# **CH<sub>3</sub>OH Masers in Massive Star-forming Regions**

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- Methanol is an alcohol, which has nearly the same geometry as water, with one H being replaced by a methyl group (-CH<sub>3</sub>).
- Since the methyl group has three equivalent H atoms, the combinations of the nuclear spins of these three H atoms create symmetry states called A and E. The A state corresponds to all spins being parallel for a total of I = 3/2, while the E state has I=1/2.
- The internal rotation of the methyl group against the HO-C framework is referred to as torsion.
- A slightly asymmetric rotor with hindered internal rotation and significant a- and b-axis dipole moments ( $\mu_a=0.885D$ ,  $\mu_b=1.44D$ ), methanol has a complex spectrum that is sensitive to IS conditions.
- 1. Observations of Methanol
- 2. Methanol Chemistry
- 3. Thermal Emission in Astronomical Sources
- 4. SMA Observations
- 5. Summary

# **1. Observations of Methanol**

#### **Rotational Energy Levels of Methanol**

Although methanol is an asymmetric rotator, it is nearly a prolate symmetric top. -> rotational level, K

Many of the rotational lines have been detected. Observable lines cover a wide range of energies and line strengths, allowing for a detailed analysis of excitation conditions and opacities.



#### Excitation and radiative transfer modeling efforts: e.g., Leurini et al. 2004, 2007

### Thermal Emissions - Gas Phase Observations



CSO 350  $\mu$ m Line Survey of Orion KL Comito et al. 2005

Even when not masing, methanol may be expected to distinctly non-LTE excitation, except under the highest density conditions, where collisions could thermalize the level populations.

### **Solid Methanol Observed**

- Methanol has six atoms 12 vibrational modes:
- They corresponds to O-H stretch (ν<sub>1</sub>), C-H stretches (ν<sub>2</sub>, ν<sub>3</sub>, ν<sub>9</sub>), C-O stretch (ν<sub>8</sub>), CH<sub>3</sub> rocks (ν<sub>7</sub>, ν<sub>11</sub>), OH bend (ν<sub>6</sub>), CH<sub>3</sub> deformations (ν<sub>4</sub>, ν<sub>5</sub>, ν<sub>10</sub>), and ν<sub>12</sub> torsion (ν<sub>1</sub> ν<sub>11</sub> : 3 10 μm)
- 3.54 μm band (C–H stretch): W3A, NGC7538(IRS1), GL2136
- 8.9 and 9.7 μm band (CH<sub>3</sub> rock and CO stretch): GL2136
- 6.85 μm (C-H bending): W3A, NGC7538(IRS9)



A typical dust grain (note the tiny scale!).



Boogert et al. 2004: (Spitzer satellite) The main ice constituents:  $H_2O$ ,  $CO_2$ , CO,  $CH_3OH$  (3.47, 6.85  $\mu$ m)

Ice Mantle:  $H_2O$ ,  $CH_3OH$  (1–30 %),  $NH_3$  (a few – 30 %),  $CO_2$ , OCS, ...

– Daughter molecules:  $CH_3CN$ ,  $HCOOCH_3$ , HCN,  $CH_3CH_2CN$ ,  $CH_3CH_2OH$ ,...

## **Methanol Masers**

- First methanol masers in 1971 toward Orion nebula (Barrett et al. 1971)
- Over 20 methanol rotational transitions have been found to be masers: in star-forming regions, associated with IR sources, molecular outflows and compact HII regions.
- Probably a sign for star-birth of massive YSOs.
- \* They are divided into two classes, I and II.
- Class I: probably produced by collisional pumping (generally well separated from the center of activity)
- Class II: probably by radiative excitation at IR (spatially well correlated with YSOs OH masers





# 2. Methanol Chemistry

## **Gas Phase Formation**

Methanol Abundance: 0.4-1 x 10<sup>-8</sup> in cold dark clouds > 10<sup>-5</sup> in hot cores
Formation in the gas phase, via the radiative association reaction: CH<sub>3</sub><sup>+</sup> + H<sub>2</sub>O → CH<sub>3</sub>OH<sub>2</sub><sup>+</sup> + hv followed by the electron recombination to CH<sub>3</sub>OH (50%) and H<sub>2</sub>CO (50%)

Miller et al. 1991, Lee et al. 1996, Turner 1998

- **Destruction** is dominated by reactions with C<sup>+</sup> (most important for 2.5 <  $A_{vo}$  < 5.0 mag), He<sup>+</sup>, H<sub>3</sub><sup>+</sup>, and UV dissociation (most important for  $A_{vo}$  < 2.5 mag)
- Many uncertainties in methanol related reactions
  - Model expectations are less by 3–4 orders of magnitudes than the observed values
  - Whether surface CH<sub>3</sub>OH can be desorbed to produce the observed gas-phase CH<sub>3</sub>OH is controversial in dark clouds.



### Solid Methanol - Grain Chemistry

- $CH_3OH$  is a "primary" ice that forms other products after nearby stars turn on.
  - Laboratory work (Bernstein et al. 1995): the mixtures of H<sub>2</sub>O/CH<sub>3</sub>OH/CO/NH<sub>3</sub> ices irradiated by UV → complex organic species ← at the expense of CH<sub>3</sub>OH as the primary carbon source
- Solid CH<sub>3</sub>OH: hydrogenation of CO (or H<sub>2</sub>CO) (Charnley et al. 1992, Caselli et al. 1994, Gibb et al. 2000).
  - may be inefficient in quiescent sources: high CO/H2O ratio source show no solid CH3OH feature (Elias 16)
  - laboratory works (Hiraoka et al. 1994)
- CH<sub>3</sub>OH formation may need energetic processing (Chiar et al. 1996)
  - -> Mainly we detect CH<sub>3</sub>OH toward massive star-forming region



#### **Desorption and Sublimation**

- Heating by CRs or UV followed by thermal evaporation of the surface molecules
- UV photodesorption: direct interaction with surface molecules



#### **Sublimation Temperature**

CO 
$$\sim$$
 20K,  $H_2S$   $\sim$  40K,  $NH_3$   $\sim$  65K,

 $H_2O$ ,  $CH_3OH \sim 100K$ 



Abundances vs. time of large O-bearing (dotted lines) and simple N-bearing (solid lines) organic molecules in hot cores following the evaporation of representative interstellar ices, T=300K (Rodgers & Charnley 2001)

- More volatile species are evaporated before more tightly bound species.
- Small-scale spatial differentiation is observed in the chemical composition of many hot cores.
- <u>N/O differences</u>: Orion KL(Hot Core, Compact Ridge), W3(OH) (Wyrowski et al. 1999), G29.96-0.02 (Pratap et al. 1999), G5.89-0.39 (Thompson & Macdonald 1999), and Sgr B2 (Nummelin et al. 2000).

## **3. Thermal Emission in Astronomical Sources**



## 4. SMA Observations towards W75N and DR21(OH)



(contour) 1.3 mm continuum, (triangles) UC HII, (+) H<sub>2</sub>O masers, (dot) OH masers [Shepherd et al. 2001]





#### Sub-Millimeter Array (SMA, 8x 6m, 0.5 km, Hawaii) 2006, W75N (230 GHz; 345 GHz), $\Theta = 1$ " (230 GHz), 2" (345 GHz)

#### **Detected Molecular Lines:** ≥ 100 transitions

- C<sup>17</sup>O, H<sup>13</sup>CO<sup>+</sup>, H<sub>2</sub>CO, CH<sub>3</sub>OH (~ 50 lines), <sup>13</sup>CH<sub>3</sub>OH
- HCOOH, HCOOCH<sub>3</sub>, CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>3</sub>CHO, CH<sub>3</sub>CH<sub>2</sub>OH
- C<sup>34</sup>S, H<sub>2</sub>CS, H<sub>2</sub>S, SO, <sup>33</sup>SO, <sup>34</sup>SO, SO<sub>2</sub>, <sup>34</sup>SO<sub>2</sub>
- SiO
- HC<sub>3</sub>N, DCN, HN<sup>13</sup>C
- CH<sub>2</sub>CHCN, CH<sub>3</sub>CH<sub>2</sub>CN, NH<sub>2</sub>CHO, ...



Table 1: Parameters of the identified continuum cores	Table 1: Parameters of the identified continu	um cores
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Source	Position <sup>b</sup>	Peak <sup>c</sup>	Total Flux	Size	$P.A.^d$	$T_{ m dust}$	$M_{ m core}$	$N_{ m H_2}$	$n_{ m H_2}$
	(", ")	(Jy/beam)	(Jy)	(" × ")	(°)	(K)	$({ m M}_{\odot})$	$(\mathrm{cm}^{-2})$	$(\mathrm{cm}^{-3})$
MM1a	(0, 0)	$0.184 \pm 0.009$	0.195	$0.97 \times 0.97$	55.7	$200\mp100$	$0.59 {}^{+0.61}_{-0.20}$	$6.2 \ ^{+6.5}_{-2.1}  imes 10^{23}$	$2.2 \ ^{+2.3}_{-0.7}  imes 10^7$
MM1b	(-0.93, 1.16)	$0.128\ {\pm}0.004$	0.462	$1.84\times1.74$	-63.1	$200 \mp 100$	$1.39  {}^{+1.47}_{-0.47}$	$1.3 \ ^{+1.3}_{-0.5}  imes 10^{23}$	$1.3 \ ^{+1.4}_{-0.4}  imes 10^{6}$

#### W75N



## Methanol Lines Observed W75N and DR21(OH)



CH3OH -A(vt=1)	7(5,3)-6(5,2) A++ <u>v</u> <sub>l</sub> =1	337545.987	326.086	485.5704
CH3OH -E	7(-2,6)-6(-2,5) E	338722.914	51.889	90.94773
CH3OH -A( <u>vt</u> =1)	7(4,4)-6(4,3) A ỵ <sub>l</sub> =1	337685.594	368.154	546.1298
CH3OH -A	7(6,2)-6(6,1) A <u>v</u> <sub>j</sub> =1	337463.624	359.210	533.2451
CH3OH -A	7(3,4)-6(3,3) A	338543.149	68.493	114.8389
CH3OH -A (s)	7(4,3)-6(4,2) A++	338512.627	89.720	145.3916
CH3OH -A (s)	7(4,4)-6(4,3) A	338512.627	89.720	145.3916
CH3OH -A( <u>vt</u> =1)	7(4,3)-6(4,2) A++ <u>v</u> <sub>l</sub> =1	337685.594	368.154	546.1298
CH3OH -E	7(6,2)-6(6,1) E	338404.593	158.155	243.8917
CH3OH -A	7(6,2)-6(6,1) A	338442.367	168.514	258.8043
CH3OH -A	7 5 3 - 6 5 2 A++	338486.322	129.721	202.9678

	Transition	NIST (MHz)	E <sub>L</sub> (cm <sup>-1</sup> )	Eu (K)
CH3OH -E	5(1,4)-4(2,2) E	216945.559	31.596	55.89267
CH3OH -A(vt=1)	6(1,5)-7(2,6) A- <u>v</u> <sub>l</sub> =1	217299.162	252.644	374.0861
CH3OH -E	20(1,19)-20(0,20) E	217886.39	346.073	508.596
СНЗОН -Е	4(2,2)-3(1,2) E	218440.05	24.31	45.47694
CH <sub>3</sub> OH -A	16(1,16)-15(2,13) A+	227814.651	219.844	327.3786
CH3OH -A	12(1,11)-12(0,12) A-+	336865.153	125.737	197.1554
CH3OH -E	33-42E	337135.858	31.595	61.66036
CH3OH -A(vt=1)	7(1,7)-6(1,6) A++ t=1	337297.483	259.825	390.1824
CH3OH -A	7(6,1)-6(6,0) A++ <u>v</u> =1	337463.624	359.210	533.2451
CH3OH -E	7(-6,2)-6(-6,1) E <u>vt</u> =1	337490.378	376.743	558.4834
CH3OH -E(vt=1)	7(3,5)-6(3,4) E <u>v</u> <sub>1</sub> =1	337519.117	323.907	482.4327
CH3OH -A(vt=1)	7(5,2)-6(5,1) A <u>v</u> t=1	337545.987	326.086	485.5704
CH3OH -E(vt=1)	7(-2,5)-6(-2,4) E <u>vt</u> =1	337605.272	287.209	429.6137
CH3OH -A(vt=1)	7(2,5)-6(2,4) A++ $\underline{v}_{1}=1$	337625.745	241.381	363.6498
CH3OH -A(vt=1)	7(2,6)-6(2,5) A <u>v</u> t=1	337635.75	241.381	363.6503
CH3OH -E(vt=1)	7 1 7 - 6 1 6 <u>vt</u> =1 E	337642.484	236.378	356.4493
CH3OH -A(vt=1)	7(3,5)-6(3,4) A++ <u>v</u> <sub>l</sub> =1	337655.174	309.104	461.1317
CH3OH -E(vt=1)	7(5,2)-6(5,1) E vt=1	337685.218	332.049	494.1602
CH3OH -E(vt=1)	7(-1,6)-6(-1,5) E <u>v</u> <sub>l</sub> =1	337707.52	321.108	478.4128
CH3OH -A(vt=1)	7(0,7)-6(0,6) A++ <u>v</u> <sub>i</sub> =1	337748.771	328.252	488.6979
CH3OH -A(vt=1)	7(1,6)-6(1,5) A <u>v</u> <sub>1</sub> =1	337969.434	259.892	390.3111
CH3OH -E	7(0,7)-6(0,6) E	338124.498	42.988	78.1069
CH3OH -E	7(-1,7)-6(-1,6) E	338344.605	37.749	70.57645
CH3OH -A	7(0,7)-6(0,6) A++	338408.718	33.876	65.00473
CH3OH -E	7(-6,1)-6(-6,0) E	338430.981	165.213	254.0523
CH3OH -A	7(6,1)-6(6,0) A++	338442.367	168.514	258.8043
CH3OH -E	7 -5 2 - 6 -5 1 E	338456.521	120.071	189.0761
CH3OH -E	7 5 -3 6 5 2 E	338475.217	128.453	201.1421
CH3OH -A	7 5 2 - 6 5 1 A-	338486.322	129.721	202.9678
CH3OH -A	7(2,6)-6(2,5) A	338512.856	60.090	102.7422
CH3OH -A	7(3,5)-6(3,4) A+	338540.824	68.493	114.8388
СНЗОН -Е	7 -3 5 6 -3 4 E	338559.963	77.468	127.7583
CH3OH -E	7(3,4)-6(3,3) E	338583.223	67.043	112.7537
CH3OH -E	7(1,6)-6(1,5) E	338614.953	48.514	86.08457
CH3OH -A	7(2,5)-6(2,4) A+	338639.807	60.096	102.7569
CH3OH -E	7(2,5)-6(2,4) E	338721.694	49.349	87.29159



















Minh et al. 2010, ApJ, in press





Minh et al. 2010, ApJ, in press





Minh et al., in preparation

DECLINATION (1950)



1" = 0.015 pc at 3 kpc 0.015 pc = 3000 AU

#### **Methanol Masers and Thermal Emission**





 $E_U$  (K)

# Summary

### • Methanol

- Oxygen chemistry
- Many transitions in radio and IR, and masers
- Traces massive star-forming activities
- More observations

- thermal emission: toward various objects, including our solar system objects chemical variations, ..
- **methanol masers:** relation with other masers, kinematics, association with other features like outflows, or other SF features, ...

probable correlation with regional chemical gradients

- More studies of its chemistry especially surface chemistry on the icy dust grains
  - ice mixture, evaporation, dissociation,..