

Combined Array for Research in Millimeter-wave Astronomy

Proposal Number

c0755

Observing Proposal Cover Sheet

General Proposal Information

| Title | | Date | TOO/Time Critical | |
|---|-------------|-------------|-------------------|------------------------|
| Continued High Resolution Mapping of HCOOH and CH ₃ OCHO toward G19.6-0.23 | | 2010-08-31 | — | |
| Scientific Category | 1cm Project | 3mm Project | 1mm Project | Level of Help Required |
| Chemistry / Interstellar Medium | — | — | X | Consultation |

Authors List

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Advisor must send a supporting letter if Thesis is checked. See Instructions.

Abstract

Chemical modeling should have predictive power for molecular composition and reaction chemistry. There is excellent progress in this area for cold sources (e.g. TMC-1); however, core chemistry continues to remain a challenge as abundances of several species are underestimated by orders of magnitude (Quan & Herbst 2007, A&A, 474, 521). Several questions remain including, 1) what is the extent of complexity in interstellar chemistry?; 2) is there a limit to molecule size, and what is that limit?; and finally, 3) can we achieve a mechanistic chemical understanding of interstellar chemistry? We propose that methyl formate, a well known interstellar species whose formation mechanism is currently in question is formed through a methyl transfer reaction leading to two different geometries of methyl formate, cis- and trans-. A consequence of this hypothesis is that when observed in the ISM in regions where we find methyl formate, formic acid should be absent. Therefore, the observed contour maps of methyl formate and formic acid should show a difference in the location of peak emission. We tested this hypothesis toward G19.61-0.23 with CARMA (proposal id: c0449). In this case, we did not have the spatial resolution or uv-coverage to detect any apparent difference in the morphology of the methyl formate and formic acid distributions. However, the results are tantalizing in the fact that there is a clear spatial separation between the methyl formate and formic acid emission peaks. This separation is $\sim 3''$ indicating that high spatial resolution observations are necessary and may in fact again support the hypothesis that a gas phase reaction of methyl formate will show a decrease in the abundance of formic acid.

Source Information

| # | Source | RA | DEC | Freq | A ¹ | B ¹ | C | D | E | SL | # Fields | Species | Imag/SNR | Flex.HA |
|--------------------------|------------|-------|--------|------|----------------|----------------|---|---|---|----|----------|---------------|----------|---------|
| 1 | G19.6-0.32 | 18:27 | -11:56 | 249 | 0 | 15 | 0 | 0 | 0 | 0 | 1 | HCOOH, etc... | Imaging | — |
| Total Hours: 15.0 | | | | | | | | | | | | | | |

Special Requirements

None

Status of Prior CARMA Observations

c0449 - High Resolution Mapping of HCOOH and CH₃OCHO toward G19.6-0.23 - Data have been analyzed and paper is in preparation.

Scientific Justification

Chemical modeling should have predictive power for molecular composition and reaction chemistry. There is excellent progress in this area for cold sources (e.g. TMC-1); however, core chemistry continues to remain a challenge as abundances of several species are underestimated by orders of magnitude (Quan & Herbst 2007, A&A, 474, 521). Furthermore, in the cold interstellar medium, dust grains develop thick mantles of ices containing H₂O, CO, CO₂, CH₄, H₂CO, and CH₃OH. When interstellar gas and dust particles collapse and heat up in the process of star formation, the surrounding envelope gradually warms up from 10K to 100-300 K. The mantles then evaporate, and new species will be produced. Some the surface species formed under cold conditions are broken up by UV radiation into radicals, which then combine to form more complex species. *Several questions remain including, 1) what is the extent of complexity in interstellar chemistry?; 2) is there a limit to molecule size, and what is that limit?; and finally, 3) can we achieve a mechanistic chemical understanding of interstellar chemistry?*

One molecule that has been extensively studied in both laboratory, theoretical and astronomical observations is methyl formate (HCOOCH₃). HCOOCH₃ was first detected in the hot molecular core SgrB2(N) by Brown et al. (1975, ApJ, 197, 29L) and subsequently detected in numerous high and low mass star forming regions. It is so ubiquitous, lines of its spectrum have been referred to interstellar "weeds". Yet despite its large abundance in the interstellar medium, chemical models that attempt to reproduce the column density of HCOOCH₃ based solely on gas-phase pathways have failed by orders of magnitude.

In our previous proposals, we have re-investigated the gas phase formation route to methyl formate because the Horn et al. (2004) paper lacked fundamental reaction networks that are known to form copious amounts of methyl formate. One reaction focused on the (acid catalyzed) Fisher esterification reaction between protonated formic acid and methanol. This reaction has two channels that correlate to cis- and trans- protonated methyl formate. The cis- and trans- geometries of methyl formate refer to the orientation of the methyl group (-CH₃) with respect to the other atoms in methyl formate. We can detect the difference in these geometries based on the spectroscopy of cis- and trans- as measured in the lab.

For interstellar chemistry, a potential problem with this process is the (calculated) reaction barrier of about 10-15 kJ/mol. As we continued our investigation into other gas phase processes, we now have looked at the reaction between protonated methanol and formic acid, so called, methyl transfer reaction. This reaction was briefly considered in the paper of Horn et al. (2004) but was ruled out as a reaction option based on SIFT experiments that indicated only proton transfer to formic acid. However, we find that there is a reaction geometry that gives a barrierless path to production of protonated methyl formate. The reaction geometry leads to the formation of protonated trans-methyl formate. In addition, the reaction geometry that would produce protonated cis-methyl formate has a reaction barrier of about 11 kJ/mol presumably due to steric repulsion in the transition state. The energetics are shown in Figure (1).

The energetics of this reaction are similar to the reaction of protonated methanol with neutral methanol to give protonated dimethyl ether (and water). For this reaction, the reaction complex is stable by 56 kJ/mol [45 kJ/mol], the transition state is 26 kJ/mol [8 kJ/mol] below the reactant energy, and the reaction is exothermic by 52 kJ/mol [35 kJ/mol]. All values are calculated. The

corresponding values for the reaction path to protonated methyl formate are given in brackets, [], above. *We propose that methyl formate is formed through this methyl transfer reaction (as illustrated in figure 1) leading to two different geometries of methyl formate, cis- and trans-. There are two consequences of this hypothesis. First, in the interstellar medium in regions where we find methyl formate, formic acid should be absent. Therefore, the observed contour maps of methyl formate and formic acid should show a difference in the location of peak emission. The second consequence is the cis- and trans- geometries of methyl formate should both be present in the same region of the ISM.*

With BIMA and now with CARMA, we have begun the investigation of this hypothesis by mapping the distribution of methanol, methyl formate, formic acid, and dimethyl ether toward select regions of the interstellar medium. Figure 2 shows the initial evidence for our hypothesis as the distribution of methyl formate and dimethyl ether show a clear difference in their distributions with respect to formic acid. These data were taken with the BIMA interferometer operating at 1mm wavelengths toward the Orion KL region and published by Liu et al. (2002, ApJ, 576, 255). Given the reaction similarities, this behavior between the three species (methyl formate, formic acid, and dimethyl ether) seems reasonable and supports our hypothesis.

We followed up these observations toward a new source, G19.61-0.23, with CARMA (proposal id: c0449). In this case, we did not have the spatial resolution or uv-coverage to detect any apparent difference in the morphology of the methyl formate and formic acid distributions (see figure 3). However, the results are tantalizing in the fact that there is a clear spatial separation between the methyl formate and formic acid emission peaks. This separation is $\sim 3''$ indicating that high spatial resolution observations are necessary and may in fact again support the hypothesis that a gas phase reaction of methyl formate will show a decrease in the abundance of formic acid.

Technical Justification

CARMA is the ideal instrument to continue this investigation into the formation chemistry of formic acid and methyl formate toward the high mass star forming region G19.6-0.2. It is also important to note that:

1. We have shown that formic acid and methyl formate are clearly both present in the G19.6-0.2 region and easily detectable with the CARMA interferometer.
2. This is a systematic attempt to investigate the formation chemistry of a large organic molecule, methyl formate.
3. The importance of this investigation is to determine the cause of the disparate high abundance of that species relative to its isomers.
4. To show, for the first time, that a systematic approach to investigate the formation of molecules in the interstellar medium CAN lead to TESTABLE observations. In general, this is NOT the way problems of interstellar chemistry are investigated.

In order to determine the compact spatial extent and more importantly the morphology of both methyl formate and formic acid, we propose to use CARMA in its B configuration operating at 1mm

wavelengths. This mapping campaign rests upon as complete uv-coverage as possible to investigate the morphology of the methyl formate and formic acid emission features. Using the CARMA RMS sensitivity calculator, in the CARMA B-array configuration centered around 249 GHz, for a single pointing at any one location, we should achieve a synthesized beam of $\sim 0.''4 \times 0.''4$, and a RMS noise level of 55 mJy/beam with 1.3 km/s spectral resolution. Figure 4 shows a table of the 4 primary molecular species and transitions that we intend to target with these observations. Yet, given the new flexibility of the CARMA correlator, we will take advantage of the available passbands and target additional transitions and molecular species (e.g. acetone and acetic acid) to continue to test our theories of mechanistic chemistry in the ISM. The noise level and spectral resolution is adequate to detect the molecular species of interest in this proposal, yet we are requesting 3 sidereal passes on source to make as high fidelity map as possible given time allocation. *Therefore, we are requesting a total of 15 hours to perform 3 single pointing observations targeting methyl formate, methanol, dimethyl ether and formic acid toward the G19.6-0.2 region.*

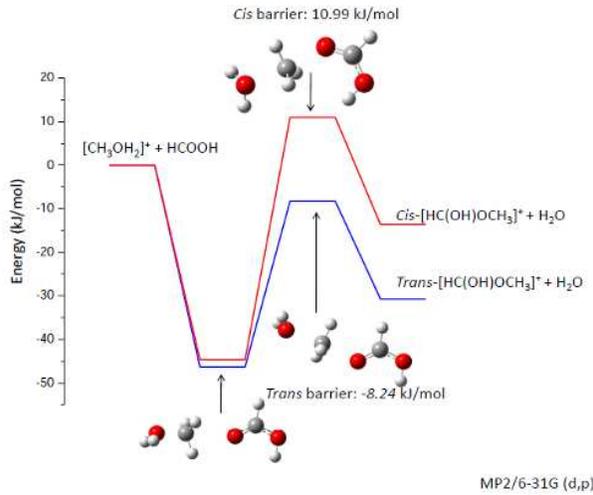


Figure 1 - Energetics involved in the formation of cis- and trans- methyl formate via methyl transfer reaction

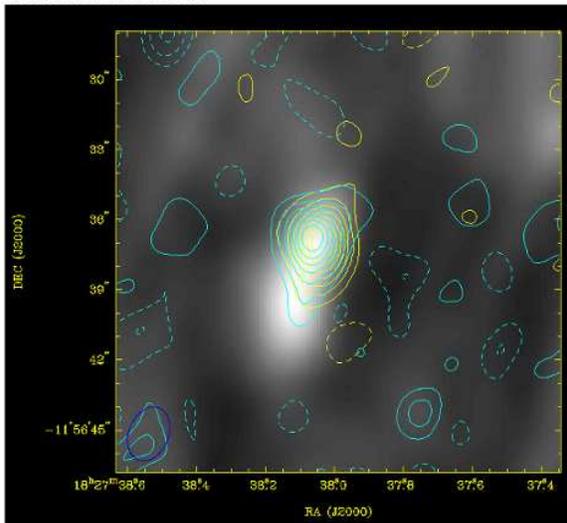


Figure 3 - Formic Acid (BLUE) and methyl formate (yellow) toward G19.6-0.2

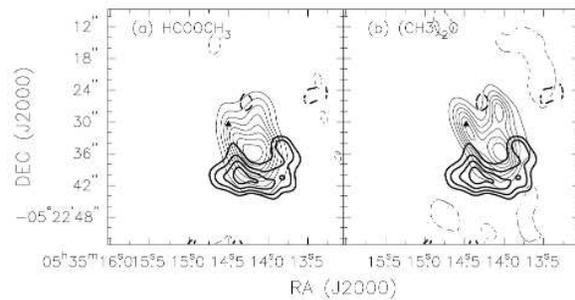


Figure 2 - BIMA 1mm observations toward the Orion Hot Core and Compact Ridge. In both cases the bold contours are from formic acid and the regular contours are from methyl formate and dimethyl ether, respectively

Table 1. Transitions

| Species | Chemical Name | Frequency (MHz) | Resolved QNs | $S_{ij}\mu^2$ (D^2) | E_{lower} (K) |
|----------------------------------|----------------|-----------------|---------------------|-------------------------|-----------------|
| HCOOH | Formic Acid | 247513.970 | 11(5,7)-10(5,6) | 17.25137 | 138.82679 |
| | | 247514.120 | 11(5,6)-10(5,5) | 17.25137 | 138.82679 |
| CH ₃ OCHO | Methyl Formate | 248749.602 | 23(1,23)-22(1,22)E | 59.32600 | 133.84865 |
| | | 248749.839 | 23(0,23)-22(0,22)E | 59.32600 | 133.84865 |
| | | 248750.551 | 23(1,23)-22(1,22)A | 59.32000 | 133.83138 |
| | | 248750.786 | 23(0,23)-22(0,22)A | 59.32000 | 133.83138 |
| CH ₃ OH $\nu_2=0$ | Methanol | 249443.344 | 7(4,4)-8(3,5)- | 1.23380 | 133.36091 |
| | | 249451.885 | 7(4,3)-8(3,6)++ | 1.23380 | 133.35947 |
| CH ₃ OCH ₃ | Dimethyl ether | 249923.816 | 15(1,14)-14(2,13)AA | 105.01789 | 100.60590 |
| | | 249924.463 | 15(1,14)-14(2,13)EE | 168.02862 | 100.60590 |
| | | 249925.110 | 15(1,14)-14(2,13)EA | 42.00716 | 100.60590 |
| | | 249925.110 | 15(1,14)-14(2,13)AE | 63.01073 | 100.60590 |

Figure 4 - Transitions of formic acid, methyl formate, dimethyl ether and methol as primary search targets for these observations.