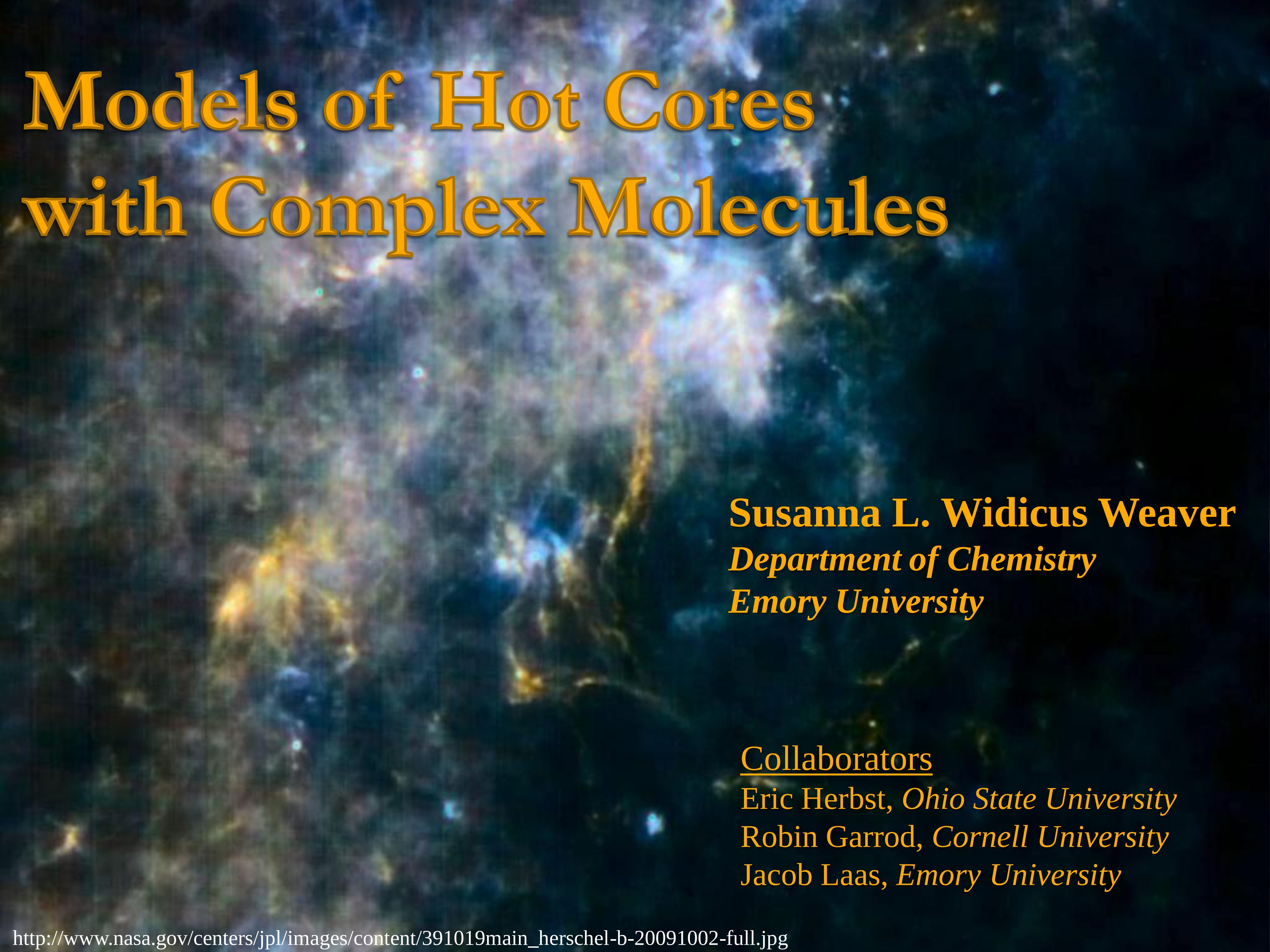


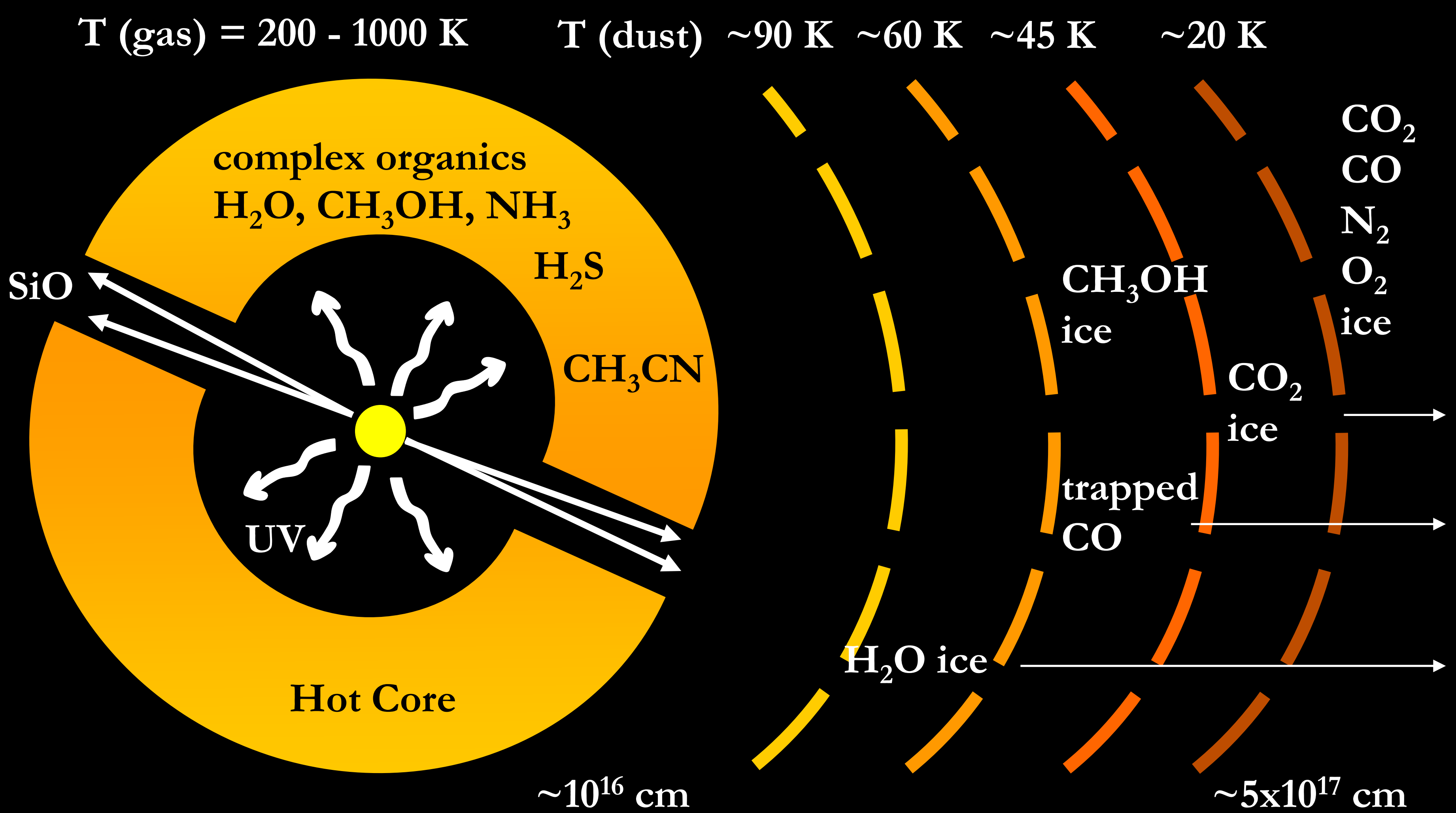
Models of Hot Cores with Complex Molecules

Susanna L. Widicus Weaver
Department of Chemistry
Emory University

<u>Collaborators</u>
Eric Herbst, *Ohio State University*
Robin Garrod, *Cornell University*
Jacob Laas, *Emory University*

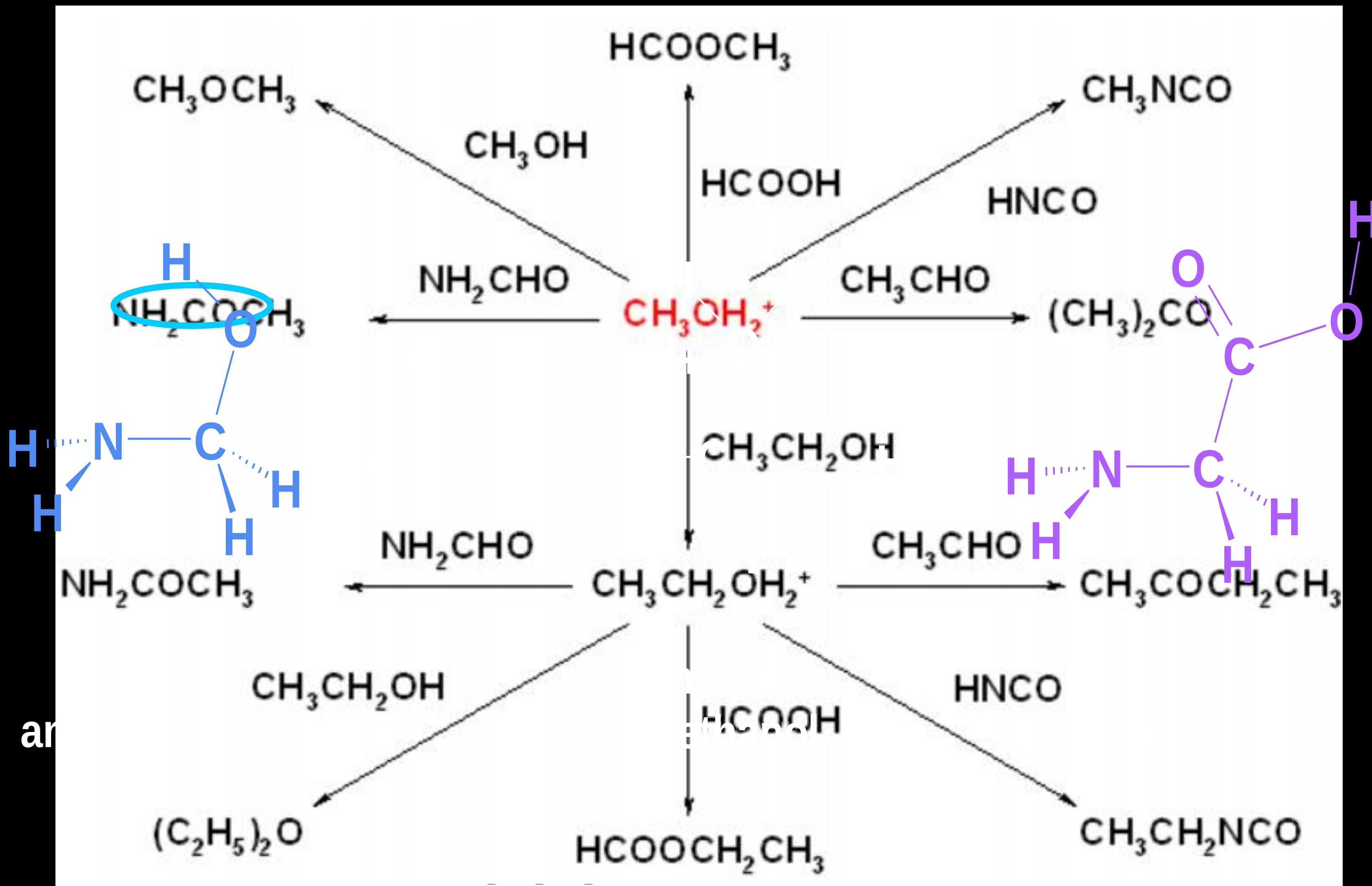
http://www.nasa.gov/centers/jpl/images/content/391019main_herschel-b-20091002-full.jpg

Schematic of a Hot Core



Adapted from van Dishoeck and Blake, Ann. Rev. Astron. & Astroph. 36, 1998

Gas Phase Reactions



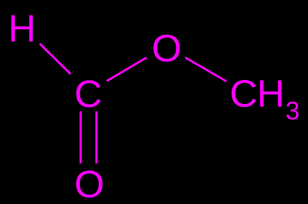
Charnley, S. (2001) Interstellar Organic Chemistry. In: *The Proceedings of the Workshop The Bridge Between the Big Bang and Biology*, (Consiglio Nazionale delle Ricerche, Italy).

The Methyl Formate Problem

- Cannot form by gas phase ion-molecule reactions   Horn et al. 2004, ApJ 611, 605

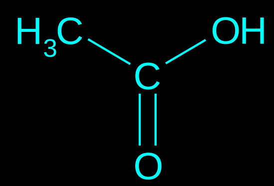
- Grain surface formation?

  Structural isomers would have similar abundances.



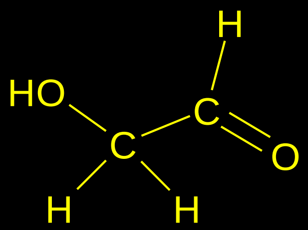
Methyl Formate

52



Acetic Acid

2



Glycolaldehyde

1

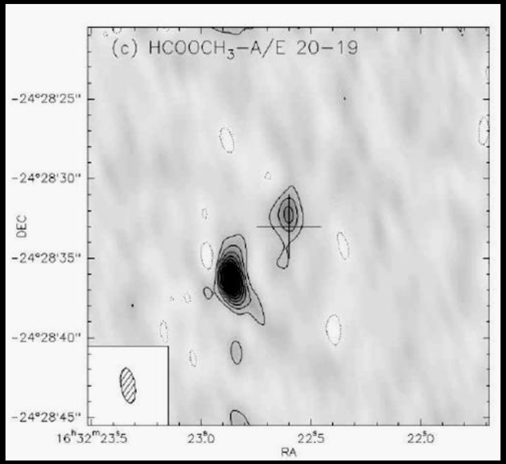
- Complex molecules observed in regions of grain mantle disruption:

  Shocked regions in the GC

  (Martín-Pintado et al.)

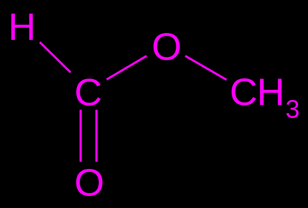
  Hot Corinos

  (Ceccarelli, Caselli, et al.)

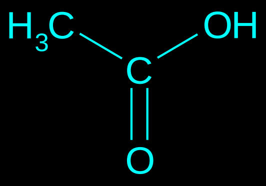


Bottinelli et al. ApJL 617, 2004

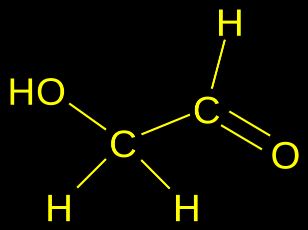
Clues from Organic Chemistry



Methyl Formate



Acetic Acid



Glycolaldehyde

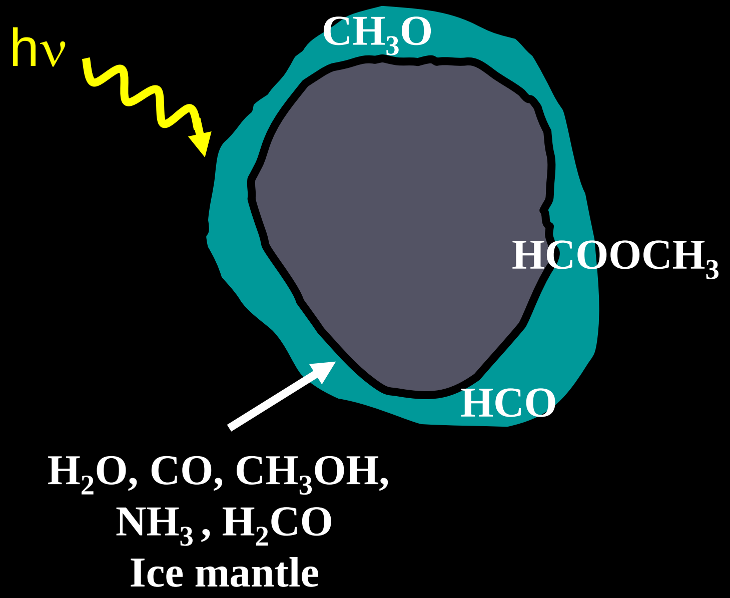
- $C_2H_4O_2$ isomers are comprised of organic functional groups:

$-CH_2OH$ $-C{=}O$ $-OCH_3$ $-OH$ $-CH_3$

- These functional groups are present in the most abundant interstellar ice components: CH_3OH, CO, H_2O, H_2CO

- What type of chemistry could drive the formation of these molecules in ices?

Grain Surface Formation



$H_2O + h\nu \longrightarrow OH + H$

$\longrightarrow H_2 + O$

$CH_3OH + h\nu \longrightarrow CH_3 + OH$

$\longrightarrow CH_3O + H$

$\longrightarrow CH_2OH + H$

$NH_3 + h\nu \longrightarrow NH_2 + H$

$H_2CO + h\nu \longrightarrow HCO + H$

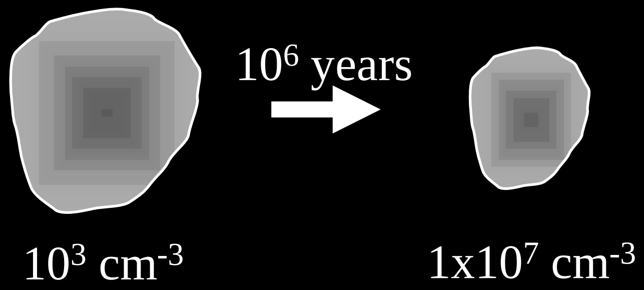
$HCO + CH_3O \longrightarrow$ **CH_3OCHO** (methyl formate)

$HCO + CH_2OH \longrightarrow$ **$HOCH_2CHO$** (glycolaldehyde)

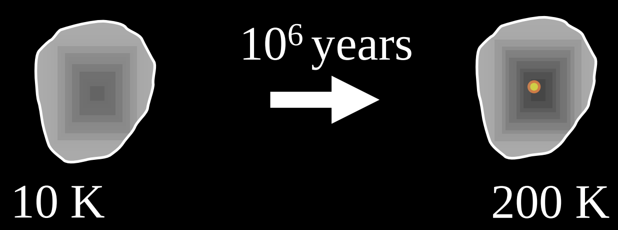
Garrod, Widicus Weaver, & Herbst, ApJ 682, 2008

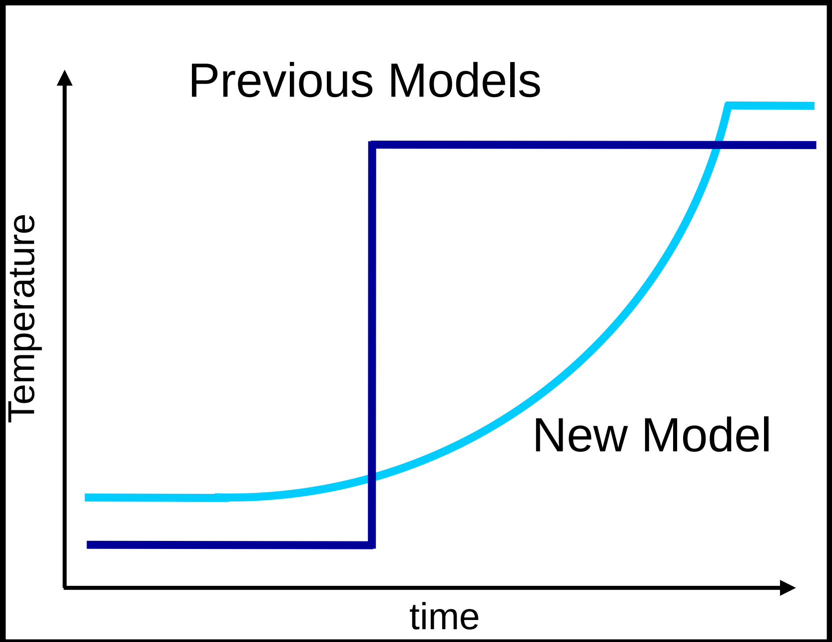
Two-Stage Hot Core Model

1. Cloud Collapse (isothermal free-fall)



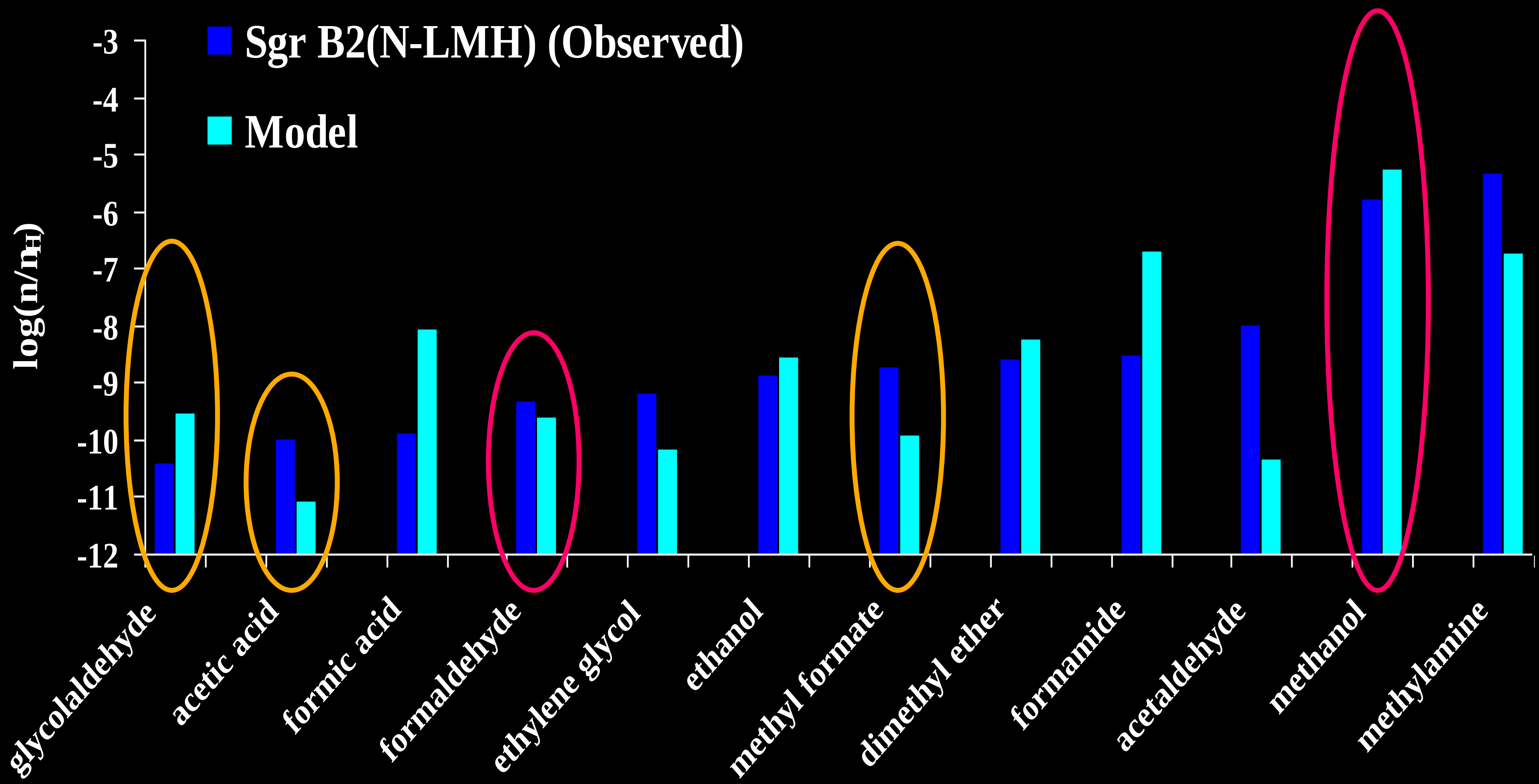
2. Warm-up (second-order power law)





Garrod, Widicus Weaver, & Herbst, ApJ 682, 2008

Results from Gas/Grain Model Including Warm-Up



CH_3OH photolysis branching ratios?

Garrod, Widicus Weaver, & Herbst, ApJ 682, 2008

There is a difference between CH_2OH and CH_3O

Values assumed for previous models:

$CH_3OH + h\nu$	$\longrightarrow$	$CH_3 + OH$	60%
	$\longrightarrow$	$CH_3O + H$	20%
	$\longrightarrow$	$CH_2OH + H$	20%

From gas phase laboratory studies, we know:

$CH_3OH + h\nu$	$\longrightarrow$	$CH_3 + OH$	< 5%
	$\longrightarrow$	$CH_3O + H$ }	~75%
	$\longrightarrow$	$CH_2OH + H$ }	
	$\longrightarrow$	$H_2CO + H$	20%

Hagege et al. Trans. Faraday Soc., **64**, 1968

This is critical for the methyl formate problem:

$$HCO + CH_3O \longrightarrow CH_3OCHO \quad \text{(methyl formate)}$$
$$HCO + CH_2OH \longrightarrow HOCH_2CHO \quad \text{(glycolaldehyde)}$$

Quantitative lab measurements of CH_3OH photolysis branching ratios are needed

Testing the Influence of CH_3OH Photodissociation Branching Ratios on COM Chemistry

- Used OSU gas/grain network and physical model from Garrod *et al.* 2008
  - ~540 chemical species, >7800 reactions, 13 reaction types

- Tested set of various BRs at different warm-up timescales

$$CH_3OH + h\nu \longrightarrow CH_3 + OH$$
$$\longrightarrow CH_3O + H$$
$$\longrightarrow CH_2OH + H$$

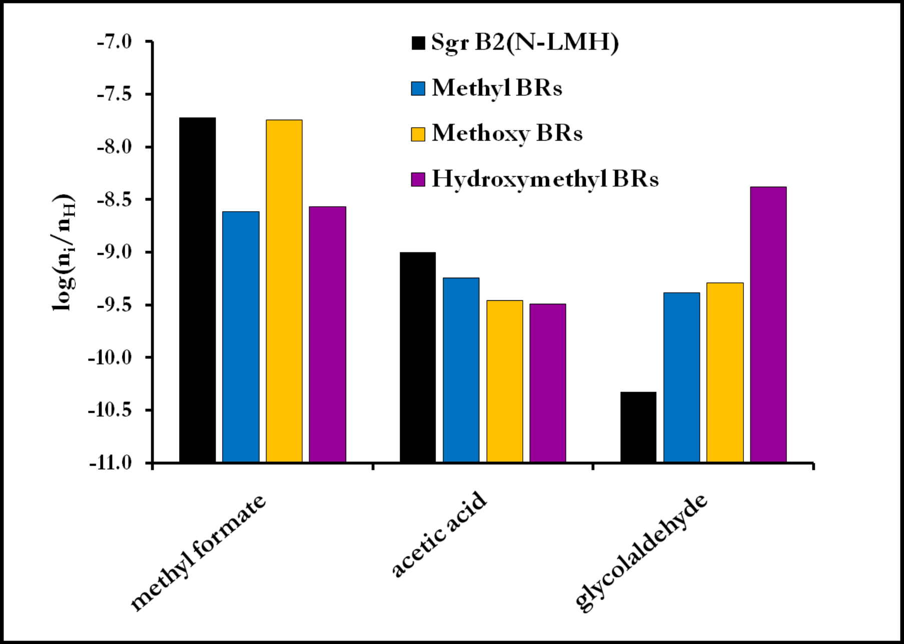
Trial	$CH_2OH:CH_3O:CH_3$ (%)
Standard[1]	20:20:60
Öberg[2]	73:15:12
Hydroxymethyl	90:5:5
Methoxy	5:90:5
Methyl	5:5:90

[1] Garrod, Widicus Weaver, & Herbst, ApJ 682, 2008
[2] Öberg *et al.*, A&A, 504, 2009

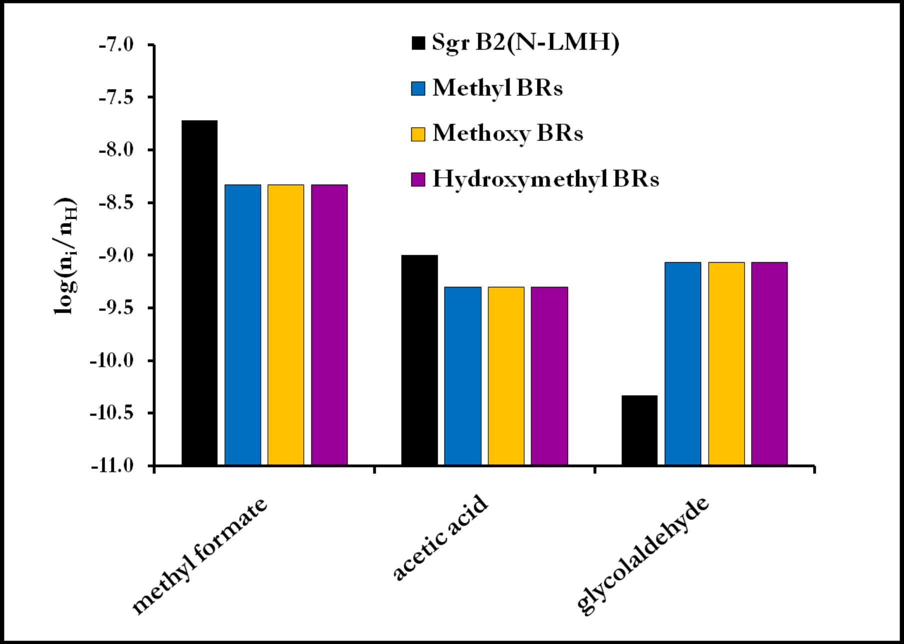
Laas, Garrod, Herbst, & Widicus Weaver, ApJ 728, 2011

Testing the Influence of CH_3OH Photodissociation Branching Ratios on COM Chemistry

Adjustment to Grain Surface BRs



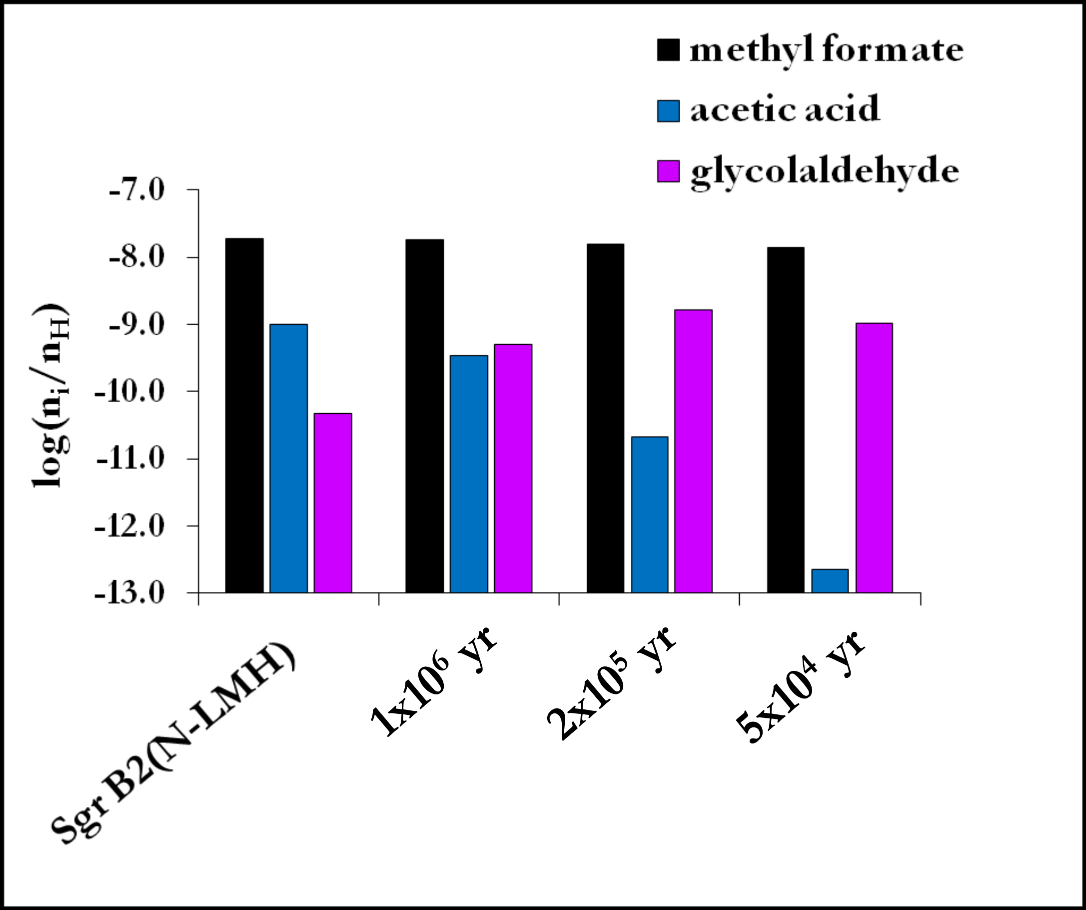
Adjustment to Gas Phase BRs



Grain surface methanol photodissociation BRs strongly influence the abundances of $C_2H_4O_2$ isomers. Gas phase methanol photodissociation BRs do not.

Laas, Garrod, Herbst, & Widicus Weaver, ApJ 728, 2011

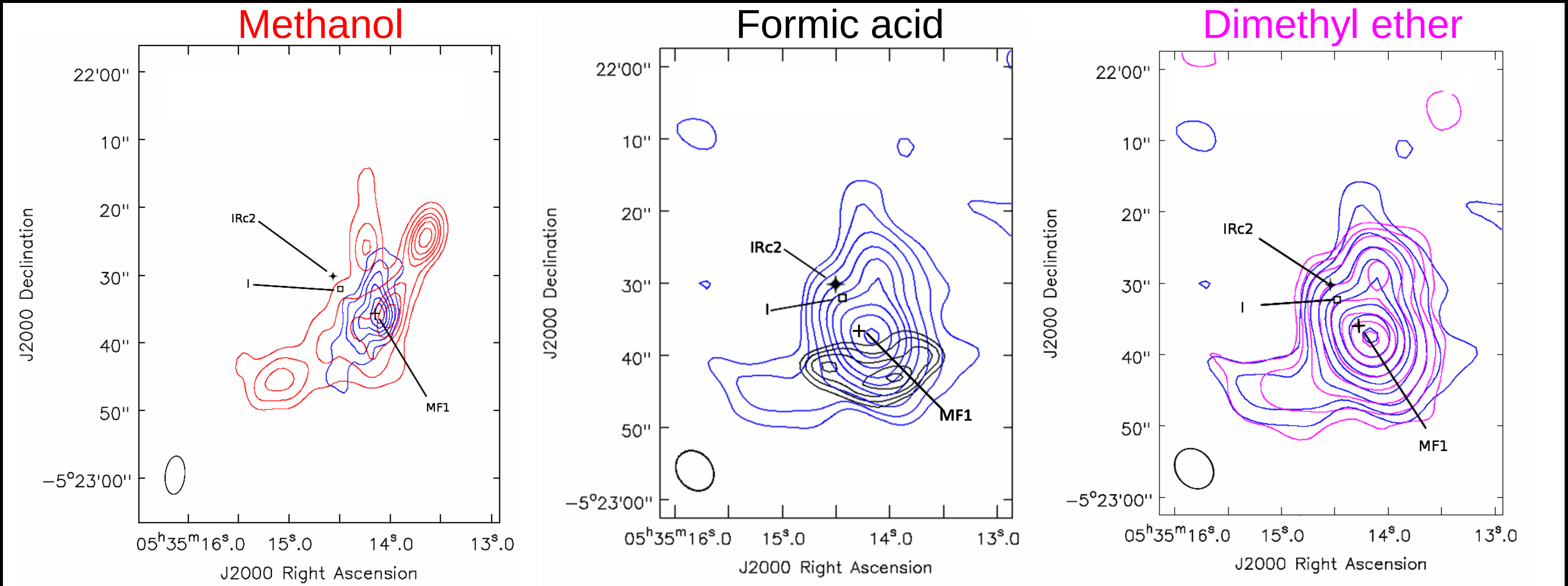
Testing the Influence of Warm-Up Timescale on COM Chemistry



Longer timescales for warm-up give better match to Sgr B2(N-LMH)

Laas, Garrod, Herbst, & Widicus Weaver, ApJ 728, 2011

Observations Indicate Additional Gas Phase Formation Routes for Methyl Formate



NRAO EVLA Demonstration 2009

Friedel and Widicus Weaver, CARMA, 2008

Dimethyl ether and methyl formate are spatially correlated.

Formic acid and methyl formate are spatially anti-correlated.

Neill et al., J. Phys. Chem., accepted

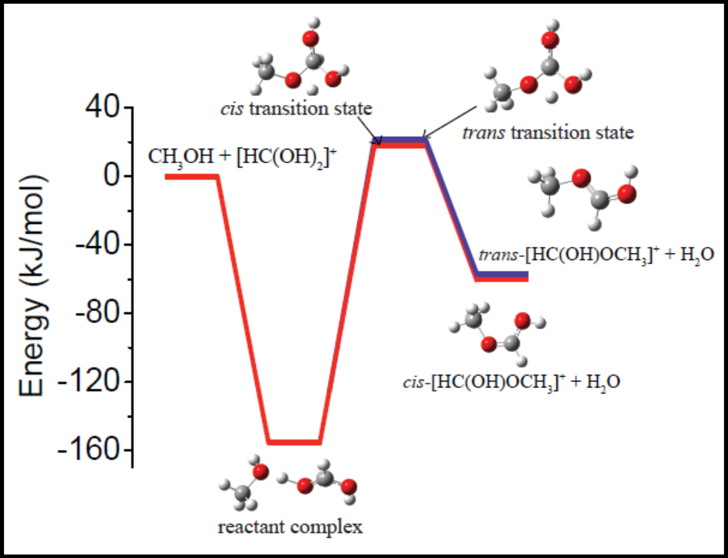
Possible Gas Phase Formation Routes for Methyl Formate

Two additional gas-phase formation routes have been proposed by Pate and coworkers:

1. Fischer esterification

   ($E_a \approx 3100$ K)

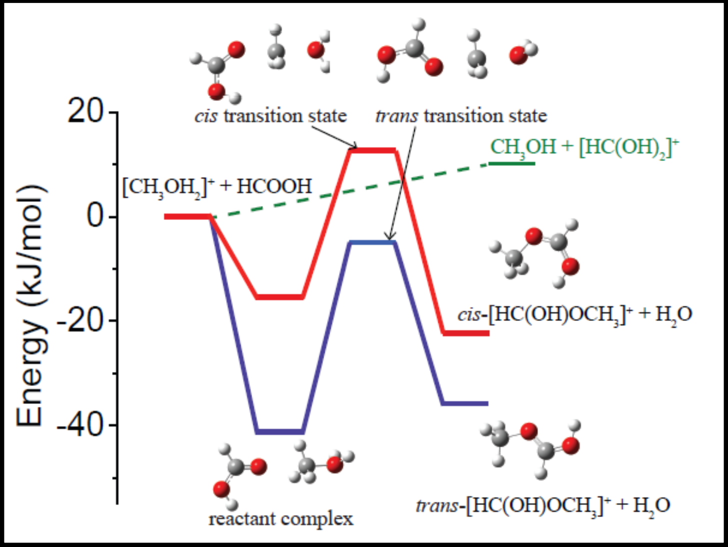
$$CH_3OH + HCOOH_2^+ \rightarrow HC(OH)OCH_3^+ + H_2O$$



2. Methyl cation transfer

   ($E_{a,cis} \approx 1320$ K, $E_{a,trans} = 0$ K)

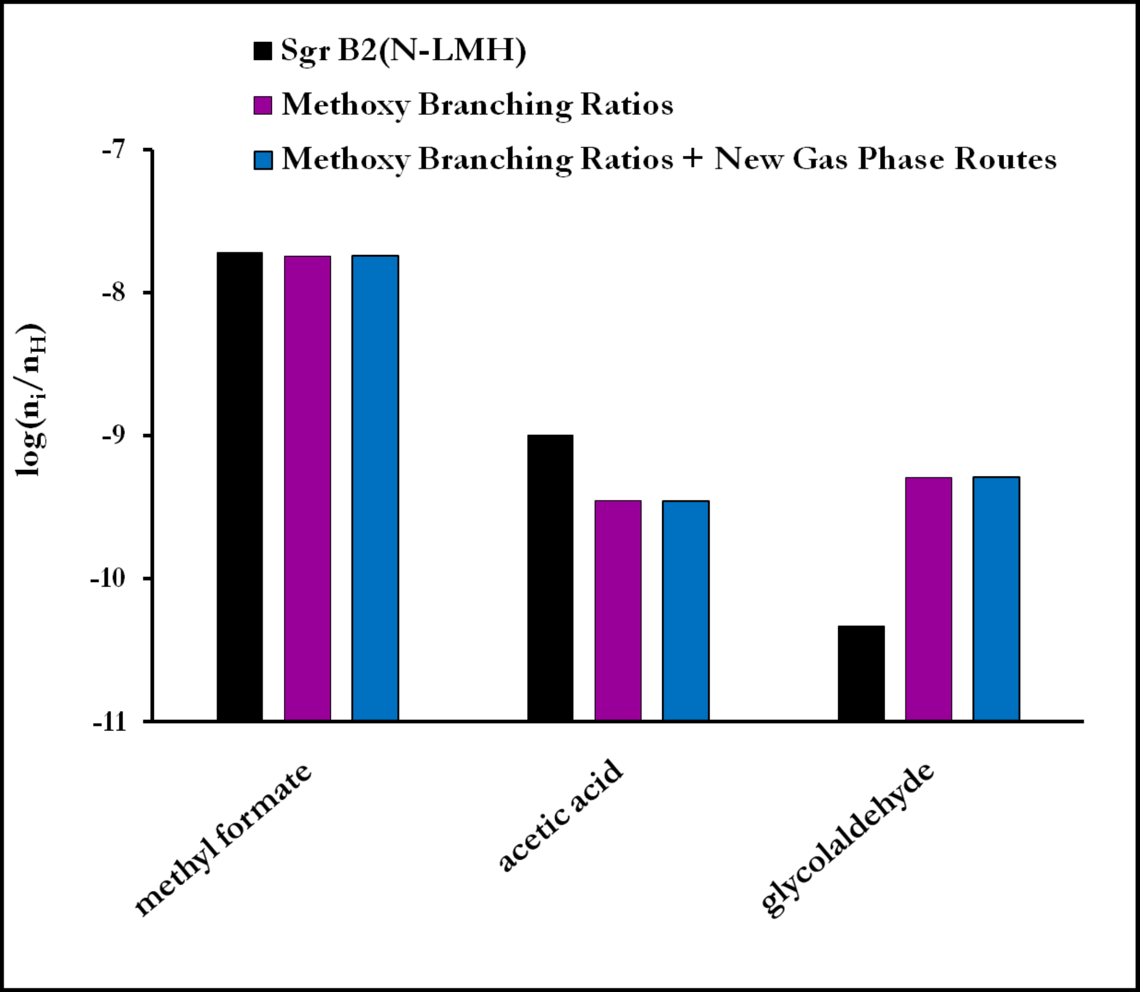
$$CH_3OH_2^+ + HCOOH \rightarrow HC(OH)OCH_3^+ + H_2O$$



Stereochemistry was also introduced to differentiate between *cis* and *trans* conformers

Neill et al., J. Phys. Chem., accepted

Grain Surface Versus Gas Phase Formation of Methyl Formate

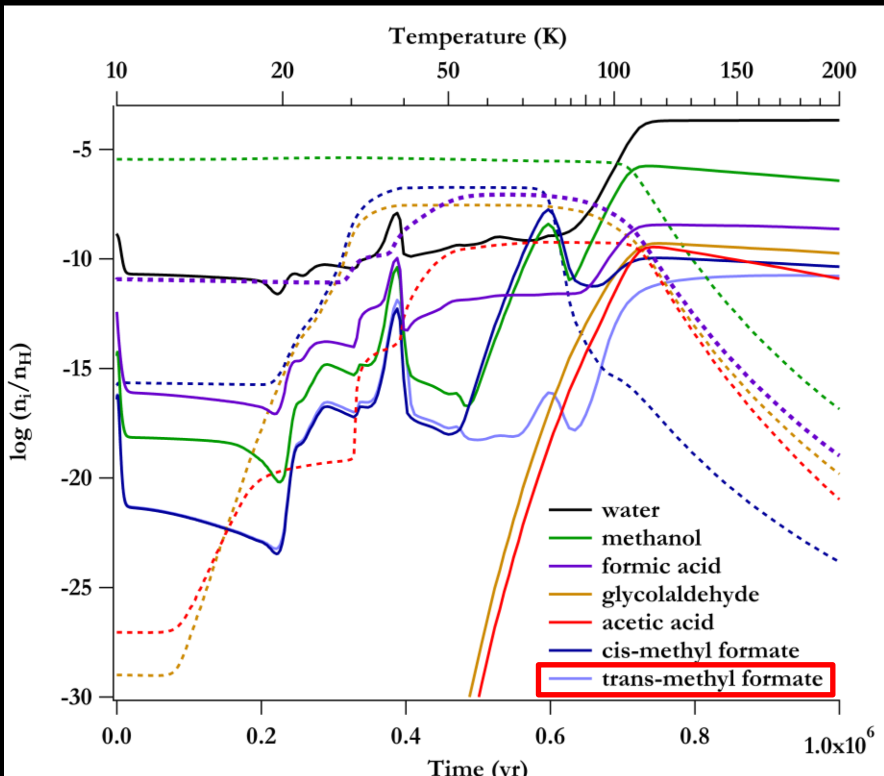


New gas phase reactions do not influence the $C_2H_4O_2$ isomers abundances

Laas, Garrod, Herbst, & Widicus Weaver, ApJ 728, 2011

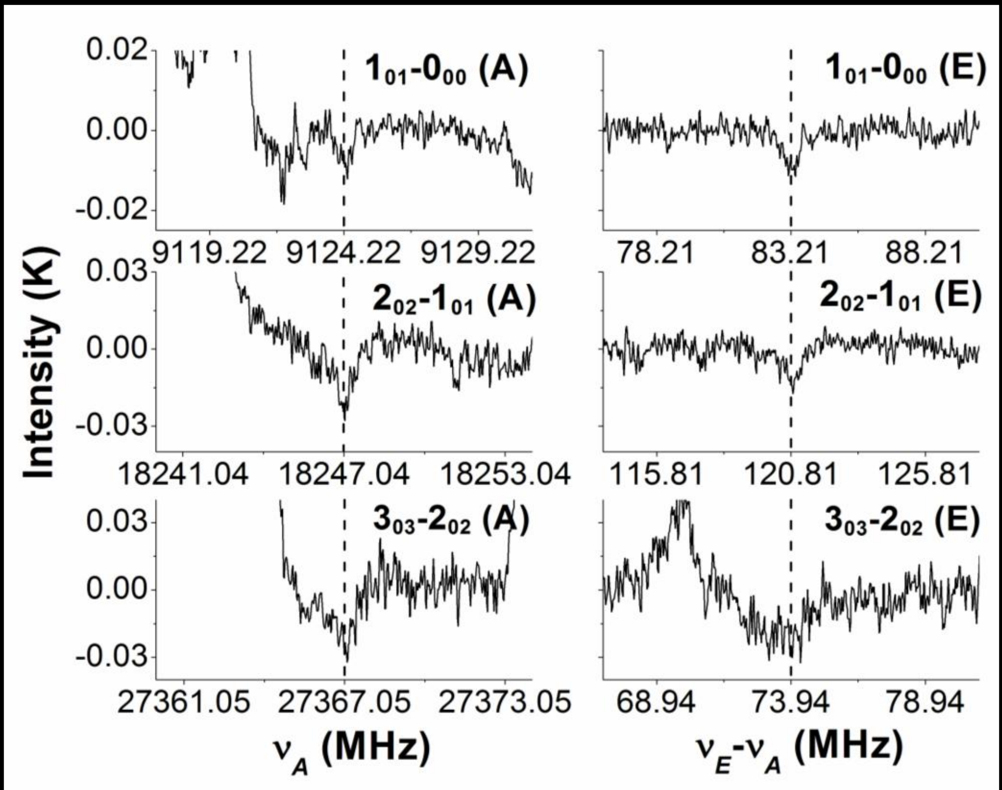
trans-Methyl Formate as a Test of Gas Phase Chemistry?

Models predict high abundance of *trans*-methyl formate in hot cores



Laas, Garrod, Herbst, & Widicus Weaver, ApJ 728, 2011

Preliminary GBT detection reported for *trans*-methyl formate in Sgr B2(N)



Neill et al., J. Phys. Chem., accepted

Summary and Future Work

- Grain surface radical-radical reactions can efficiently form COMs during warm-up phase of star formation

  Extend chemical network to include more grain surface chemistry

- Timescale for warm-up greatly influences COM abundances

  Gas/grain networks need to be incorporated into models for other types of sources

- Methanol photodissociation branching ratios also greatly influence COM abundances

  Lab measurements of key rates, intermediates are needed

- Additional gas-phase pathways to *cis*-methyl formate are not efficient

  Stereoisomers of other molecules need to be included in the chemical network

- The stereoisomer *trans*-methyl formate may be abundant, and would trace warm gas-phase chemistry in hot cores

  Preliminary detection reported, imaging studies are next step

- Additional direct tracers of grain surface or gas chemistry and more observations are needed for comparison

  More comprehensive observational studies of a variety of sources are needed

Acknowledgements

The Widicus Weaver Group:
Brian Hays, Le Zhong, Cate Levey, Jay Kroll, Max Farina, Jake Laas, Brett McGuire, Mary Radhuber, Brandon Carroll (not pictured)

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Michael McCarthy, CfA
Anthony Remijan, NRAO
Douglas Friedel, UIUC/CARMA

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