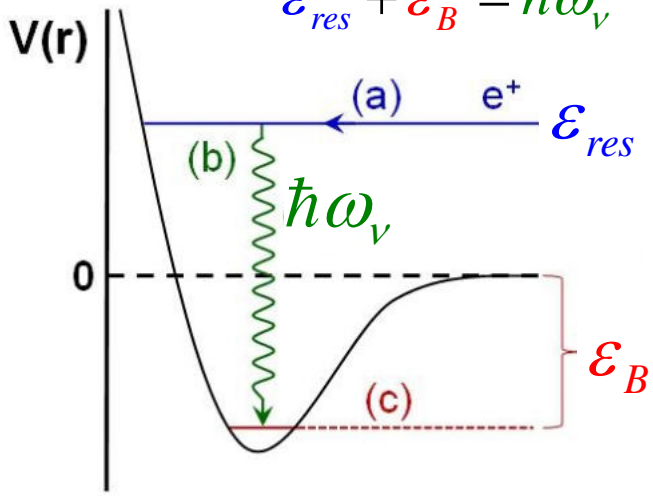
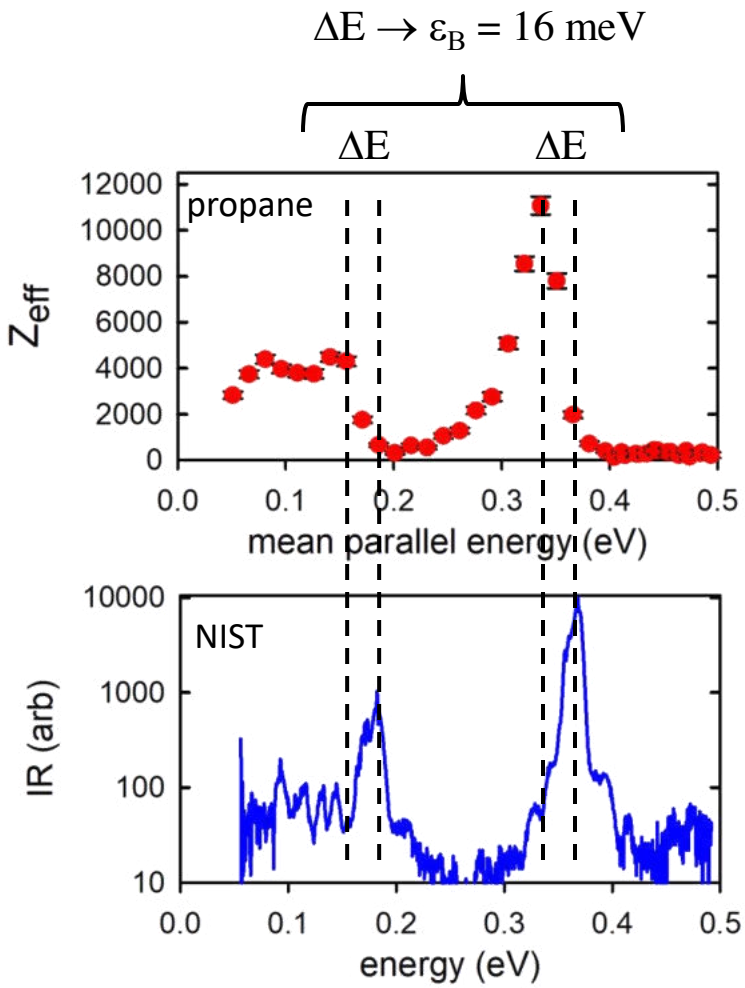


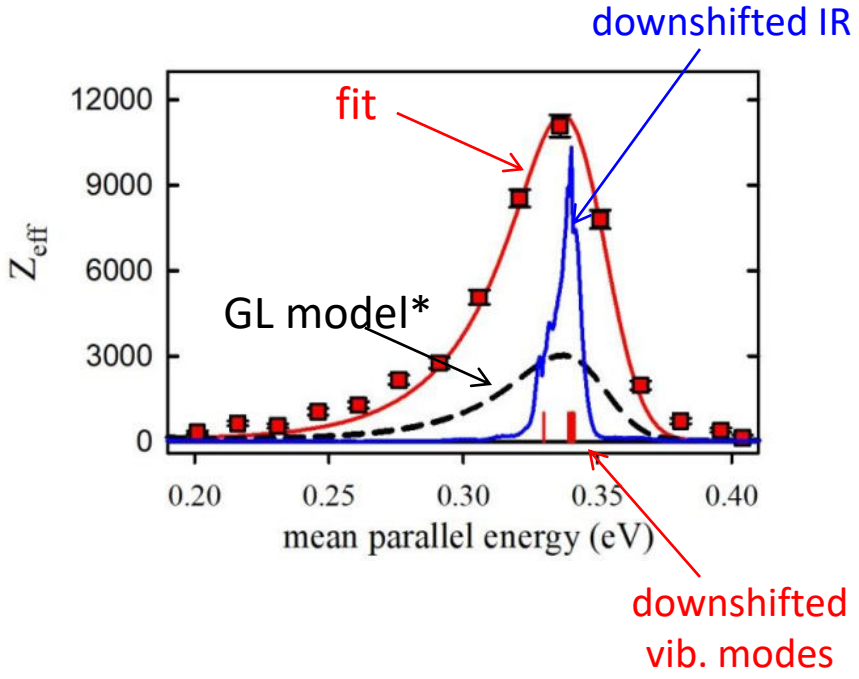
Measurement of binding energy!

$$\varepsilon_B = \Delta\varepsilon$$

*Gribakin 2002 and Gribakin and Lee 2006

Propane Spectra Fitting

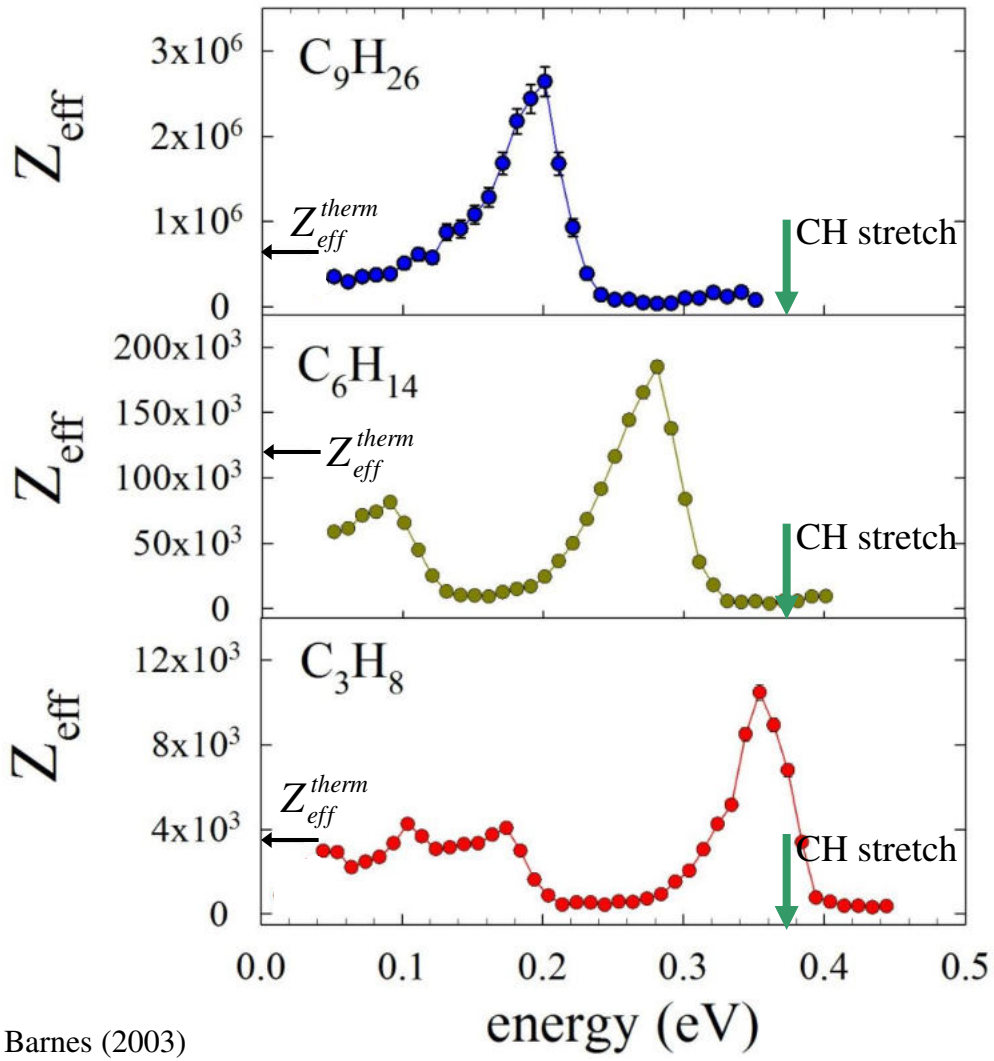




Using dipole active vibrational modes and the known beam distribution, can fit the VFR's for each molecule → **shift gives ε_B.**

*Gribakin and Lee 2006

Bound States for Alkanes



Barnes (2003)

Bound States for Alkanes

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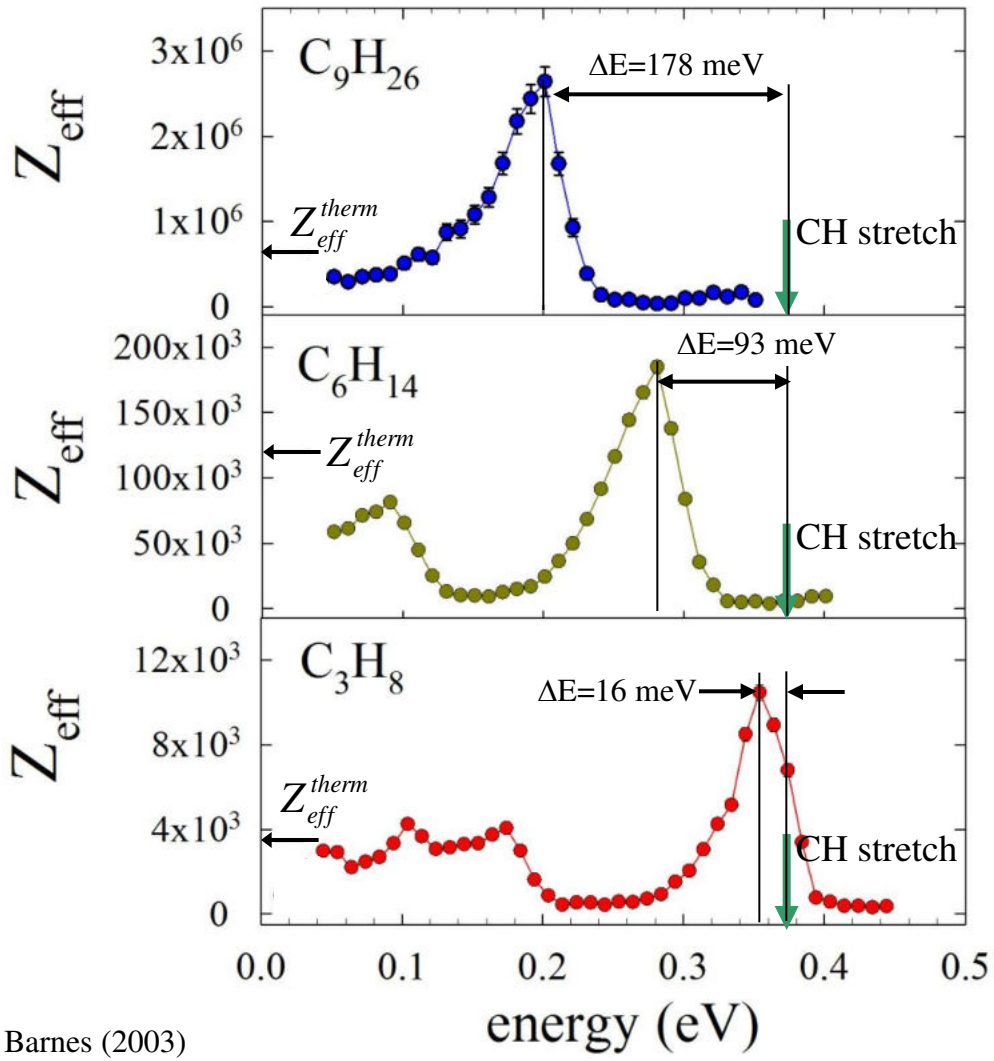

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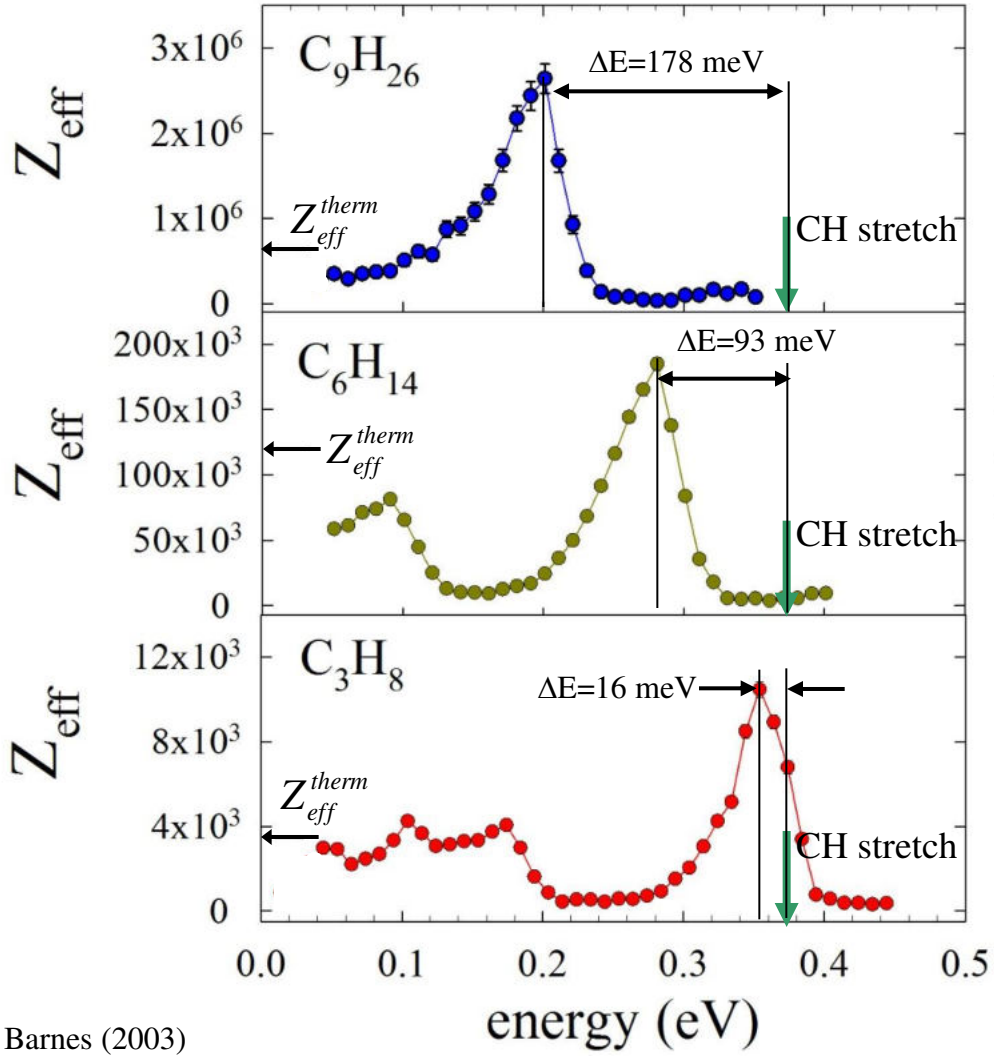

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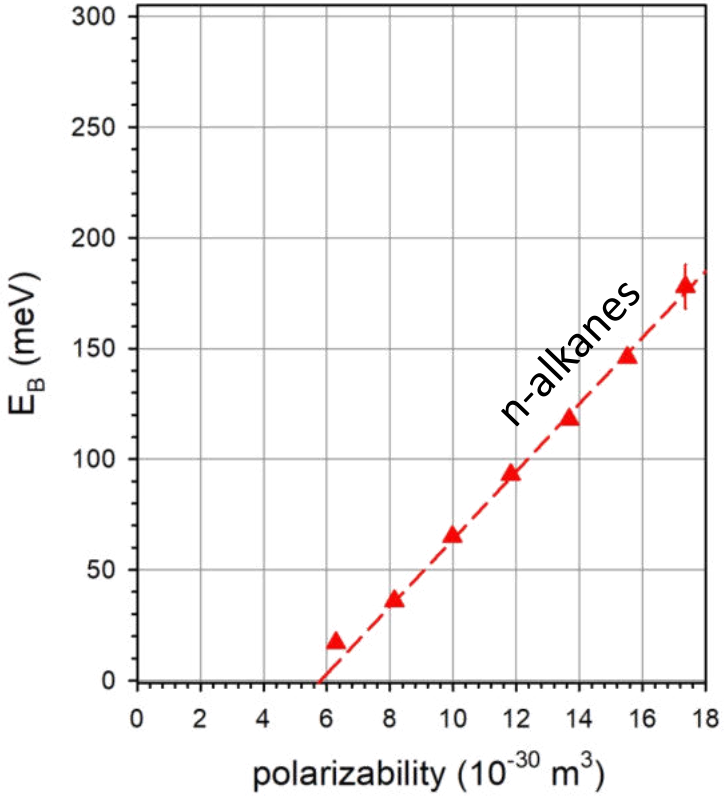

For some recent modeling of the alkanes, see Swann and Gribakin, PRL (2019)

Overview of Measured E_B

> 90 molecules total

- **n-alkanes**
- **alkane-isomers**
- **cyclo-alkanes**
- **aromatics**
- **formates**
- **acetates**
- **aldehydes**
- **ketones**
- **alcohols**
- **nitriles**
- **amides**
- **halo-substitutions (F, Cl, Br)**

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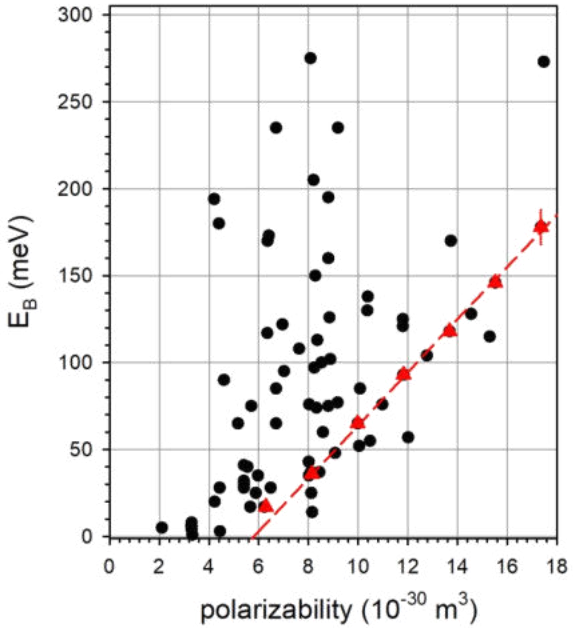

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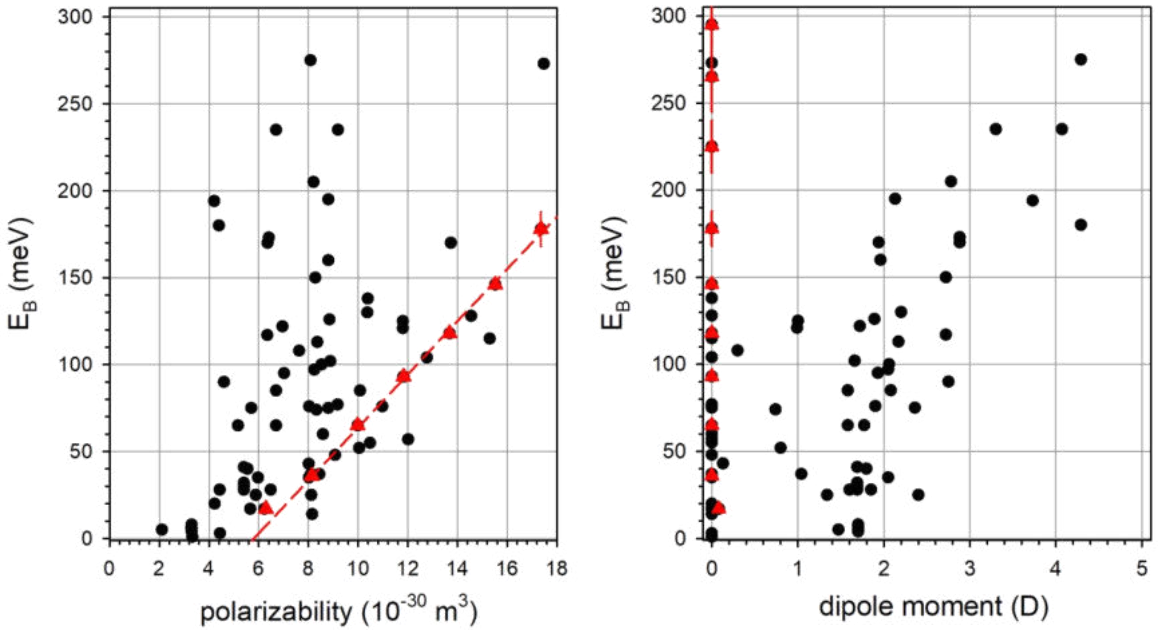

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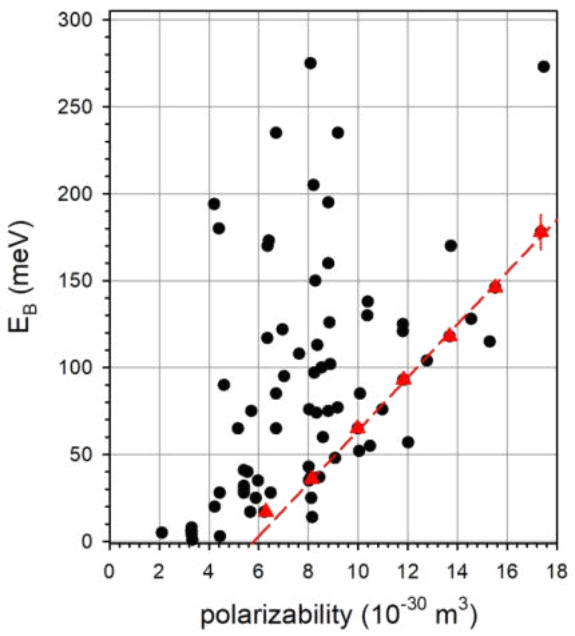

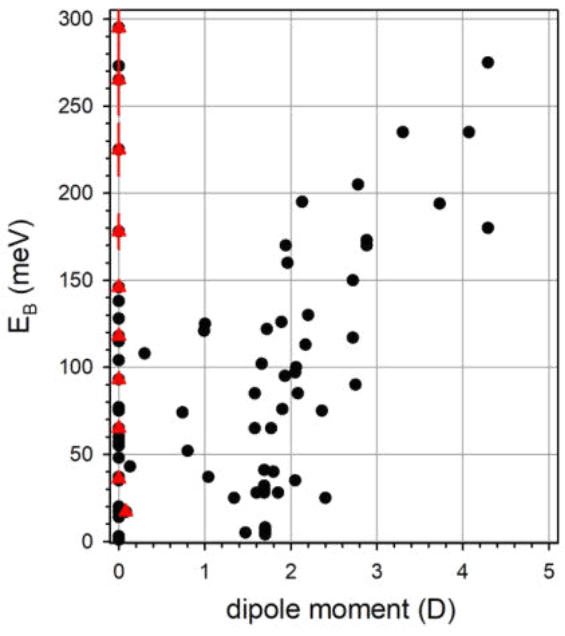

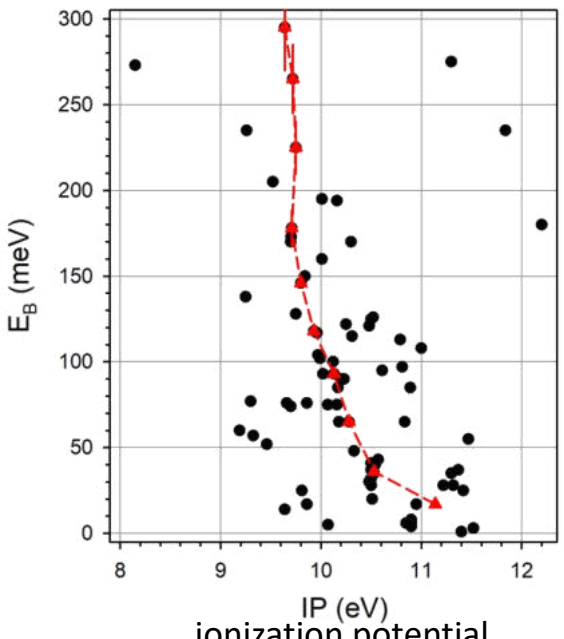

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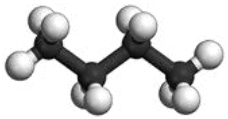
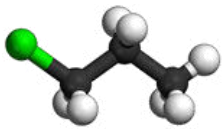
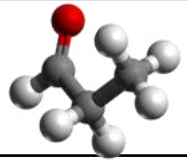
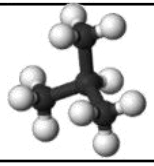
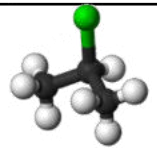
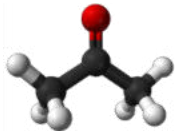
Study #1: Isomer Comparison

	butane C_4H_{10}
	1-cl.propane C_3H_7Cl
	propanal C_3H_6O
	isobutane C_4H_{10}
	2-cl.propane C_3H_7Cl
	acetone C_3H_6O

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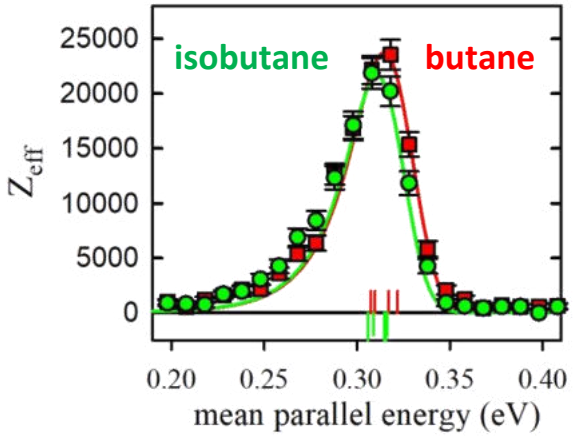
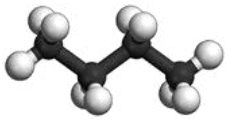
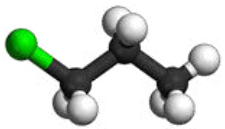
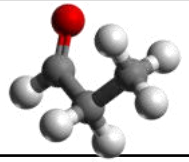
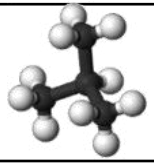
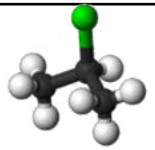
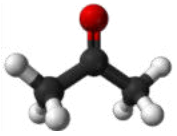


	butane C_4H_{10} **E_B = 37 meV**		1-cl.propane C_3H_7Cl		propanal C_3H_6O
	isobutane C_4H_{10} **E_B = 41 meV**		2-cl.propane C_3H_7Cl		acetone C_3H_6O

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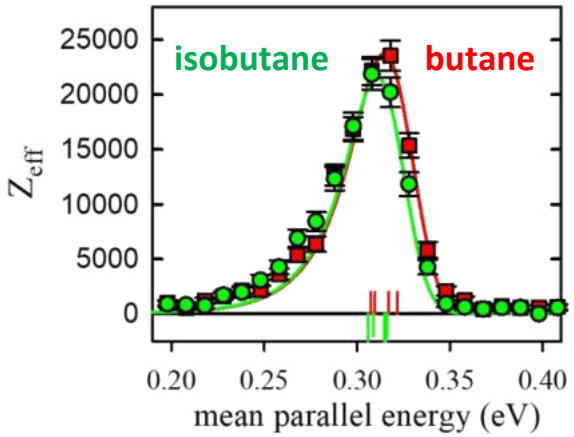
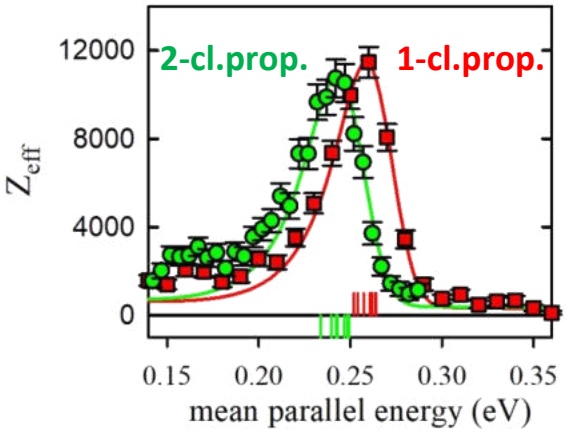
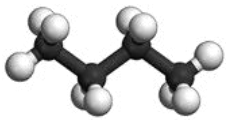
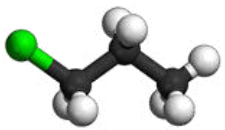
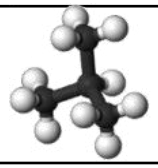
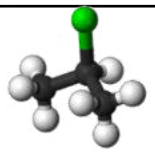
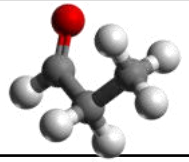
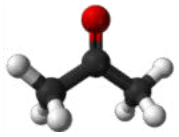
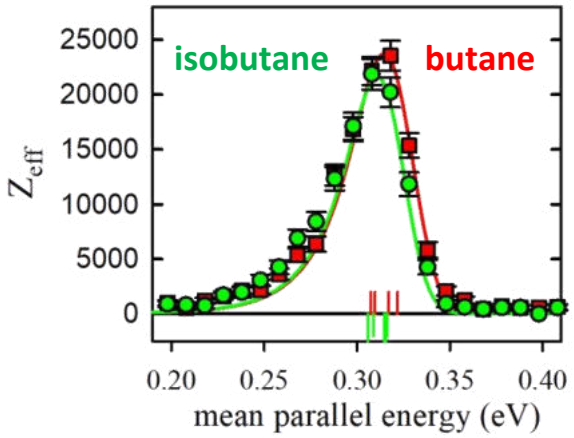


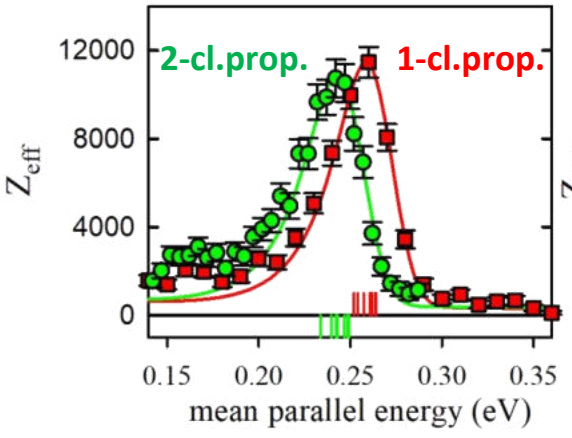


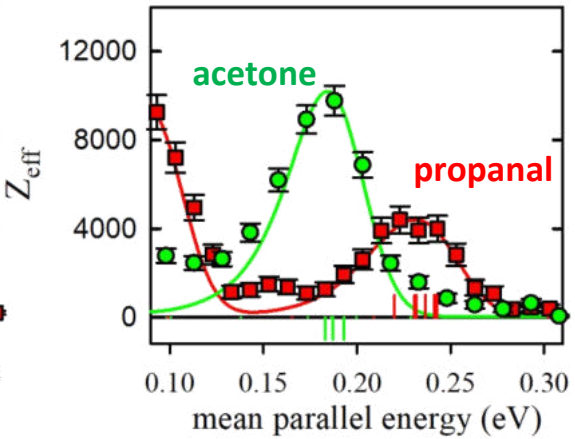
	butane C_4H_{10}	 1-cl.propane C_3H_7Cl
	E_B = 37 meV	**E_B = 95 meV**
	isobutane C_4H_{10}	 2-cl.propane C_3H_7Cl
	E_B = 41 meV	**E_B = 115 meV**

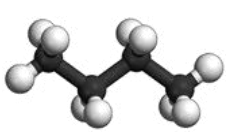
	propanal C_3H_6O
	acetone C_3H_6O

Study #1: Isomer Comparison

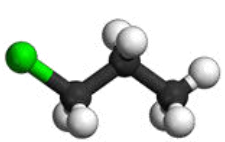




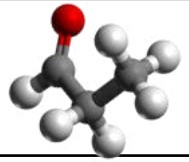




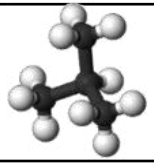
butane
C_4H_{10}
E_B = 37 meV



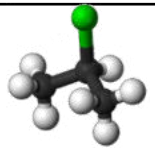
1-cl.propane
C_3H_7Cl
E_B = 95 meV



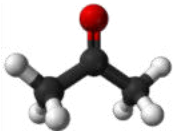
propanal
C_3H_6O
E_B = 120 meV



isobutane
C_4H_{10}
E_B = 41 meV



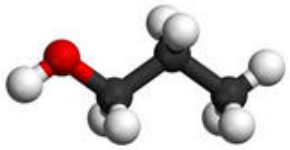
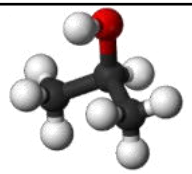
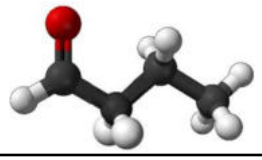
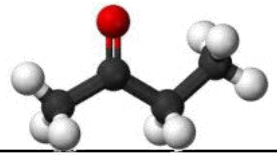
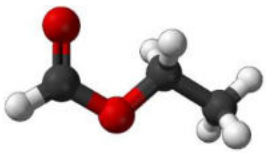
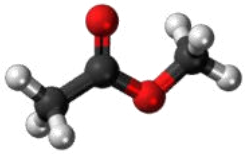
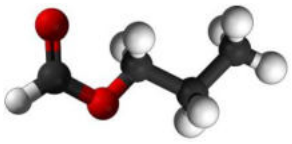
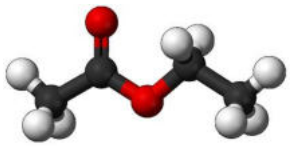
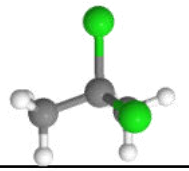
2-cl.propane
C_3H_7Cl
E_B = 115 meV



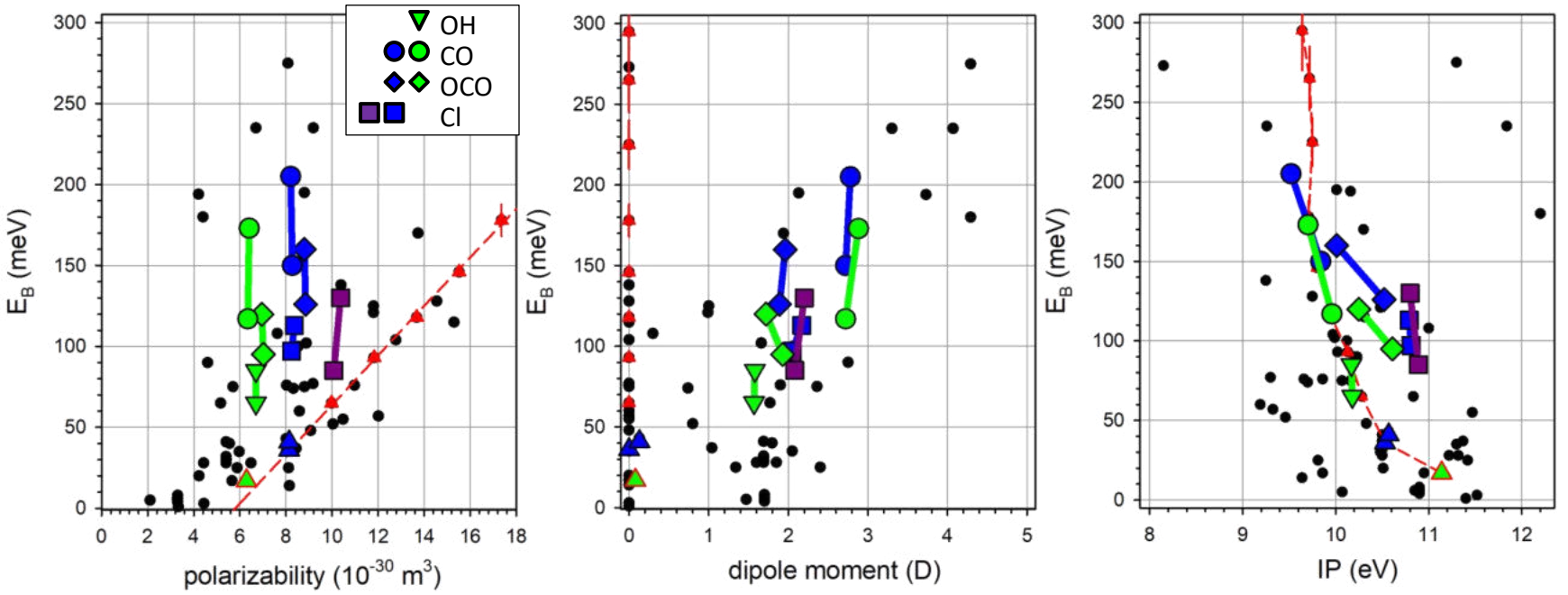
acetone
C_3H_6O
E_B = 170 meV

Key Result: The molecule with the substitution closer to the middle has a larger E_B.

More Isomer Pair Comparisons

	1-propanol C_3H_7OH E_B = 70 meV	2-propanol C_3H_7OH E_B = 90 meV	
	butanal C_4H_8O E_B = 140 meV	2-butanone C_4H_8O E_B = 195 meV	
	ethyl formate $C_3H_6O_2$ E_B = 100 meV	methyl acetate $C_3H_6O_2$ E_B = 125 meV	
	propyl formate $C_4H_8O_2$ E_B = 125 meV	ethyl acetate $C_4H_8O_2$ E_B = 160 meV	
	1,3-dichl.propane $C_3H_6Cl_2$ E_B = 85 meV	2,2-dichl.propane $C_3H_6Cl_2$ E_B = 130 meV	

Summary: Isomer Pairs



Generic trends:

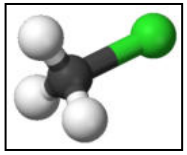
- E_B increases with α
- E_B increases with μ
- E_B decreases with IP

} But this is not enough!

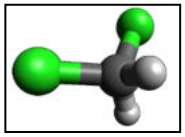
The geometry (shape) of the molecule also plays an important role in determining E_B.

Study #2: Chlorine Substitutions*

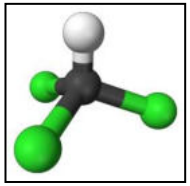
CH3Cl



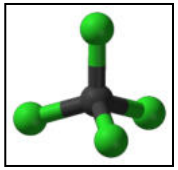
CH2Cl2



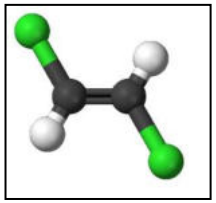
CHCl3



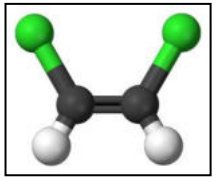
CCl4



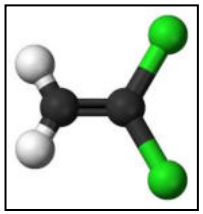
C2H2Cl2
1,2-trans



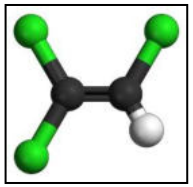
C2H2Cl2
1,2-cis



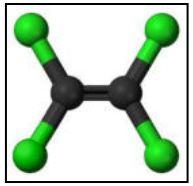
C2H2Cl2
1,1



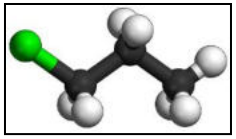
CHCl3

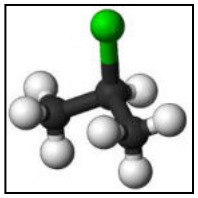


C2Cl4

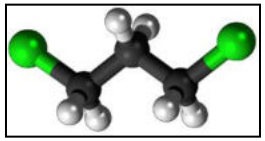


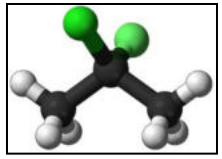
C3H7Cl
1- vs 2- cl.propane





C3H6Cl2
1,3- vs 2,2- dcl.prop.

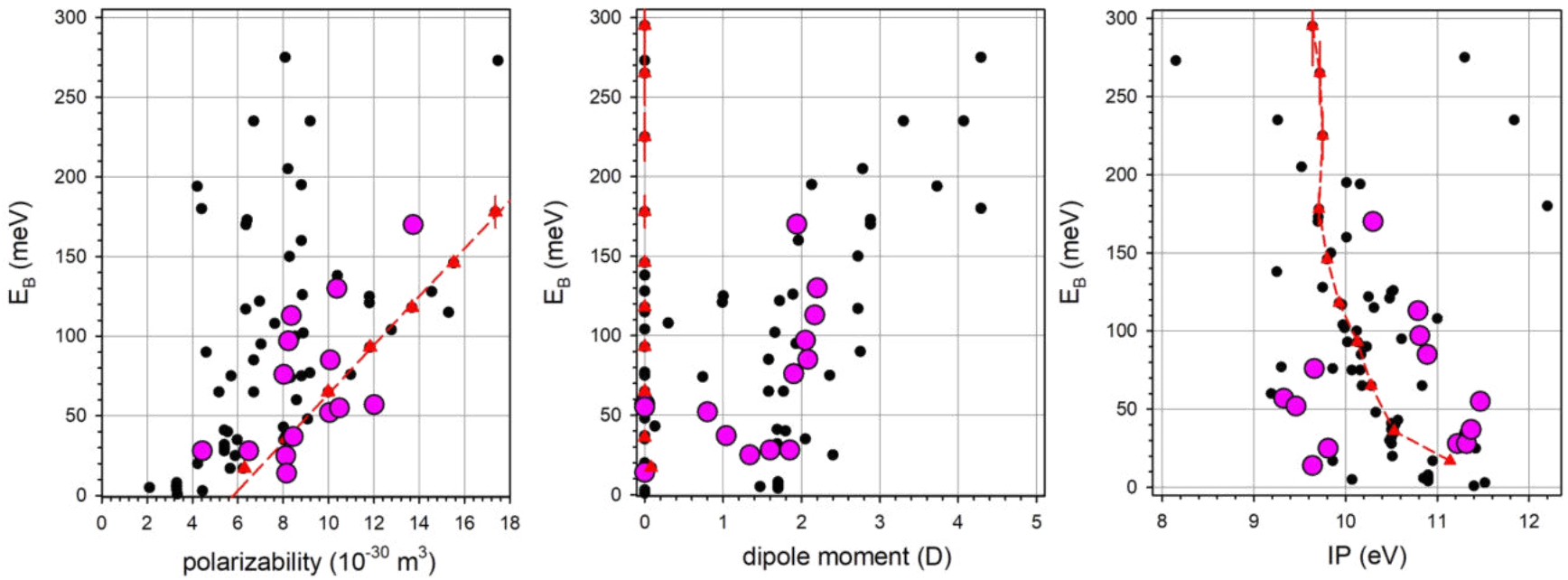




- E_B data for 14 molecules with various levels of chlorine substitution
- Use effective potential model to calculate E_B and positron wavefunction.

*Swann et al. (2021)

Study #2: Chlorine Substitutions*



- E_B data for 14 molecules with various levels of chlorine substitution
- Use effective potential model to calculate E_B and positron wavefunction.

*Swann et al. (2021)

Effective Potential Model*

Molecule treated in the Born-Oppenheimer approximation, electronic structure found from static Hartree-Fock with 6-311++G(d,p) Gaussian basis, obtaining the double occupied electron orbits, $\varphi_i(\mathbf{r})$.

Potential given by two parts

$$V(\mathbf{r}) \equiv V_{\text{static}}(\mathbf{r}) + V_{\text{cor}}(\mathbf{r})$$

Electrostatic potential

$$V_{\text{static}}(\mathbf{r}) = \underbrace{\sum_{A=1}^{N_\alpha} \frac{Z_A}{|\mathbf{r}-\mathbf{r}_A|}}_{\text{atoms}} - \underbrace{2\sum_{i=1}^{N/2} \int \frac{|\varphi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\tau'}_{\text{electrons}}$$

Solve the Schrodinger equation

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

Solve for ε and $\psi(\mathbf{r})$

Correlation energy from bond polarizability (α) and cutoff (ρ_A)

$$V_{\text{cor}}(\mathbf{r}) = -\sum_{A=1}^{N_\alpha} \frac{\alpha_A}{2|\mathbf{r}-\mathbf{r}_A|^4}\left[1 - \exp\left(-\frac{|\mathbf{r}-\mathbf{r}_A|^6}{\rho_A^6}\right)\right]$$

Fit

Key feature – includes the full molecular geometry

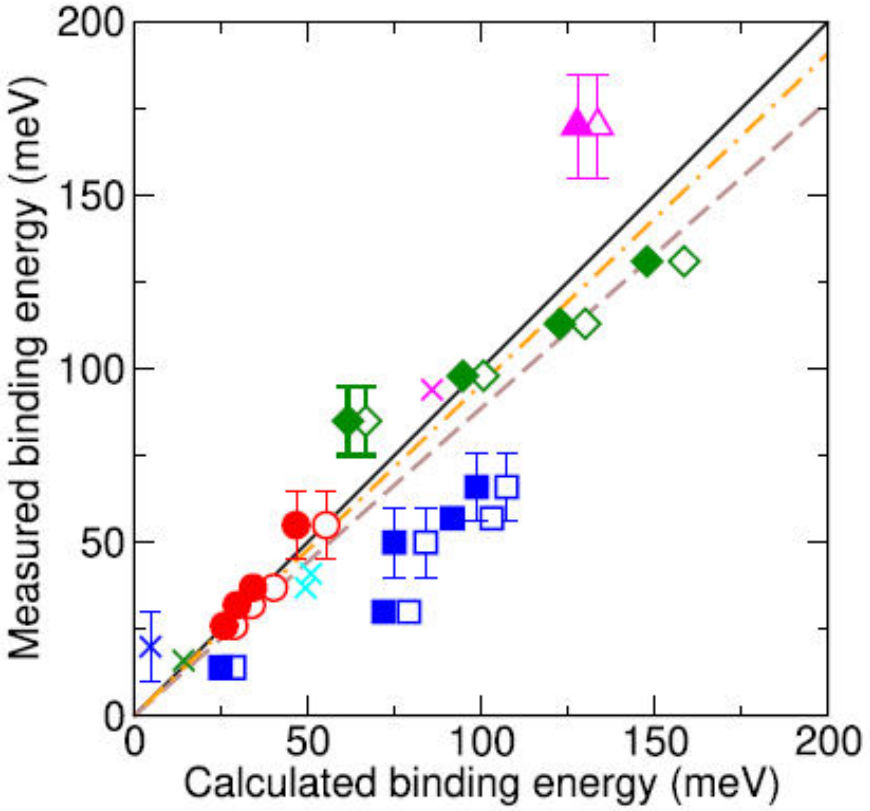
*Swann and Gribakin (2020)

Comparison of Model to Measurements*

Choose cutoff: $\rho_{Cl} = 2.20 \rightarrow \varepsilon_B^+$

$\rho_{Cl} = 2.24 \rightarrow \varepsilon_B^-$

Molecule	Formula	ε_b^+ (meV)	ε_b^- (meV)	ε_b^{exp} (meV)
Methyl chloride	CH_3Cl	28.91	26.00	26 ± 6
Methylene chloride	CH_2Cl_2	33.90	29.66	32 ± 4
Chloroform	$CHCl_3$	40.31	34.31	37 ± 3
Carbon tetrachloride	CCl_4	55.34	46.68	55 ± 10[a]
Vinyl chloride	C_2H_3Cl	54.08	49.78	
trans-1,2-Dichloroethylene	$C_2H_2Cl_2$	28.84	24.89	14 ± 3
Vinylidene chloride	$C_2H_2Cl_2$	79.24	71.89	30 ± 5
cis-1,2-Dichloroethylene	$C_2H_2Cl_2$	107.4	98.68	66 ± 10[a]
Trichloroethylene	C_2HCl_3	84.04	75.04	50 ± 10[a]
Tetrachloroethylene	C_2Cl_4	103.1	91.66	57 ± 6
n-Propyl chloride	C_3H_7Cl	100.7	94.71	98 ± 4
Isopropyl chloride	C_3H_7Cl	130.0	122.7	113 ± 5
1,2-Dichloropropane	$C_3H_6Cl_2$	52.65	47.38	
1,3-Dichloropropane	$C_3H_6Cl_2$	66.80	61.69	85 ± 10[a]
1,1-Dichloropropane	$C_3H_6Cl_2$	131.9	122.6	
2,2-Dichloropropane	$C_3H_6Cl_2$	158.5	147.8	131 ± 4
n-Butyl chloride	C_4H_9Cl	125.2	118.9	
sec-Butyl chloride	C_4H_9Cl	181.4	172.8	
Isobutyl chloride	C_4H_9Cl	145.3	138.2	
tert-Butyl chloride	C_4H_9Cl	195.5	186.1	
n-Hexyl chloride	$C_6H_{13}Cl$	133.6	127.7	170 ± 15[a]



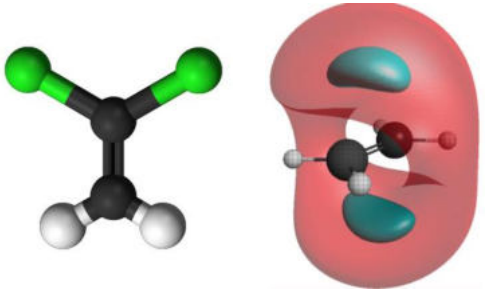
Result: Overall agreement is pretty good

*Swann et al. (2021)

Wavefunctions*

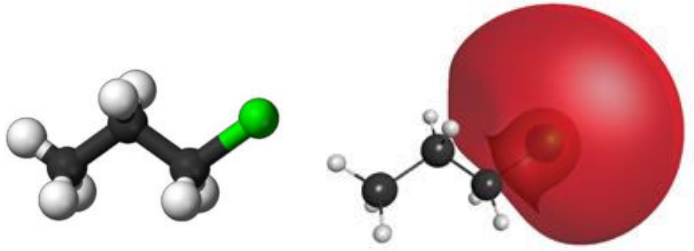
1,1-DCE

ε_B (calc) ≈ 72 meV
ε_B (meas) ≈ 30 meV



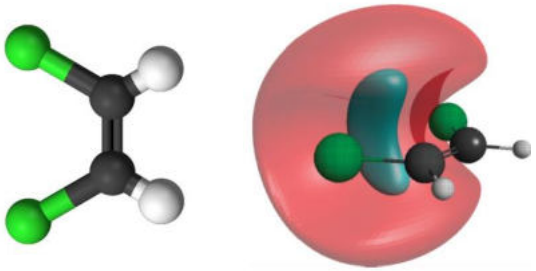
1-cl.prop.

ε_B (calc) ≈ 95 meV
ε_B (meas) ≈ 98 meV



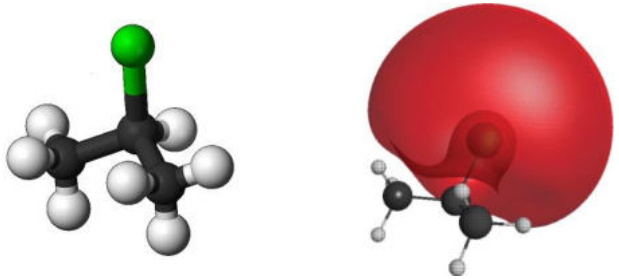
cis-1,2-DCE

ε_B (calc) ≈ 99 meV
ε_B (meas) ≈ 60 meV



2-cl.prop.

ε_B (calc) ≈ 123 meV
ε_B (meas) ≈ 113 meV



*Swann et al. (2021)

Wavefunctions*

1,1-DCE

ε_B (calc) ≈ 72 meV
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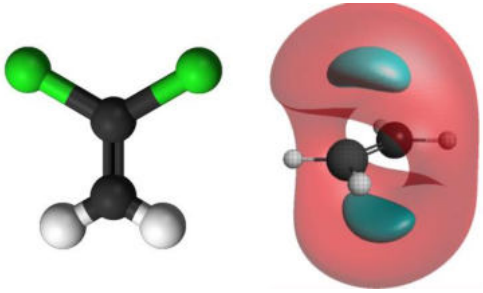
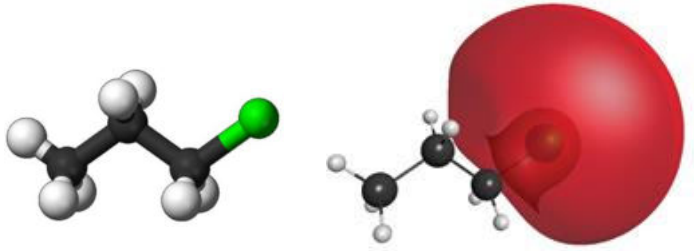


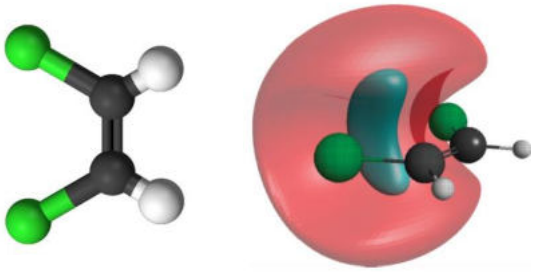
1-cl.prop.

ε_B (calc) ≈ 95 meV
ε_B (meas) ≈ 98 meV



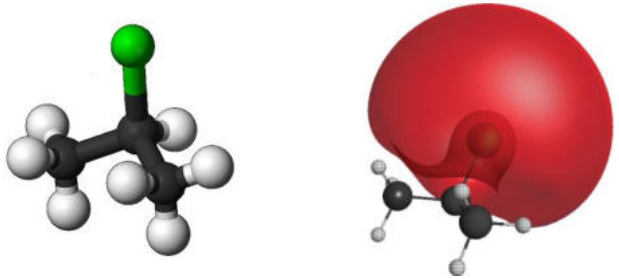
cis-1,2-DCE

ε_B (calc) ≈ 99 meV
ε_B (meas) ≈ 60 meV



2-cl.prop.

ε_B (calc) ≈ 123 meV
ε_B (meas) ≈ 113 meV



Certain geometries enable the positron to sample more of the molecule and leading to a higher binding energy.

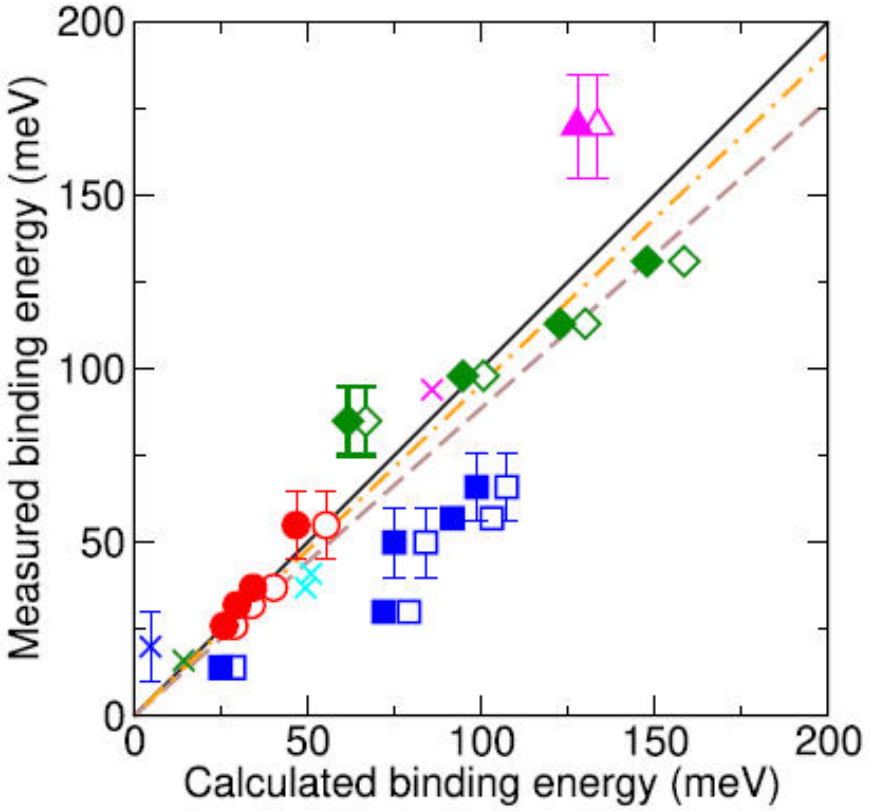
*Swann et al. (2021)

Comparison of Model to Measurements*

Choose cutoff: $\rho_{Cl} = 2.20 \rightarrow \varepsilon_B^+$

$\rho_{Cl} = 2.24 \rightarrow \varepsilon_B^-$

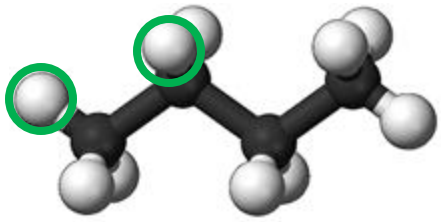
Molecule	Formula	ε_b^+ (meV)	ε_b^- (meV)	ε_b^{exp} (meV)
Methyl chloride	CH_3Cl	28.91	26.00	26 ± 6
Methylene chloride	CH_2Cl_2	33.90	29.66	32 ± 4
Chloroform	$CHCl_3$	40.31	34.31	37 ± 3
Carbon tetrachloride	CCl_4	55.34	46.68	55 ± 10[a]
Vinyl chloride	C_2H_3Cl	54.08	49.78	
trans-1,2-Dichloroethylene	$C_2H_2Cl_2$	28.84	24.89	14 ± 3
Vinylidene chloride	$C_2H_2Cl_2$	79.24	71.89	30 ± 5
cis-1,2-Dichloroethylene	$C_2H_2Cl_2$	107.4	98.68	66 ± 10[a]
Trichloroethylene	C_2HCl_3	84.04	75.04	50 ± 10[a]
Tetrachloroethylene	C_2Cl_4	103.1	91.66	57 ± 6
n-Propyl chloride	C_3H_7Cl	100.7	94.71	98 ± 4
Isopropyl chloride	C_3H_7Cl	130.0	122.7	113 ± 5
1,2-Dichloropropane	$C_3H_6Cl_2$	52.65	47.38	
1,3-Dichloropropane	$C_3H_6Cl_2$	66.80	61.69	85 ± 10[a]
1,1-Dichloropropane	$C_3H_6Cl_2$	131.9	122.6	
2,2-Dichloropropane	$C_3H_6Cl_2$	158.5	147.8	131 ± 4
n-Butyl chloride	C_4H_9Cl	125.2	118.9	
sec-Butyl chloride	C_4H_9Cl	181.4	172.8	
Isobutyl chloride	C_4H_9Cl	145.3	138.2	
tert-Butyl chloride	C_4H_9Cl	195.5	186.1	
n-Hexyl chloride	$C_6H_{13}Cl$	133.6	127.7	170 ± 15[a]



*Swann et al. (2021)

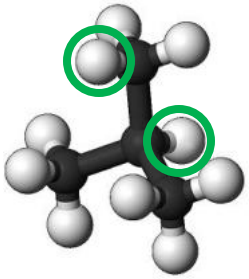
More Model Results*

butane

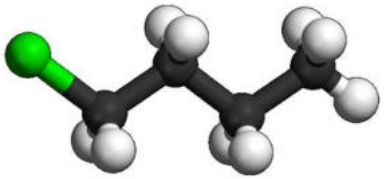


Calc: E_B = 49 meV

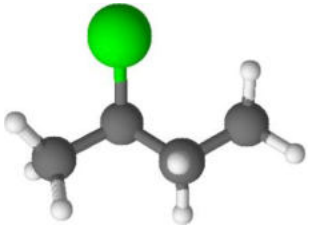
isobutane



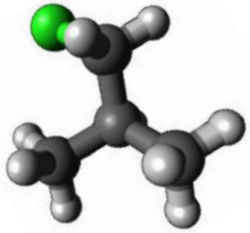
Calc: E_B = 51 meV



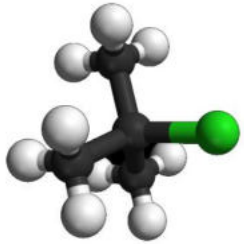
Calc: E_B = 120 meV



Calc: E_B = 175 meV



Calc: E_B = 140 meV

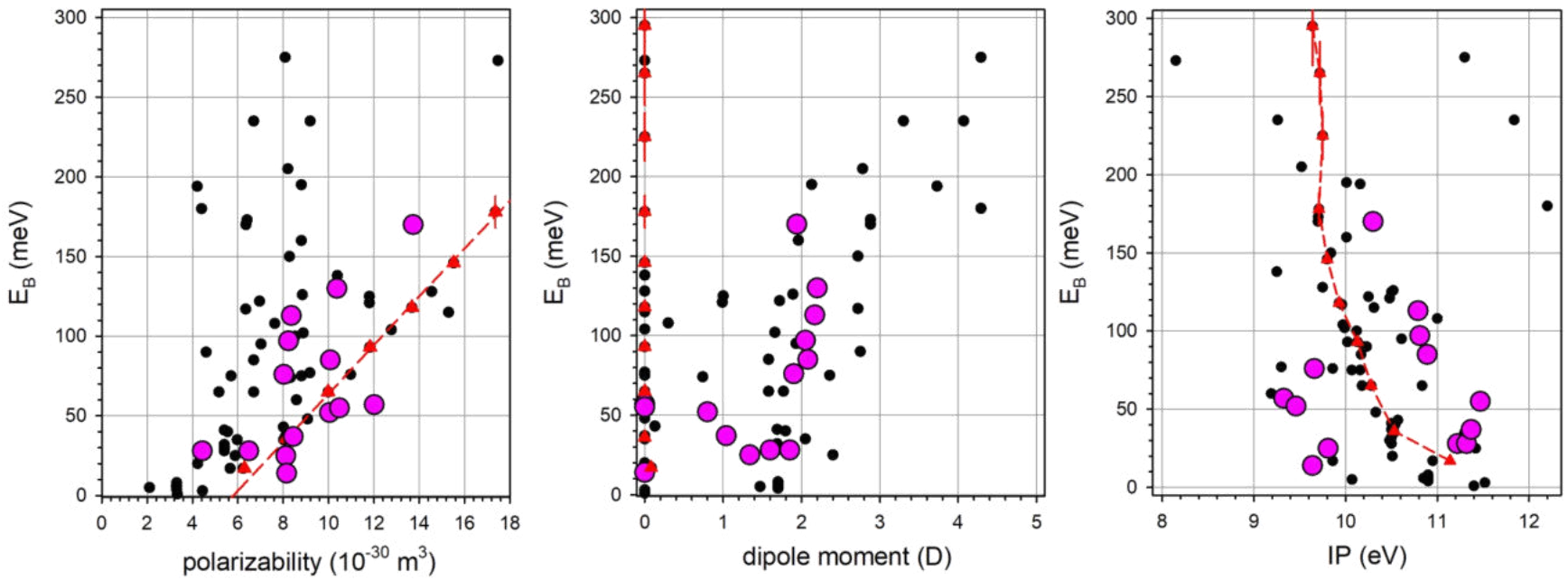


Calc: E_B = 190 meV

As before, the molecule with the substitution closer to the middle has a larger E_B.

*Swann et al. (2021)

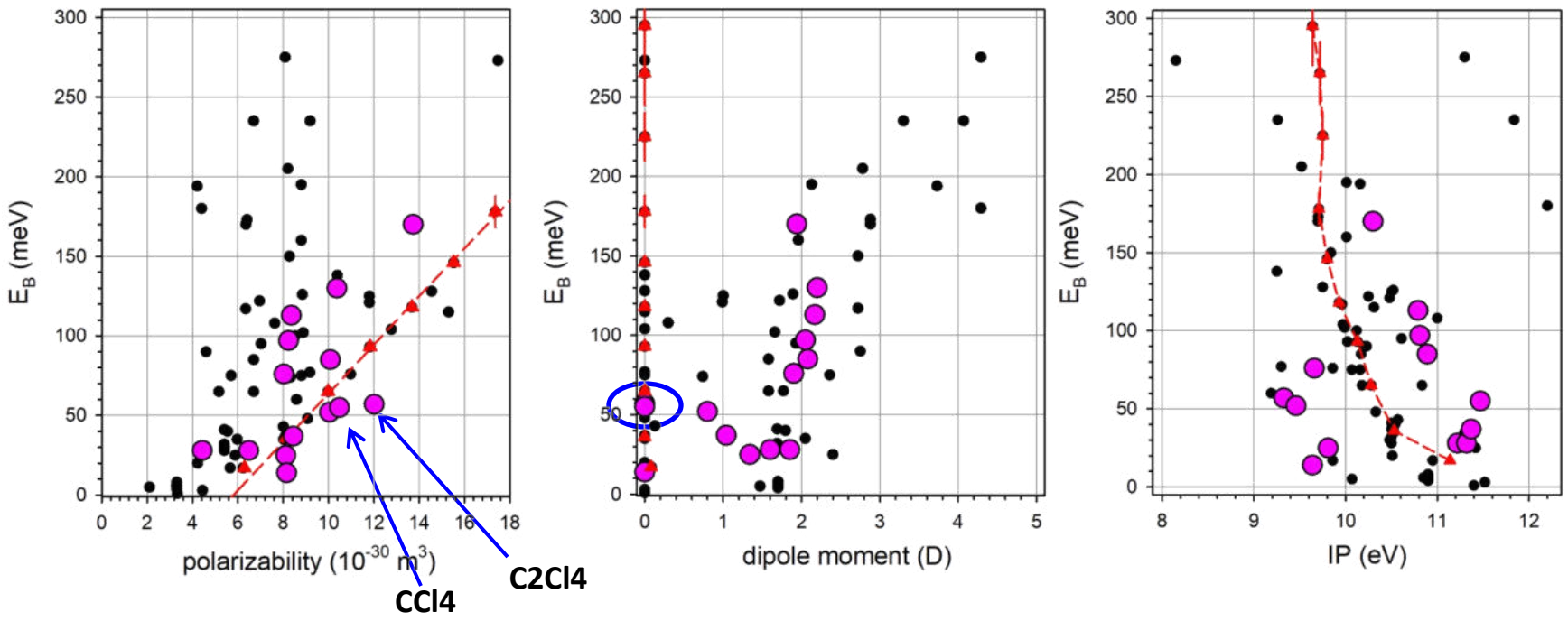
Study #2: Chlorine Substitutions*



- E_B data for 14 molecules with various levels of chlorine substitution

*Swann et al. (2021)

Study #2: Chlorine Substitutions*



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*Swann et al. (2021)

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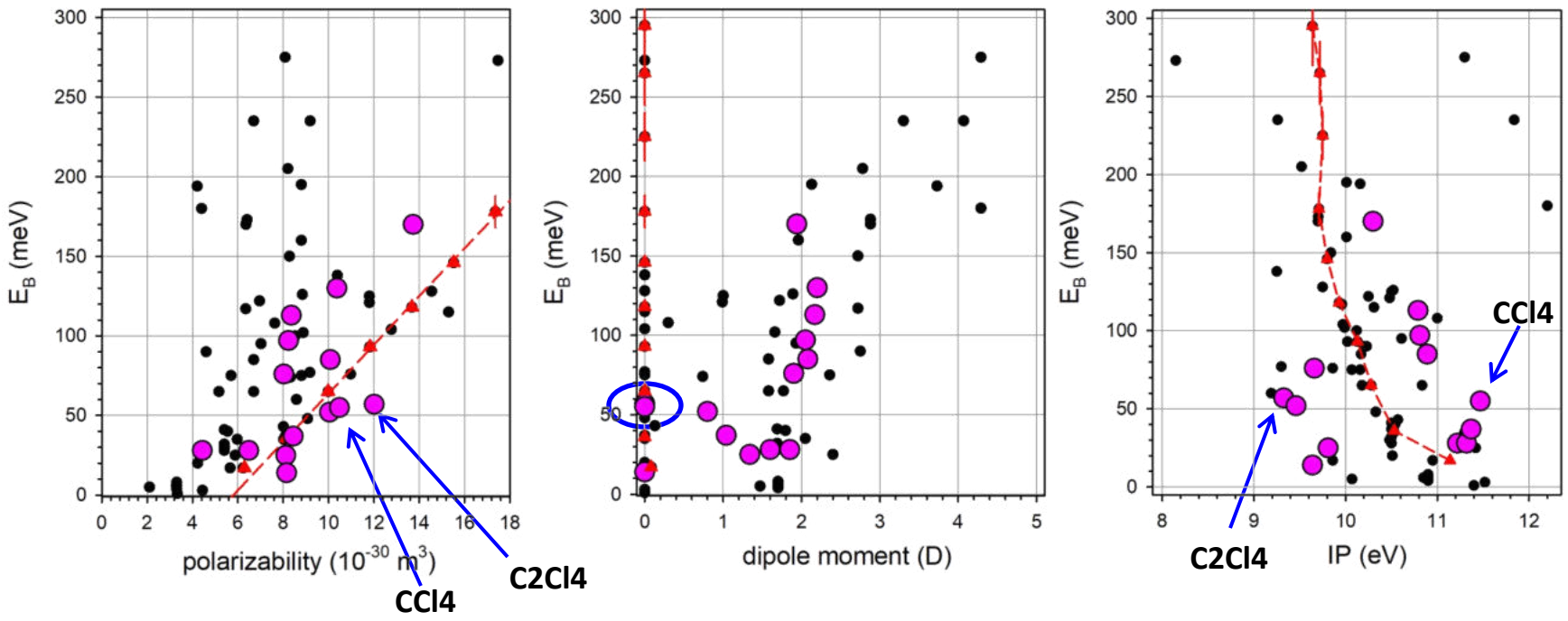

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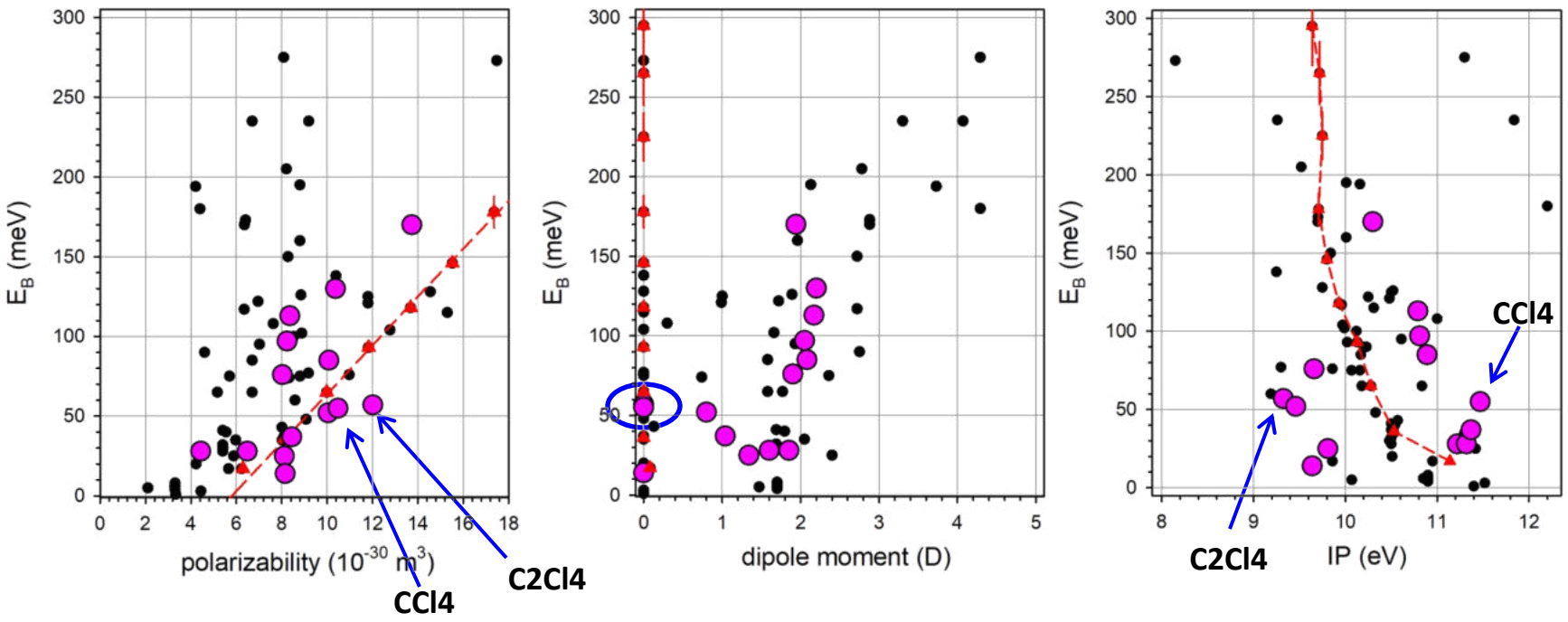
*Swann et al. (2021)

Study #2: Chlorine Substitutions*



- E_B data for 14 molecules with various levels of chlorine substitution
- **Clearly, the global parameters are not enough!**

*Swann et al. (2021)

Broad Range of Calculations!

Positron–electron correlation polarization potential

Sugiura, Takayanagi, Kita and Tachikawa, Eur. Phys. J. D 73, 162 (2019)

Sugiura, Suzuki, Otomo, Miyazaki , Takayanagi and Tachikawa, J. Comp. Chem. 41, 1576 (2020)

Suzuki, Otomo, Iida, Sugiura, Takayanagi and Tachikawa, Phys. Rev. A 102, 052830 (2020).

Effective potential calculations

Swann and Gribakin, J. Chem. Phys. 149, 244305(2018)

Swann and Gribakin, Phys. Rev. Lett. 123, 113402 (2019)

Swann and Gribakin, J. Chem. Phys. 153, 184311 (2020)

} alkanes

Swann and Gribakin , Phys. Rev. A 101, 022702 (2020)

Swann, Gribakin, Danielson, Ghosh, Natisin and Surko, Phys. Rev. A 104, 012813 (2021)

chlorine Study

Machine-learning predictions of positron binding to molecules

Amaral and Mohallem, Phys. Rev. A 102, 052808 (2020)

Many-body theory of positron binding to polyatomic molecules

Hofierka, Cunningham, Rawlins, Patterson and Green, arXiv preprint 2105.06959 (2021)

includes virtual positronium!

Conclusions and Future Work

- Using a select group of molecules it was shown that the molecular geometry has a significant effect on the binding energy that cannot be captured by using average molecular parameters
  → parametric fits are unlikely to provide an adequate description.

- Recent theoretical work using model potentials are having good success, in particular when they use the full molecular geometry in the calculation.

- Looking at broader range of molecules, including analysis using other molecular parameters (e.g., molecular orbitals, ionization potential, quadrupole moments, etc.), and combined with model potential calculations may enable new understanding of the positron-molecule interaction.

- Next up – focus on understanding the spectra (VFR amplitude) using the cryo-beam.
  (See Soumen Ghosh poster #6)

For more information, visit

positrons.ucsd.edu