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). Methyl formate, CH_3OCHO, was first detected in the hot molecular core Sgr B2(N) by Brown et al. (1975, ApJ, 197, 29L) and has subsequently been detected in numerous high and low mass star forming regions. It is so ubiquitous that lines of its spectrum have been referred to as interstellar "weeds". Yet despite its large abundance in the interstellar medium, current chemical models that attempt to reproduce the column density of CH_3OCHO based solely on gas-phase pathways have failed by orders of magnitude.

Calculations of the reaction profiles for several possible gas-phase routes of CH_3OCHO have failed to find a reaction pathway with a barrier low enough to be important in interstellar environments (Horn et al. 2004, ApJ, 611, 605). Consequently, the formation mechanisms have focused on radical-radical reactions on the surfaces of grains. However, chemical maps in the literature suggest that there is a gas phase formation of CH_3OCHO in a reaction that involves formic acid, HCOOH. This reaction process is inferred from the anti-correlation of the spatial distribution of HCOOH and CH_3OCHO. A previously published example in the Orion CR is shown in Figure 1. These data were taken with the BIMA interferometer operating at 1 mm wavelengths published by Liu et al. (2002, ApJ, 576, 255). The anti-correlated density distribution of HCOOH and CH_3OCHO has also been observed in maps of IRAS 16293-2422 (Remijan & Hollis, 2006, ApJ, 637, 37L) and is weakly evident in recent CARMA maps of G19 (analysis in progress). These observations suggest a gas phase reaction process to form CH_3OCHO is a common reaction process in the interstellar medium.

Recently, electronic structure theory was used to examine possible reaction pathways that produce CH_3OCHO from the reaction of HCOOH and CH_3OH and two possible reaction routes have been identified: acid-catalyzed Fisher esterification, a reaction of protonated formic acid ($HCOOH_2^+$) and methanol and the methyl transfer reaction, a reaction of protonated methanol ($CH_3OH_2^+$) and neutral formic acid. Both reactions have two channels that correlate to cis- and trans- protonated methyl formate. For interstellar chemistry, a potential problem with the Fisher Esterification reaction is the calculated reaction barrier of about 10-15 kJ/mol. However, with the methyl transfer reaction, ab initio calculations indicate the production of protonated trans-methyl formate through a barrierless reaction. The energetics are shown in Figure 2. This reaction pathway is similar to the well-known reaction between neutral methanol and its protonated form ($CH_3OH_2^+$) to form protonated dimethyl ether ($CH_3O(H^+)CH_3$). We therefore propose that methyl formate is formed through this methyl transfer reaction as illustrated in Figure 2 leading to two different geometries, cis- and trans-. Production of neutral methyl formate (CH_3OCHO) would come from a proton transfer to a high-abundance molecule with a higher proton affintiy, such as CS, or through dissociative electron recombination. The latter process can deposit large amounts of energy in the neutral product that may lead to conformational isomerization to the more stable cis isomer or dissociation (Hamberg et al. 2010, A&A, 514, A83). However, the details of the electron recombination are not known experimentally for CH_3OCHO.

We have used the literature results to support the case for ion-molecule gas phase formation of CH_3OCHO in the Orion CR. From ab initio quantum chemistry, the more probably reaction pathway is the methyl cation transfer reaction between neutral HCOOH and protonated methanol. As support for the proposed reaction, the BIMA map (Figure 1) demonstrates the presence of HCOOH and CH_3OCHO in the Orion CR. As further support for the proposed reaction, the Orion maps of H. Beuther et al. using the SMA (Beuther et al. 2005, ApJ, 632, 355) show that there is a local density maximum of methanol in the reaction region implied by Figure 1 and thus this co-reactant can be placed in this spatial region.

The chemistry could be driven by a molecular outflow interacting with the dense cloud, as suggested by recent mapping studies. The outflow (Wang et al. 2010,. ApJ, 713, 1192; Plambeck et al. 2009, ApJ, 704, L25) could produce enhanced ionization and higher yields of protonated species. This conjecture is supported by recent survey results from the IRAM 30m telescope that show that the ratio of protonated CS (HCS^+) to CS is relatively high in the CR region and a factor of 4 higher than observed in the Orion hot core, for example (Tercero et al. 2010, A&A). The maps of Beuther et al. show that there is also a local maximum in the column densities of CS (and thioformaldehyde, H_2CS) in the CR region. Both of these could serve as proton acceptors in reactions to produce neutral CH_3OCHO.

Finally, if the proposed methyl cation reaction between HCOOH and protonated methanol occurs, then it is also expected that there will be enhanced production of $(CH_3)_2O$ in the same spatial region via the similar proton transfer reaction between protonated methanol with neutral methanol (Bouchoux & Choret, 1997, Rapid Communications in Mass Spectrometry, 11, 1799). The maps in Figure 1 show that $(CH_3)_2O$ is present. The maps of Beuther et al. also demonstrates the strong coincidence between these species.

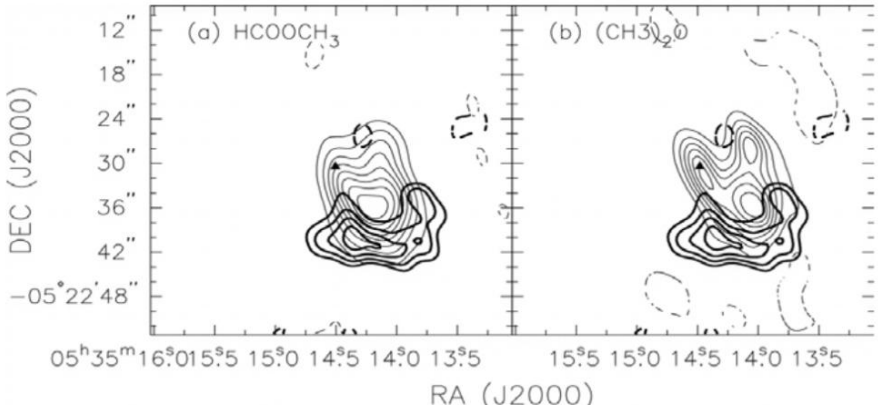

Figure 1: BIMA array maps of the Orion KL region showing the distribution of CH_3OCHO (left, light contours) with respect to HCOOH (left bold contours). The right panel shows $(CH_3)_2O$ (light) with respect to HCOOH (bold).

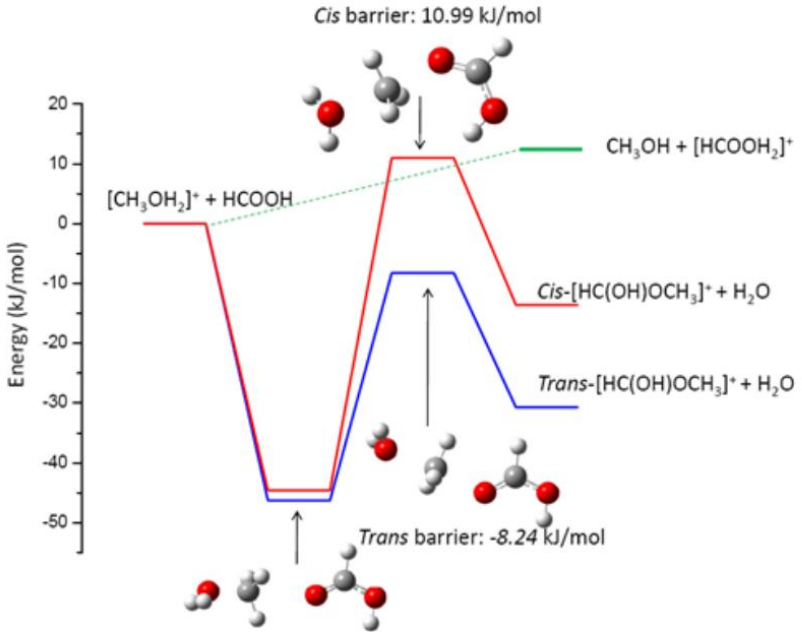

Figure 2: Methyl cation transfer formation of cis- and trans-methyl formate. The cis barrier is 10.99 kJ mol^{-1} whereas the trans barrier is -8.24 kJ mol^{-1}

Technical Justification

If this new proposed chemical model is correct, there is large kinetic formation of protonated trans-methyl formate and if conformation is largely preserved in the neutralization reactions (electron recombination or proton transfer to a species like CS), then we predict that "unusually" large amounts of this conformer would be present where this chemistry occurs.

Using a pulsed discharge nozzle and Fourier transform microwave spectroscopy techniques, the spectrum of the "trans" conformer of CH_3OCHO has been characterized for the first time in the laboratory. The predicted frequencies for select transitions at mm wavelengths are presented in Table 1.

Table 1: Predicted frequencies for select transitions of the A state of trans-methyl formate

Transition	ν (GHz)
$10_{0,10} \rightarrow 9_{0,9}$	91.011
$11_{0,11} \rightarrow 10_{0,10}$	100.06
$11_{1,10} \rightarrow 10_{1,9}$	102.085
$12_{1,12} \rightarrow 11_{1,11}$	107.429
$12_{0,12} \rightarrow 11_{0,11}$	109.093

Figure 3 shows the detection of 2 of 9 lines of the trans form of CH_3OCHO that have currently been observed towards SgrB2N using the GBT. The weakness here is that the detection is within a region in which there are currently no high resolution maps to suggest this reaction. Therefore, to confirm the proposed scheme above, trans-methyl formate needs to be observed in the Orion CR and thus we request time on the Arizona Radio Observatory 12m telescope to observe the five transitions listed in Table 1 in an effort to confirm the reaction chemistry outlined in this proposal.

We would like to obtain a sensitivity of 10 mK of a 3 sigma noise level. With T_{sys} ~250 K, using the 1 MHz filterbanks, this sensitivity can be theoretically be obtained in about ~3 hours of total integration time per transition, or ~1.5 hour total telescope time, assuming parallel observing mode. Therefore, we request 12 hours of total telescope time, allowing for overhead, tuning, and pointing. At the 12m telescope, Orion KL can be tracked for ~9 hrs a day and thus we request 2 observing slots to cover 12 hours at the 12m telescope between the hours of 1-10 LST to test the presence of trans-methyl formate in this source.

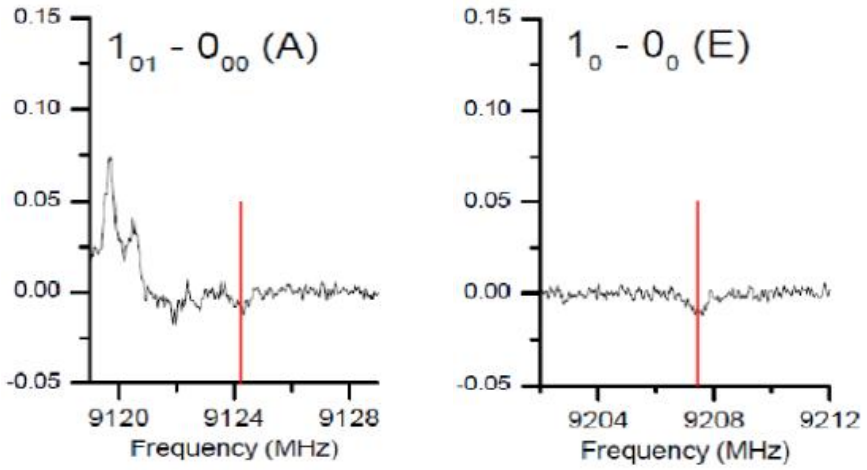

Figure 3: Detection of trans-methyl formate from the GBT PRIMOS survey towards SgrB2N