

# From SURE to GREF through Bourbon St.: Great Years!!





# Halogenated Hydrocarbons and Halomethanediols: A Study of the Atmospheric Implications of Proposed Replacements for Chlorofluorocarbons (CFCs)

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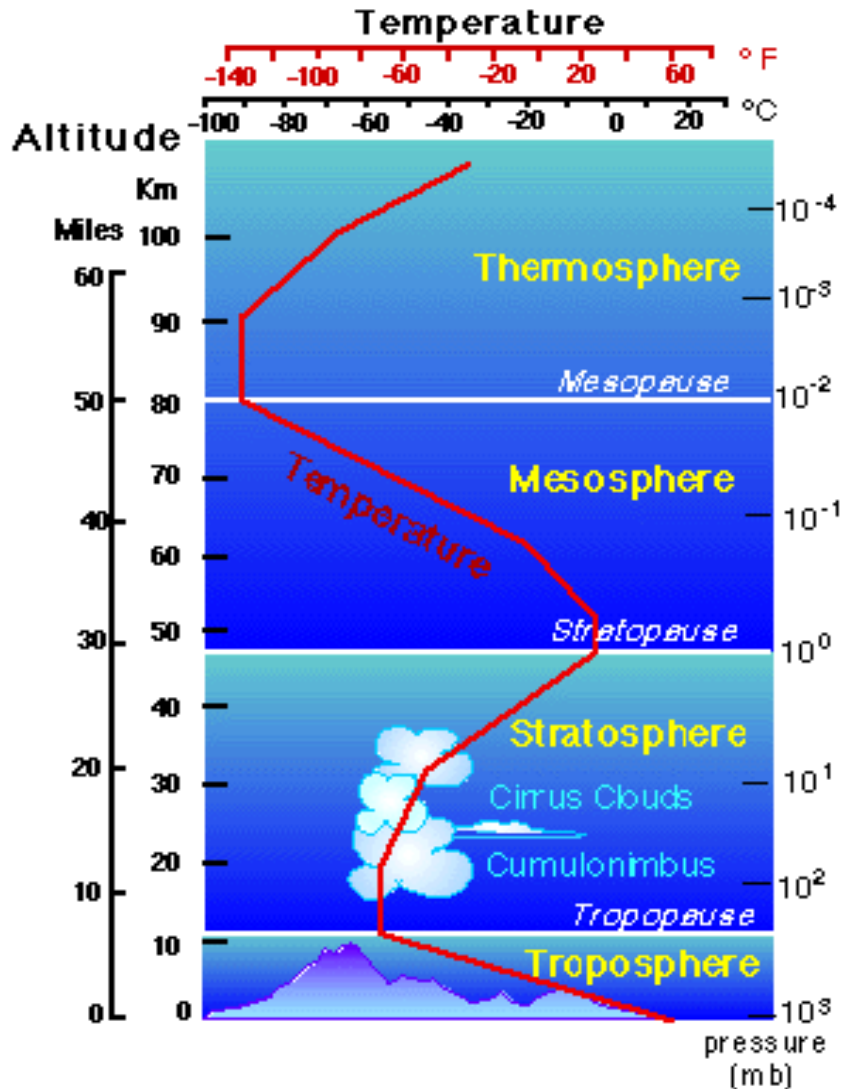
# Outline

- ✓ Atmospheric Chemistry
- ✓ Research Interests and Approach
- ✓ Taste of My Research
  - ✓ Atmospheric Oxidation Mechanisms of Bromoethane and Bromopropane
  - ✓ Structure and Vibrational Spectra of Bromine Reservoir Species from the Atmospheric Oxidations of Bromoethane and Bromopropane
  - ✓ Atmospheric Modeling of Bromopropane
  - ✓ Methylhydroperoxide ( $\text{CH}_3\text{OOH}$ )
  - ✓ Conformational Topography of Halomethanediols  $\text{XCH}(\text{OH})_2$  ( $\text{X} = \text{H}, \text{F}, \text{Cl}$ )
- ✓ Conclusions





# Atmospheric Layers



- Variations are due to alterations in the chemical and physical nature of the atmosphere with altitude.
- Troposphere contains about 75% of the total mass of the atmosphere.
- Stratosphere is also called the ozone layer.





# Atmospheric Chemistry ??

- Study of the atmosphere and its chemistry
  - Experimental studies of atmospheric processes
  - *Ab initio* calculations
  - Climate modeling





# Halogenated Compounds

- CFCs, chlorinated and brominated compounds
- Potential environmental effects
  - Tropospheric and Stratospheric chemistry
- Replacement





# Research Interest & Approach

- Gas phase reactions involving halogens that can be responsible for the catalysis of ozone depletion.
  - Chemical removal mechanisms and energetics of gas phase reactions involving halogens.
  - Characterization of the potential energy surface (PES) of the proposed mechanisms for the degradation of the halogenated hydrocarbons and their by-products.
- High level molecular orbital *ab initio* calculations



Method	Method Type	Advantages	Disadvantages	Best for
Molecular Mechanics	<ul style="list-style-type: none"> <li>•uses classical physics</li> <li>•relies on force-field with embedded empirical parameters</li> </ul>	<ul style="list-style-type: none"> <li>•Computationally least intensive - fast and useful with limited computer resources</li> <li>•can be used for molecules as large as enzymes</li> </ul>	<ul style="list-style-type: none"> <li>•particular force field applicable only for a limited class of molecules</li> <li>•does not calculate electronic properties</li> <li>•requires experimental data (or data from <i>ab initio</i>) for parameters</li> </ul>	<ul style="list-style-type: none"> <li>•large systems (thousands of atoms)</li> <li>•systems or processes with no breaking or forming of bonds</li> </ul>
Semi-Empirical	<ul style="list-style-type: none"> <li>•uses quantum physics</li> <li>•uses experimentally derived empirical parameters</li> <li>•uses approximation extensively</li> </ul>	<ul style="list-style-type: none"> <li>•less demanding computationally than <i>ab initio</i> methods</li> <li>•capable of calculating transition states and excited states</li> </ul>	<ul style="list-style-type: none"> <li>•requires experimental data (or data from <i>ab initio</i>) for parameters</li> <li>•less rigorous than <i>ab initio</i> methods</li> </ul>	<ul style="list-style-type: none"> <li>•medium-sized systems (hundreds of atoms)</li> <li>•systems involving electronic transitions</li> </ul>
<i>Ab Initio</i>	<ul style="list-style-type: none"> <li>•uses quantum physics</li> <li>•mathematically rigorous, no empirical parameters</li> <li>•uses approximation extensively</li> </ul>	<ul style="list-style-type: none"> <li>•useful for a broad range of systems</li> <li>•does not depend on experimental data</li> <li>•capable of calculating transition states and excited states</li> </ul>	<ul style="list-style-type: none"> <li>•computationally expensive</li> </ul>	<ul style="list-style-type: none"> <li>•small systems (tens of atoms)</li> <li>•systems involving electronic transitions</li> <li>•molecules or systems without available experimental data ("new" chemistry)</li> <li>•systems requiring rigorous accuracy</li> </ul>



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# *Ab initio* Calculations

- Software
  - Gaussian 03
- Geometry optimizations and frequency calculations
  - Levels of theory and basis sets
- Single point energy calculations





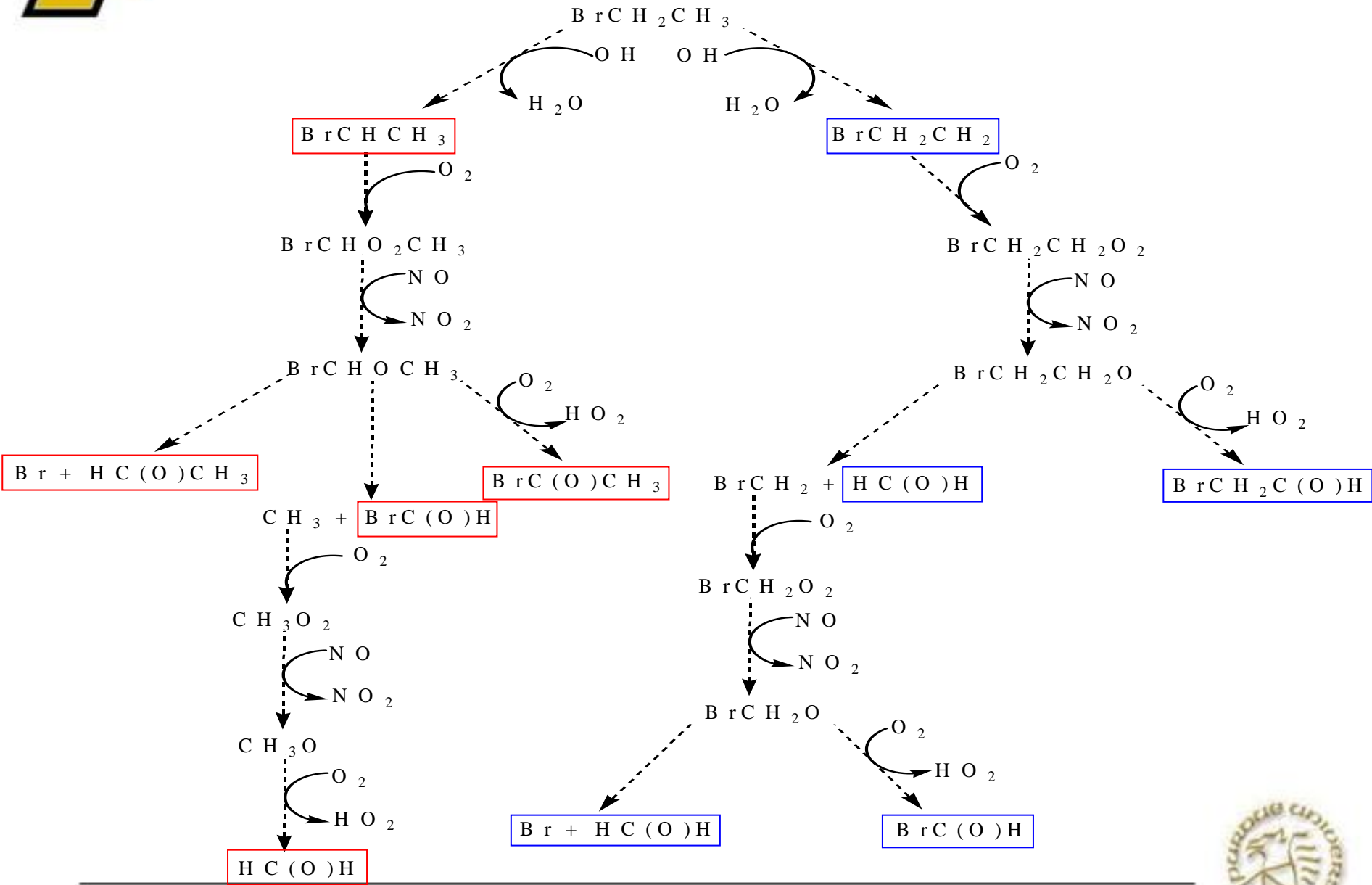
# Levels of Theory

- Hartree-Fock (HF)
  - Simplest and least expensive *ab initio* wavefunction
- Møller-Plesset (MP) Perturbation Theory
  - Second-order Møller-Plesset (MP2) perturbation theory
  - Least-expensive traditional method including electron correlation
- CCSD(T)
  - Coupled-cluster, singles and doubles with approximate triples
  - Most popular high-level (i.e., lots of electron correlation) method
  - Very expensive (e.g. bromopropane's TS)
  - Describes a calculation that gives the same energy for two atoms (or molecular fragments) separated by a large distance as is obtained from summing the energies for the atoms (or molecular fragments) computed separately

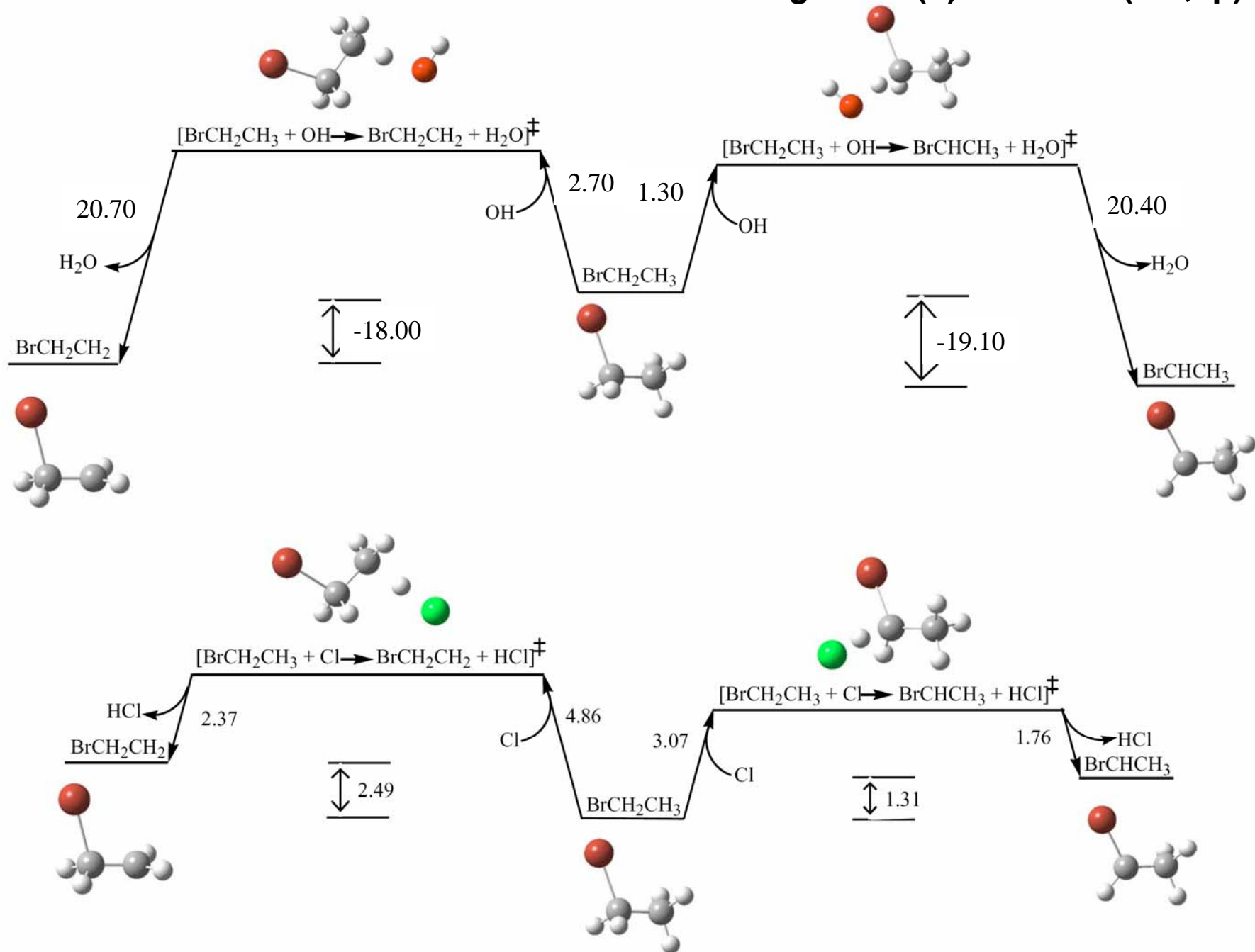


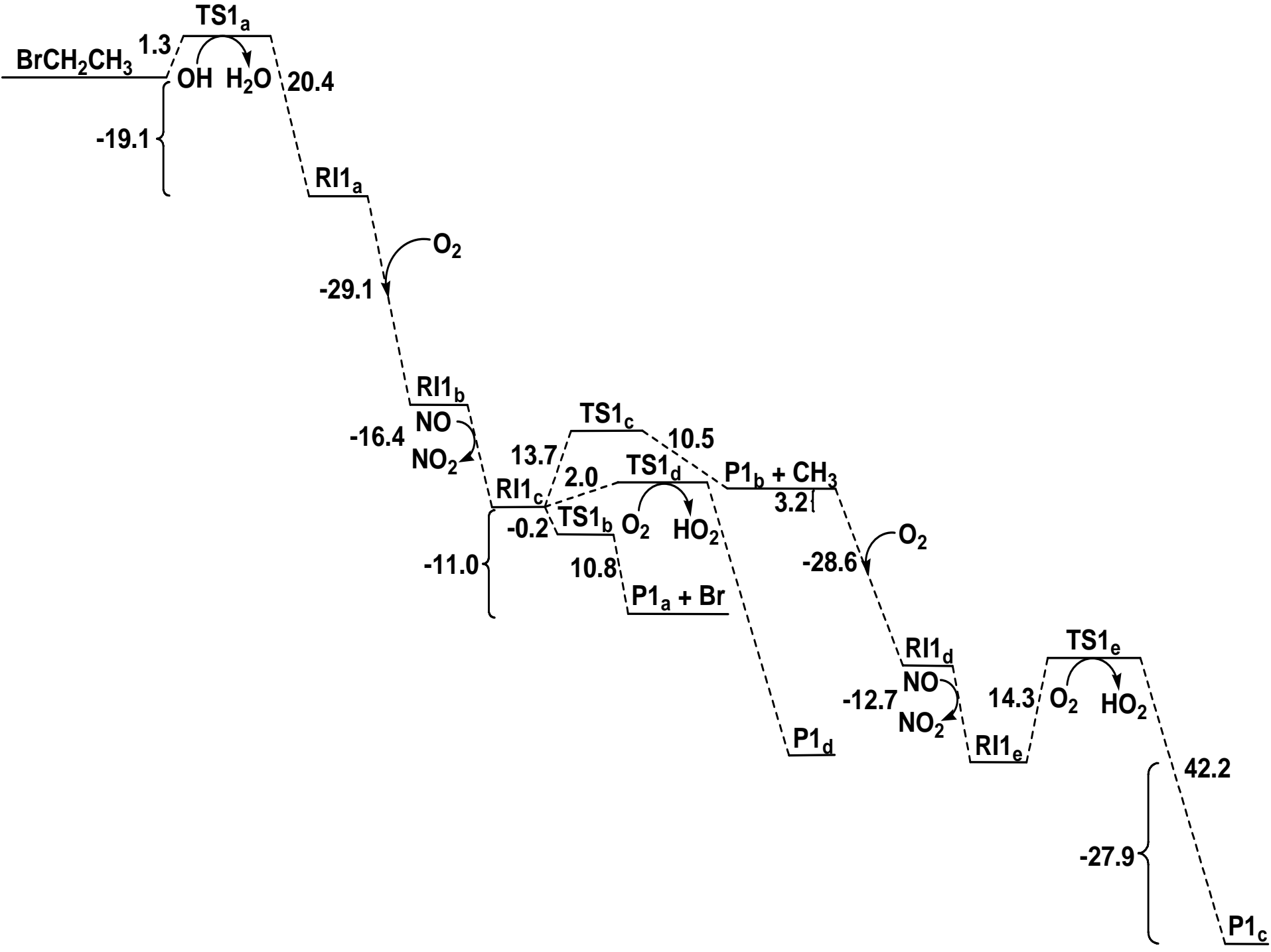


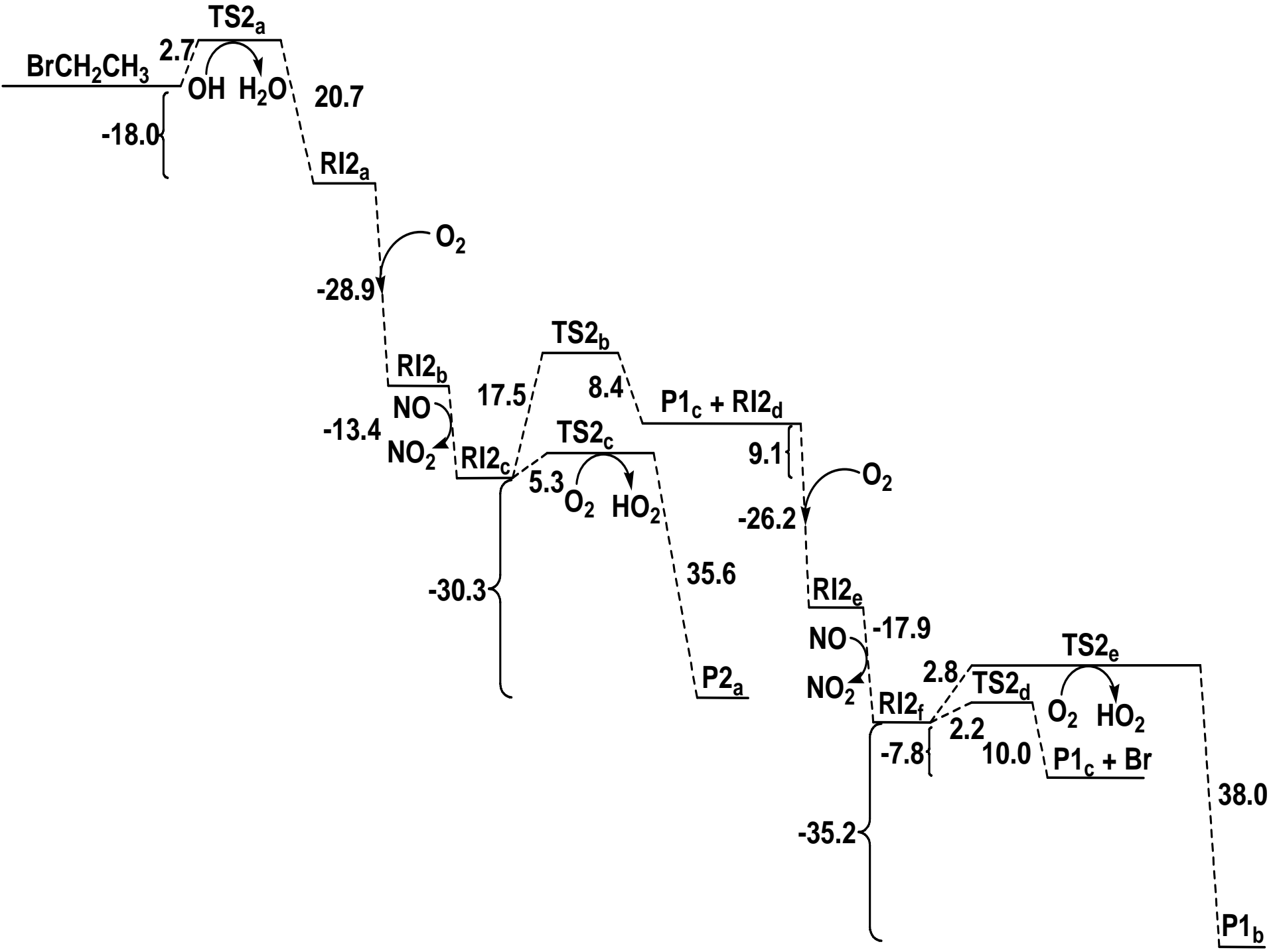
# Atmospheric Degradation of Bromoethane



# PES for the reaction of Bromoethane + OH / Cl using CCSD(T)/6-311++G(2df,2p)







# Atmospheric Degradation of Bromoethane





# What is Bromopropane?

- Short-lived halocarbon
- Possible replacement for CFCs
- Toxic effects
  - Male and female reproductive and hematopoietic organs
  - Neurotoxicity





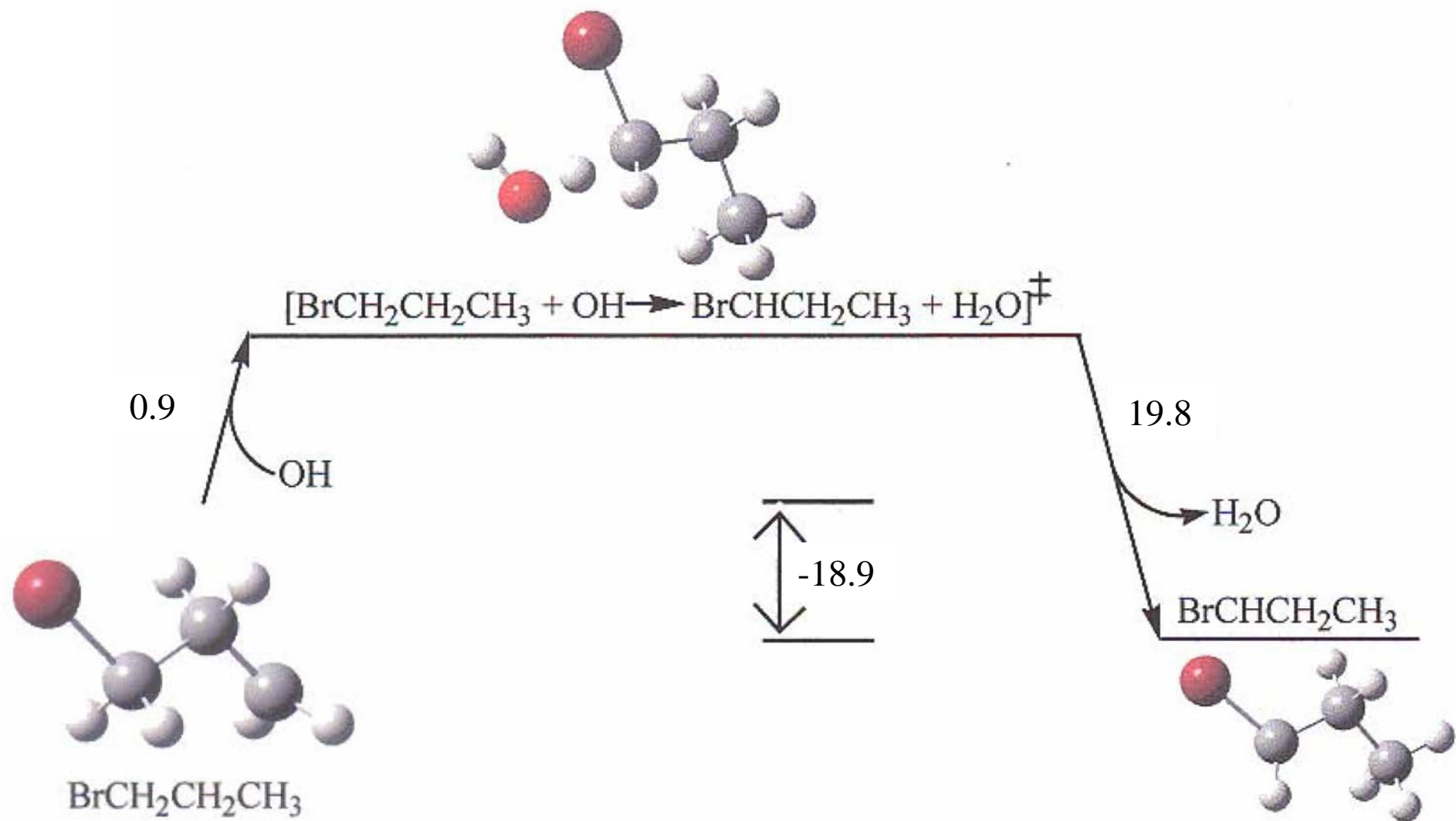
# Why Bromopropane?

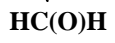
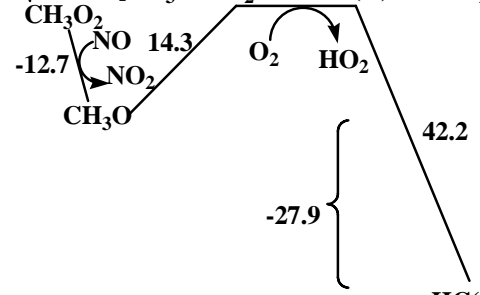
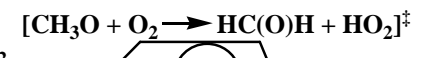
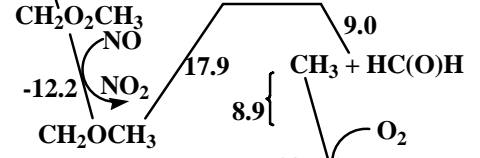
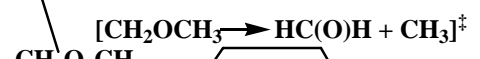
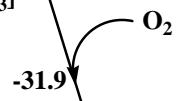
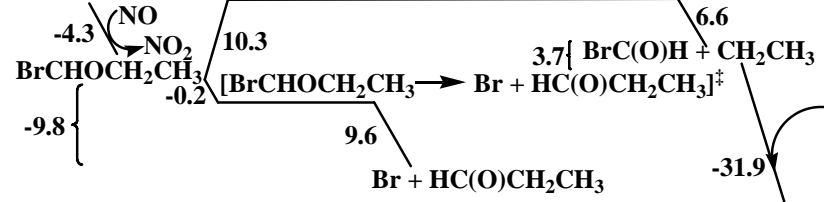
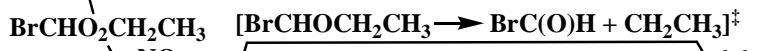
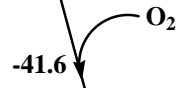
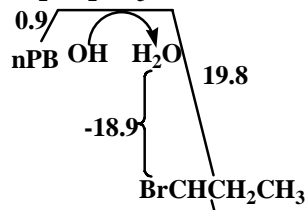
- Catalytic ozone destruction
- Release of Br atoms
- Atmospheric lifetime
- Ozone Depletion Potentials (ODP)



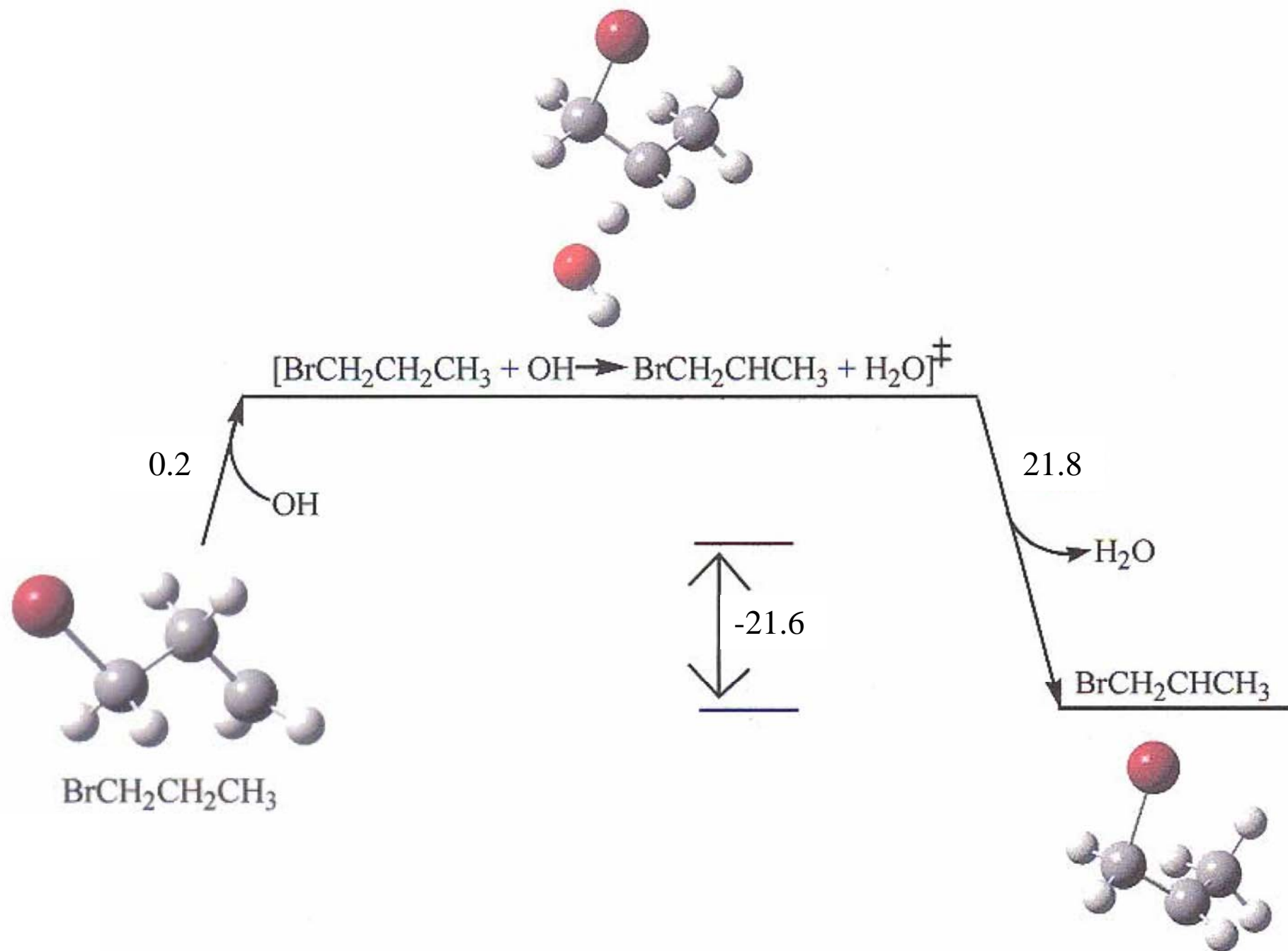


PES for the reaction of Bromopropane + radical OH using CCSD(T)/6-311++G(2df,2p)



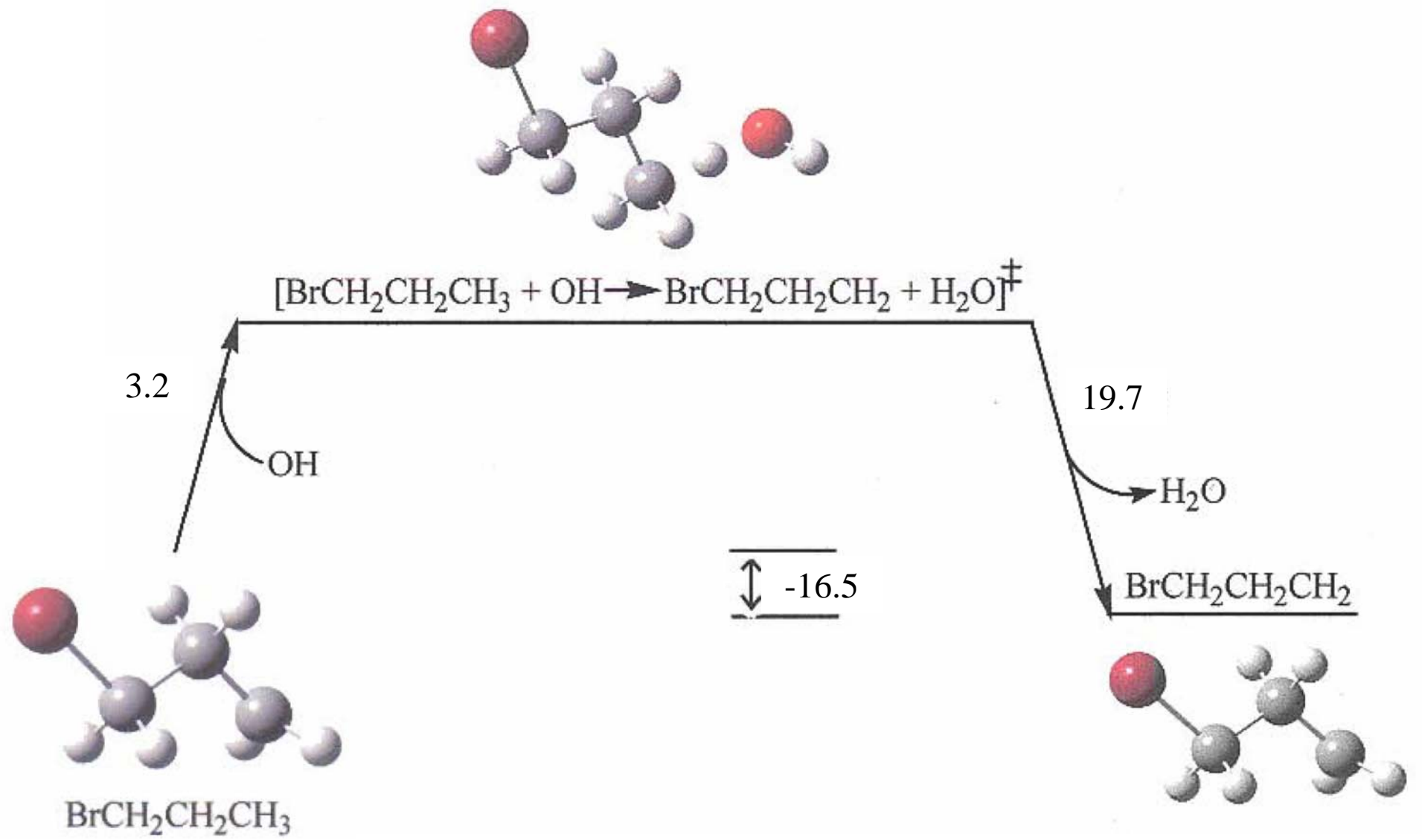


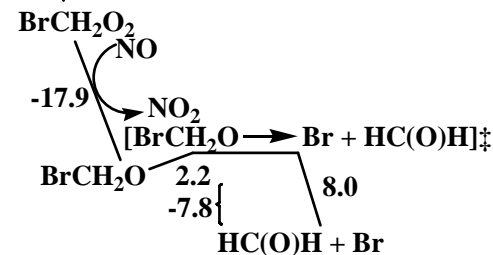
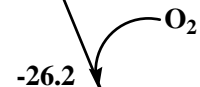
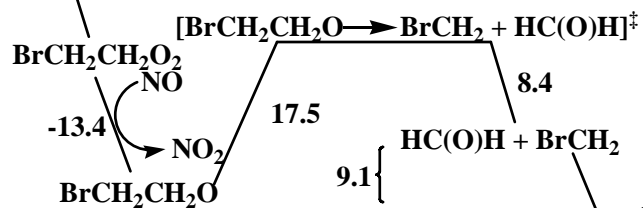
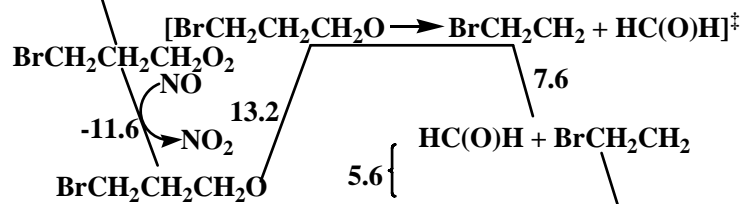
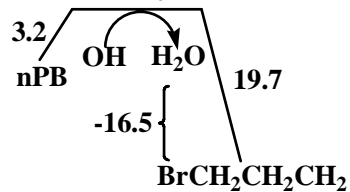
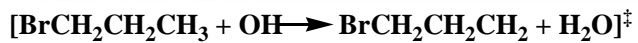
PES for the reaction of Bromopropane + radical OH using CCSD(T)/6-311++G(2df,2p)





PES for the reaction of Bromopropane + radical OH using CCSD(T)/6-311++G(2df,2p)









# Structure and Vibrational Spectra of Bromine Reservoir Species from the Atmospheric Oxidations of Bromoethane and Bromopropane

**Table 1. Rotational Constants (MHz) of the Reservoir Species**

Species	Level of Theory								
	MP2/6-31G(d)			QCISD/6-31G(d)			B3LYP/6-311++G(3df,3pd)		
	A	B	C	A	B	C	A	B	C
<b>Aldehydes</b>									
HC(O)H	287167	37972	33538	285427	38136	33641	284869	39232	34483
BrC(O)H	73742	3982	3778	73514	3981	3777	75345	3997	3796
HC(O)CH <sub>3</sub>	56528	10092	9043	56316	10065	9020	57515	10179	9132
BrCH <sub>2</sub> C(O)H	24018	1925	1859	24536	1895	1831	23112	1940	1873
BrCH <sub>2</sub> CH <sub>2</sub> C(O)H	20333	974	966	20843	958	947	21566	955	944
<b>Ketones</b>									
BrC(O)CH <sub>3</sub>	9985	2980	2328	9995	2972	2324	10150	2955	2321
BrC(O)CH <sub>2</sub> CH <sub>3</sub>	8274	1545	1323	8317	1536	1318	8401	1525	1311
BrCH <sub>2</sub> C(O)CH <sub>3</sub>	7421	1603	1422	7394	1584	1406	7517	1560	1386

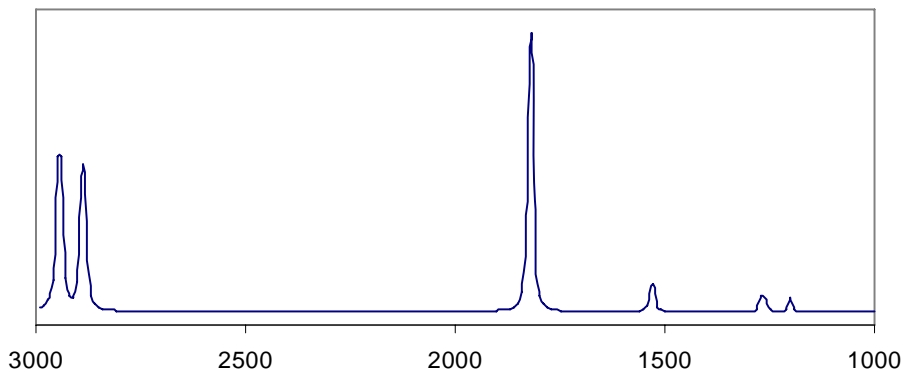
**Among molecules with the same amount of heavy atoms, aldehydes will have higher values for A than ketones; whereas the inverse is true for B and C.**



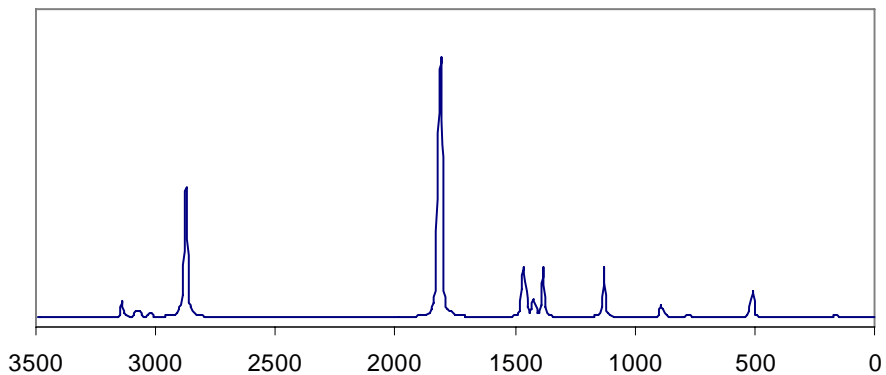


# Theoretical IR Spectra for Aldehydes

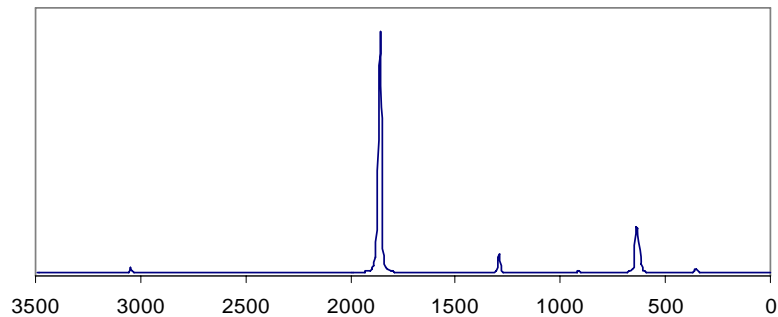
HC(O)H



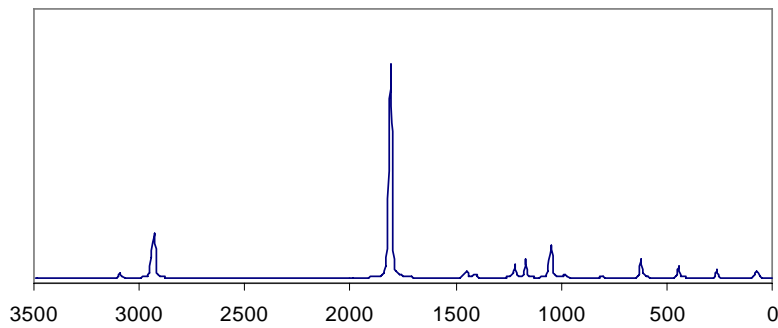
HC(O)CH<sub>3</sub>



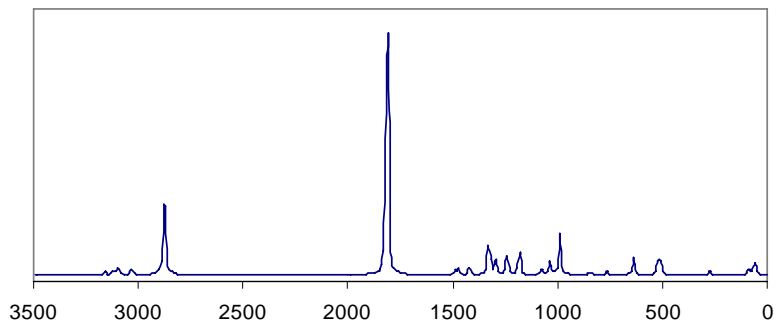
BrC(O)H



BrCH<sub>2</sub>C(O)H



BrCH<sub>2</sub>CH<sub>2</sub>C(O)H

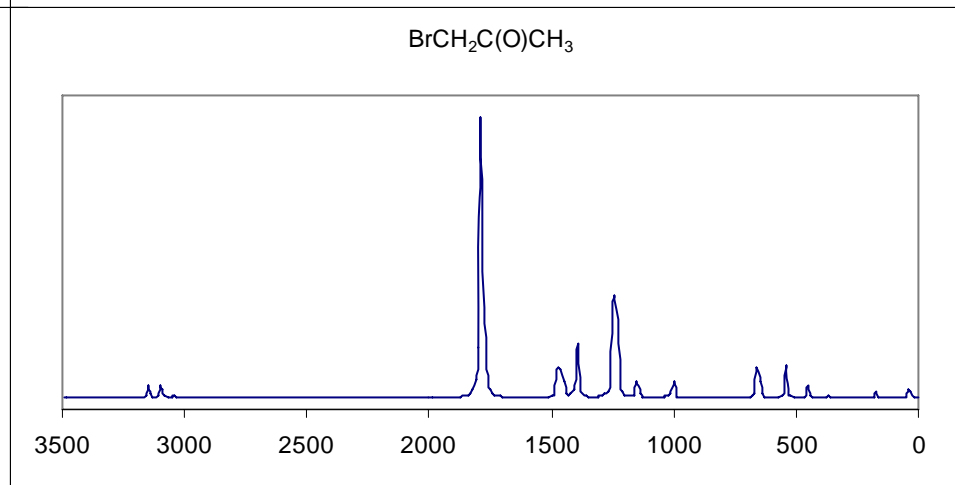
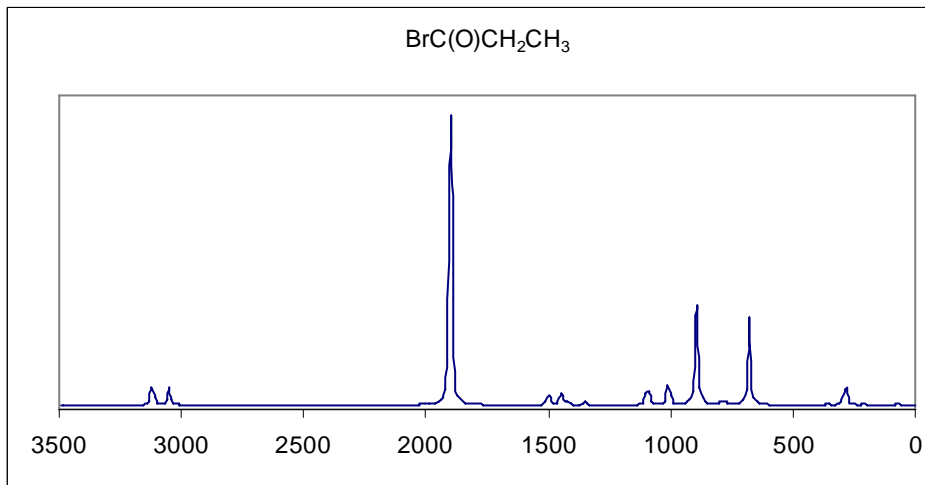
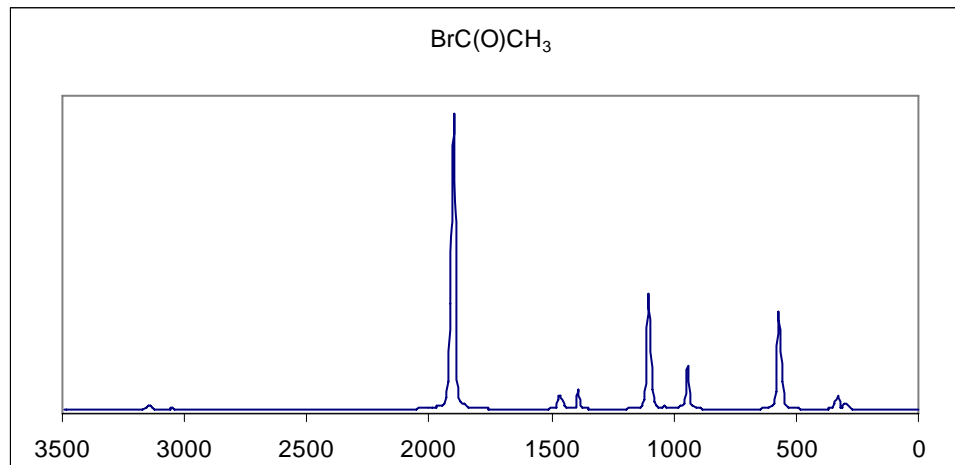


**Symmetric CO stretch ~1800 cm<sup>-1</sup>**  
**CBr stretch ~ 600 cm<sup>-1</sup>**



# Theoretical IR Spectra for Ketones

**Symmetric CO stretch  $\sim 1800\text{ cm}^{-1}$**   
**CBr stretch  $\sim 600\text{ cm}^{-1}$**





# To submit...

- Theoretical calculations are required!
- Obtain IR spectrum with prominent peaks and  
specify the assignments for a peak at 1700 cm<sup>-1</sup> and a peak at 3000 cm<sup>-1</sup>  
bromine
- Literature values for  $\Delta H_{\text{vap}}$  and  $\Delta H_{\text{f}}^{\circ}$  and  
HC

**Draft**

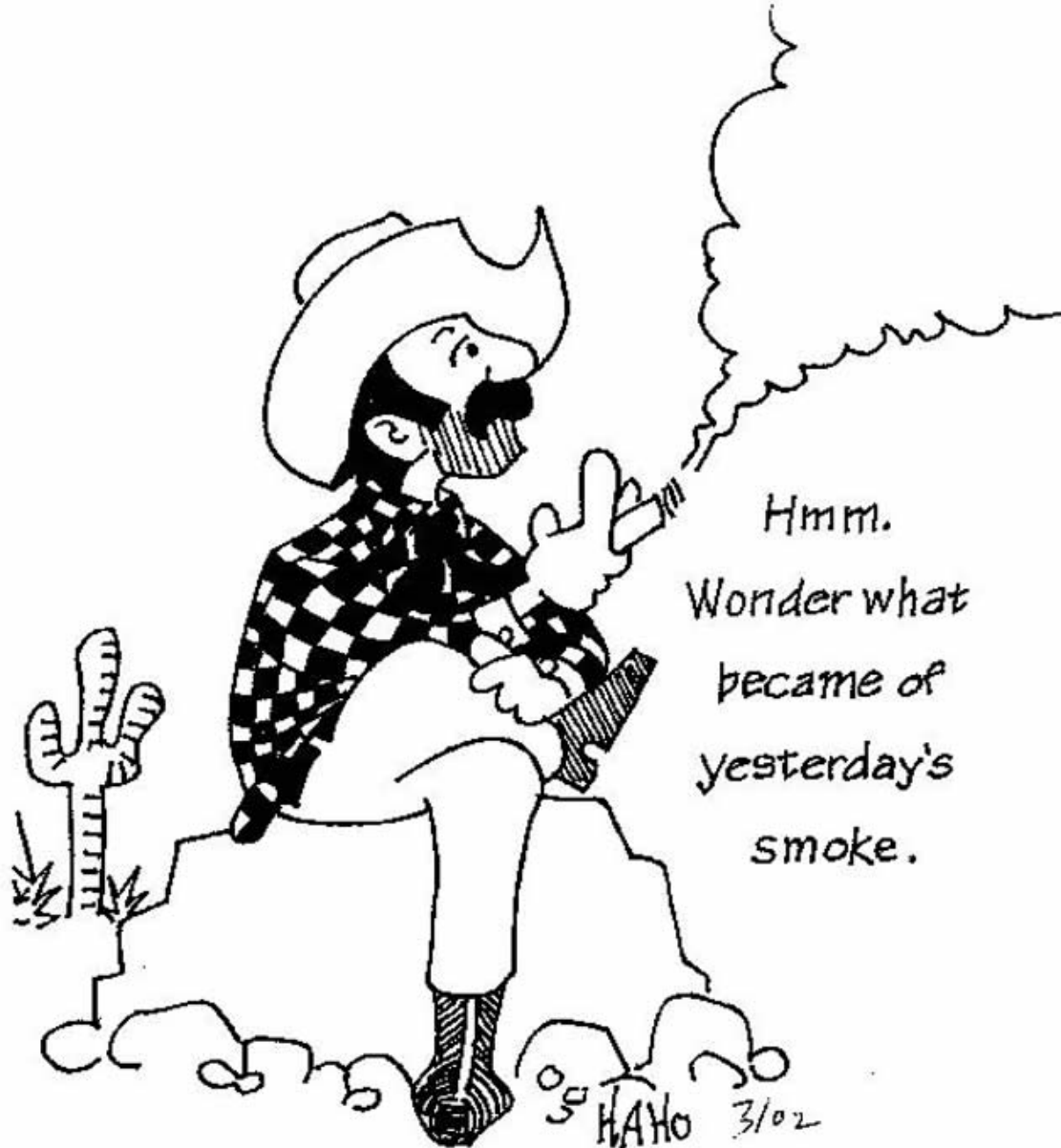




ILLINOIS

UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

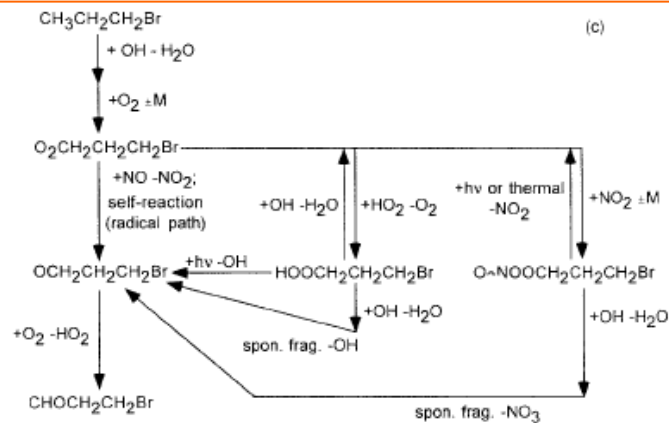
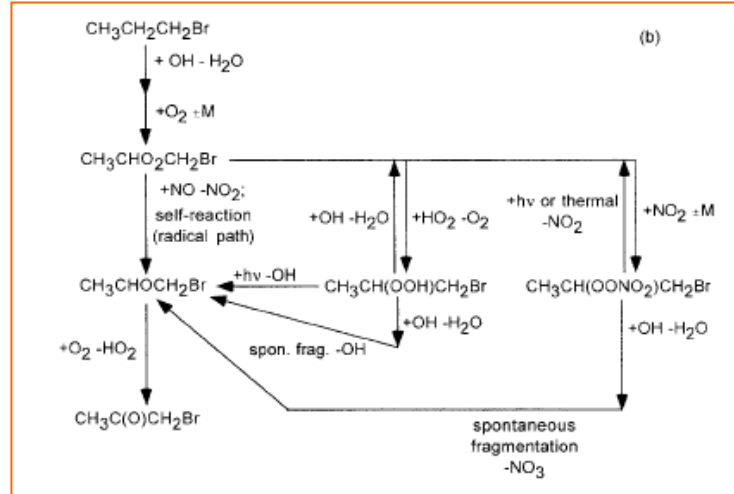
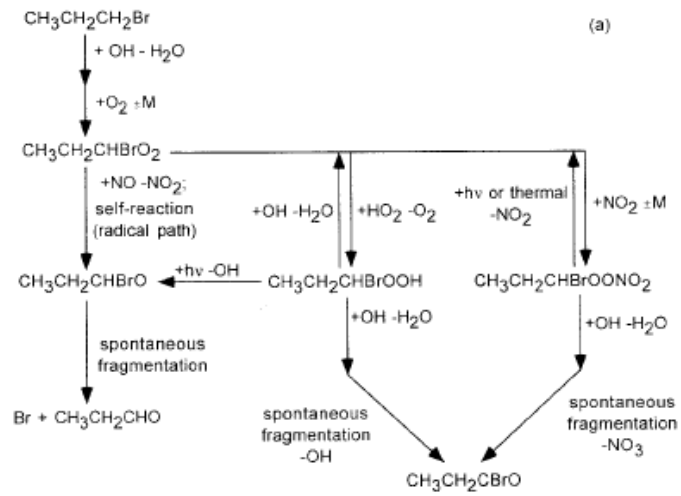




Hmm.  
Wonder what  
became of  
yesterday's  
smoke.

05 HAHo 3/02







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# 2D Atmospheric Modeling

- MOZART2-2D
  - 2D: less computationally expensive
  - All thermal and photochemical reactions
    - Rate constants: JPL and Multiwell
    - Thermal: Arrhenius values
    - Photochemical: Absorption cross sections
    - Analogous treatment





**Table 1.** Estimates of Reaction Rate Constants and Mass Accommodation Coefficients for the Degradation Chemistry of *n*-Propyl Bromide

Reaction <sup>a</sup>	Rate Constant in Appropriate Units <sup>b</sup> or Analogous Compound	Reference
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br + OH → CH <sub>3</sub> CH <sub>2</sub> CHBrO <sub>2</sub> + H <sub>2</sub> O CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br + OH → CH <sub>3</sub> CH(O <sub>2</sub> )CH <sub>2</sub> Br + H <sub>2</sub> O CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br + OH → O <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br + H <sub>2</sub> O RCHBrO <sub>2</sub> + NO → RCHO + NO <sub>2</sub> RXCHO <sub>2</sub> + NO → RXCO + NO <sub>2</sub> + HO <sub>2</sub> <sup>c</sup> XC(O)O <sub>2</sub> + NO → X + CO <sub>2</sub> + NO <sub>2</sub> XO <sub>2</sub> + NO <sub>2</sub> + M → XOONO <sub>2</sub> + M	4.0 × 10 <sup>-12</sup> exp (300/T) 1.8 × 10 <sup>-12</sup> exp (300/T) 7.3 × 10 <sup>-12</sup> exp (300/T) three body <sup>d</sup> with k <sub>0</sub> = 1.3 × 10 <sup>-20</sup> (T/300) <sup>-6.2</sup> k <sub>∞</sub> = 8.8 × 10 <sup>-12</sup> g = 0.31	<i>Kwok and Atkinson</i> [1995] distribution; <i>Nelson et al.</i> [1997] total  <i>DeMore et al.</i> [1997] for <i>T</i> dependence; <i>Atkinson et al.</i> [1997] for preexponential factors <i>Atkinson et al.</i> [1997]
XC(O)O <sub>2</sub> + NO <sub>2</sub> + M → XC(O)OONO <sub>2</sub> + M	three body <sup>d</sup> with k <sub>0</sub> = 2.7 × 10 <sup>-28</sup> (T/300) <sup>-7.1</sup> k <sub>∞</sub> = 1.2 × 10 <sup>-11</sup> (T/300) <sup>-0.9</sup> g = 0.30	<i>Atkinson et al.</i> [1997]
XOONO <sub>2</sub> → XO <sub>2</sub> + NO <sub>2</sub> XC(O)OONO <sub>2</sub> → XC(O)O <sub>2</sub> + NO <sub>2</sub> 2R <sub>1</sub> R <sub>2</sub> CBrO <sub>2</sub> → 2R <sub>1</sub> C(O)R <sub>2</sub> + 2Br + O <sub>2</sub> 2RXCHO <sub>2</sub> → 2RC(O)X + O <sub>2</sub> + 2HO <sub>2</sub> <sup>c</sup> 2XC(O)O <sub>2</sub> → 2X + 2CO <sub>2</sub> + O <sub>2</sub> XOOH + OH → XO <sub>2</sub> + H <sub>2</sub> O RXCHOOH + OH → RC(O)X + OH + H <sub>2</sub> O XCH <sub>2</sub> OOH + OH → XCHO + OH + H <sub>2</sub> O XC(O)OOH + OH → XC(O)O <sub>2</sub> + H <sub>2</sub> O XC(O)OH + OH → X + CO <sub>2</sub> + H <sub>2</sub> O	9 × 10 <sup>15</sup> exp (-10,450/T) 4 × 10 <sup>16</sup> exp (-13,600/T) 3.3 × 10 <sup>-11</sup> 3.9 × 10 <sup>-12</sup> 2.9 × 10 <sup>-12</sup> exp (500/T) 2.66 × 10 <sup>-12</sup> exp (200/T) 3.8 × 10 <sup>-13</sup> exp (200/T) 7.6 × 10 <sup>-13</sup> exp (200/T) 2.66 × 10 <sup>-12</sup> exp (200/T) 3.0 × 10 <sup>-13</sup> exp (255/T)	<i>Atkinson</i> [1994] <i>Atkinson</i> [1994] <i>Atkinson et al.</i> [1997] <i>Atkinson et al.</i> [1997] <i>DeMore et al.</i> [1997] <i>DeMore et al.</i> [1997]
OH + XCHO, RCBRO, CH <sub>3</sub> C(O)CH <sub>2</sub> Br, XC(O)OONO <sub>2</sub> , as well as OH + XC(O)OH or XC(O)OOH at H along X		<i>Kwok and Atkinson</i> [1995]; section 3.11 of text <i>Kwok and Atkinson</i> [1995]
Photolysis reactions		
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br + <i>hν</i> CH <sub>3</sub> C(O)CH <sub>2</sub> Br + <i>hν</i> CH <sub>3</sub> CH <sub>2</sub> CBrO + <i>hν</i> , CHOCH <sub>2</sub> CH <sub>2</sub> Br + <i>hν</i> , CHOCH <sub>2</sub> CBrO + <i>hν</i> , ZCOCH <sub>2</sub> CBrO + <i>hν</i> , CHOC(O)CH <sub>2</sub> Br + <i>hν</i> , CH <sub>3</sub> C(O)CBrO + <i>hν</i> , CHOC(O)CBrO + <i>hν</i> , ZC(O)C(O)CH <sub>2</sub> Br + <i>hν</i> , ZC(O)C(O)CBrO + <i>hν</i> CHOCBrO + <i>hν</i> , ZC(O)CBrO + <i>hν</i> XOOH + <i>hν</i> , XC(O)OOH + <i>hν</i> except when X contains adjacent C=O XOONO <sub>2</sub> + <i>hν</i> , XC(O)OONO <sub>2</sub> + <i>hν</i> except when X contains adjacent C=O	CH <sub>3</sub> Br + <i>hν</i> CH <sub>3</sub> C(O)CH <sub>3</sub> + <i>hν</i> CH <sub>3</sub> CH <sub>2</sub> CHO + <i>hν</i>  CH <sub>3</sub> C(O)CHO + <i>hν</i>  CHOCHO + <i>hν</i> CH <sub>3</sub> OOH + <i>hν</i>  CH <sub>3</sub> C(O)OONO <sub>2</sub> + <i>hν</i>	<i>DeMore et al.</i> [1997] <i>Gierczak et al.</i> [1998] <i>Atkinson et al.</i> [1997]  <i>Atkinson et al.</i> [1997]  <i>Atkinson et al.</i> [1997] <i>DeMore et al.</i> [1997]  <i>DeMore et al.</i> [1997]
Mass accommodation coefficients for "α-based" rainout		
CH <sub>3</sub> C(O)CH <sub>2</sub> Br XCHO	CH <sub>3</sub> C(O)CH <sub>3</sub> CH <sub>3</sub> CH <sub>2</sub> CHO (3-carbon) or CH <sub>3</sub> CHO (2-carbon)	<i>DeMore et al.</i> [1997] <i>DeMore et al.</i> [1997]
RCBrO XC(O)OH XOOH XC(O)OOH XOONO <sub>2</sub> XC(O)OONO <sub>2</sub> CHOC(O)CBrO XO <sub>2</sub> and other radicals	0.0 CH <sub>3</sub> C(O)OH CH <sub>3</sub> OOH CH <sub>3</sub> C(O)OOH CH <sub>3</sub> C(O)OONO <sub>2</sub> CH <sub>3</sub> C(O)OONO <sub>2</sub> CH <sub>3</sub> CHO 0.0	<i>DeMore et al.</i> [1997] <i>DeMore et al.</i> [1997] <i>DeMore et al.</i> [1997] <i>DeMore et al.</i> [1997] <i>DeMore et al.</i> [1997] <i>Schweitzer et al.</i> [1998]

<sup>a</sup>R, R<sub>1</sub>, R<sub>2</sub> = alkyl group not containing Br; X = brominated alkyl group; Z = OH, OOH, or OONO<sub>2</sub>.

<sup>b</sup>"Appropriate units": s<sup>-1</sup> for photolysis or first-order thermal decomposition, cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> for second-order reactions or third-order reactions (including the k<sub>0</sub>[M] low-pressure terms). *T* is in K, [M] is in molecules cm<sup>-3</sup>.

<sup>c</sup>An additional O<sub>2</sub> not shown on the left side reacts instantly with the initially formed radical to produce HO<sub>2</sub> (see section 3.7).

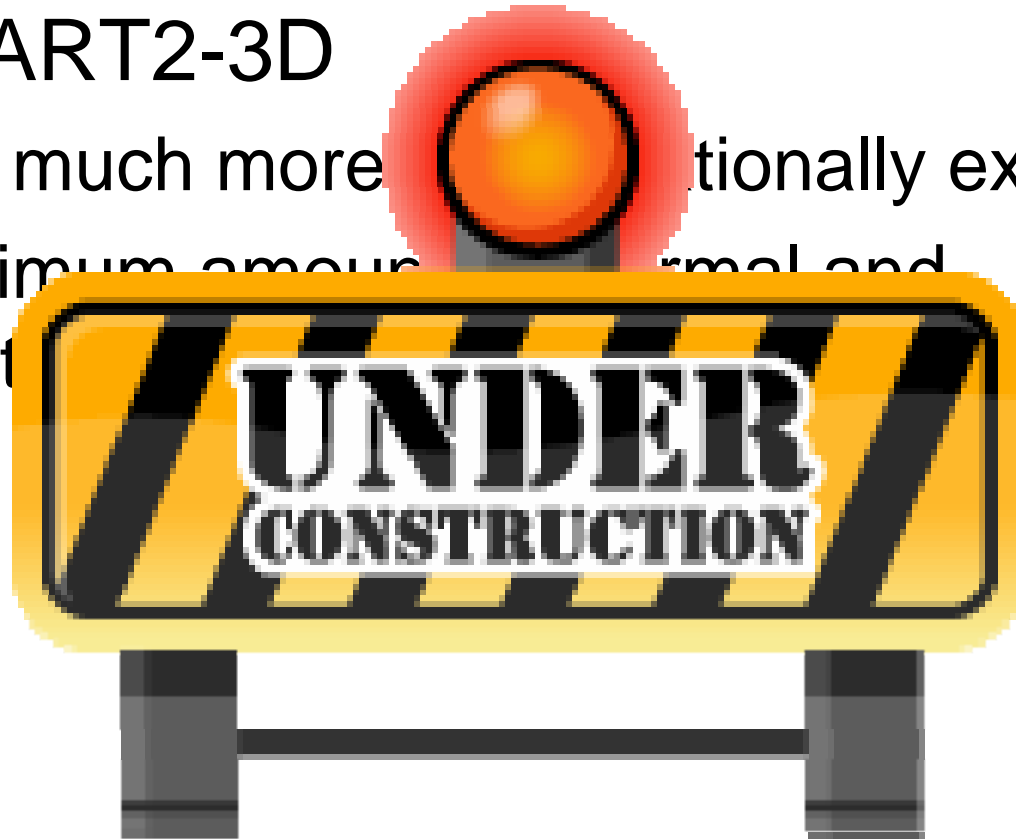
<sup>d</sup>"Three-body" rate constant given by the Troe expression,  $k = k_0[M]k_\infty / (k_0[M] + k_\infty)$  with  $f = \log_{10}(g)(1 + [\log_{10}(k_0[M]/k_\infty)]^2)^{-1}$ .





# 3D Atmospheric Modeling

- MOZART2-3D
  - 3D: much more computationally expensive
  - Minimum amount of thermal and phot





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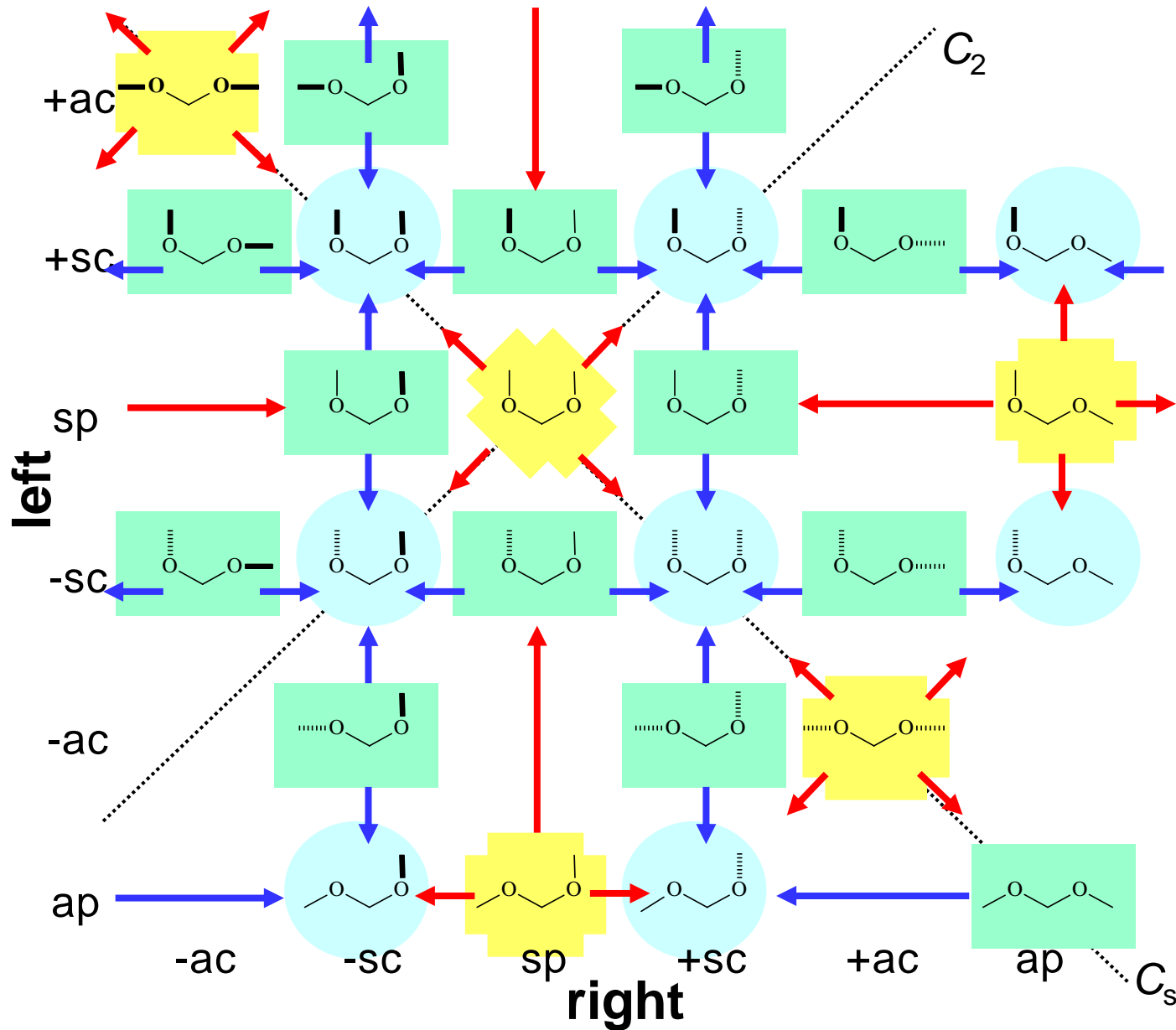
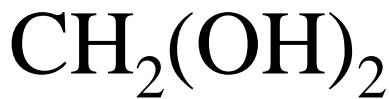




# Conformational Topography of Halomethanediols $XCH(OH)_2$ ( $X = H, F, Cl$ )

- Long story short...
  - $CF_3CHXY$  (where  $X, Y = H, F$  or  $Cl$ )
    - Proposed CFC alternative
  - Degrades to carbonyl compounds:  $HXCO$
  - $HXCO + H_2O \longrightarrow XCH(OH)_2$
- Methodology: *Ab initio* calculations!!
  - 2 optimizations (HF & MP2) + 3 SP calculations
  - CCSD(T)/cc-PVTZ//MP2/6-311+G(d,p)

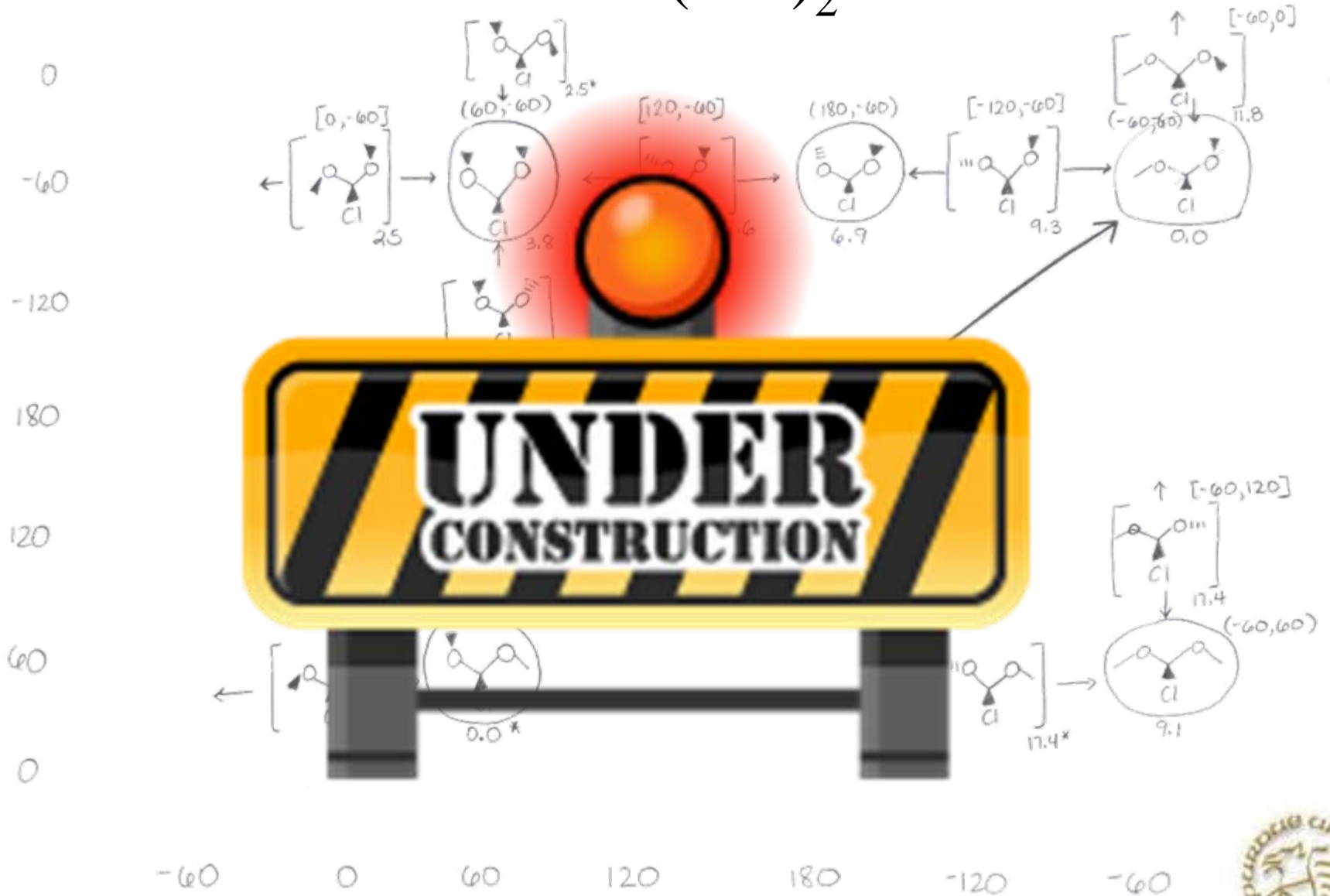




ap (antiperiplanar), sp (synperiplanar), ac (anticlinal), sc (synclinal)



# $\text{ClCH}(\text{OH})_2$



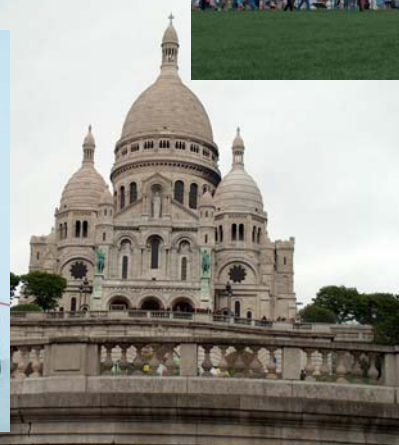
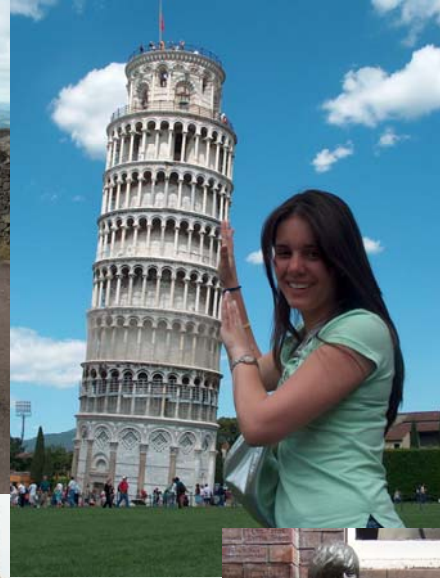


It is nice to work while you

TRAVEL!!!



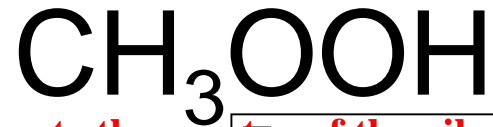
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**P**

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The purpose of the studies was to generate the spectra of the vibration overtone states of the methyl hydroperoxide, examine the dissociation spectral profile and characterization of the product state distribution.

- Synthesize CH<sub>3</sub>OOH
- Lasers alignment
- SPECTRA!!!

Vibrational mediated photodissociation was used to study this organic peroxide's photochemistry. The studies were performed by exciting the  $\nu = 2$  and 3 OH vibration modes. Dissociation light in the visible region was used to initiate dissociation, which was followed by probing the dissociation OH fragment using laser induced fluorescence (LIF).

- Data Analysis
- Simulations

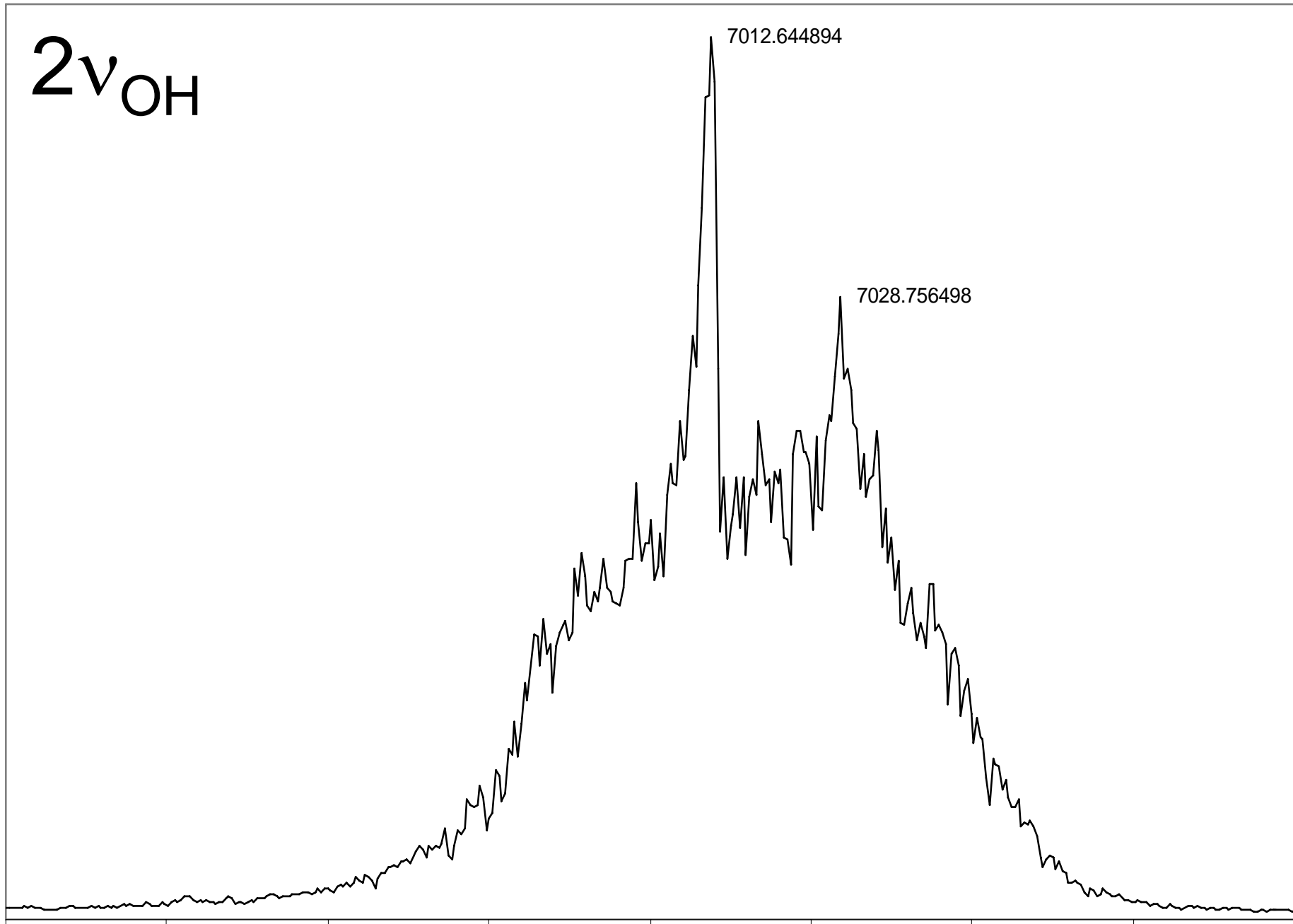


$2\nu_{\text{OH}}$

7012.644894

7028.756498

6925 6945 6965 6985 7005 7025 7045 7065 7085



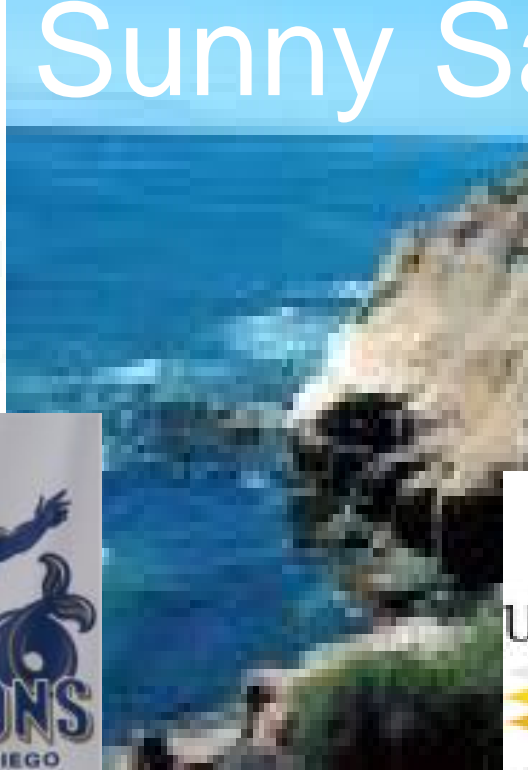
3v<sub>OH</sub>

**Draft**

10080 10130 10180 10230 10280 10330 10380 10430 10480



# Sunny San Diego!!



SAN DIEGO ZOO





# Conclusions

- I love to work while I am traveling!!
- Graduate school + GREF = Great experience!!
- When it does not work...
  - Don't get discouraged, but also be realistic...
- Experience
  - Computational chemistry
  - Laser Induced Fluorescence (LIF)
  - Atmospheric modeling
- Missing = Post Doc
  - In situ studies of halogenated compounds in the marine environment...marine biological activity is the major source of brominated compounds...





# Acknowledgments

- Dr. Joseph S. Francisco and Francisco Research Group (Purdue University)
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- Dr. Ian Williams and Williams Research Group (Bath University)
- Dr. Donald Wuebbles and Wuebbles Research Group (UIUC)
- Rose and Alex for...





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# FOOD

# ANYONE??!!

QUESTIONS?? =>

