MkIV ground-based measurements of Ethene (Ethylene; C$_2$H$_4$)

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C$_2$H$_4$ has been previously measured by ACE (e.g., Herbin et al., 2009) and from the ground in fires (Paton-Walsh et al., 2005; Rinsland et al., 2005).

Best IR feature of C$_2$H$_4$ is Q-branch of nu$_7$ band (CH$_2$ wag) at 948 cm$^{-1}$. This is 7 times stronger than any feature in the 3000 cm$^{-1}$ region.

Ethylene images from PNNL
Defined a 14 cm$^{-1}$ wide window which include several strong lines of CO$_2$ and H$_2$O. CO$_2$ lines are T-dependent, one lies directly overlies C$_2$H$_4$ Q-branch.
Fitting done using GFIT, NCEP model, ATM linelist (i.e., TCCON methodology).
C$_2$H$_4$ Q-branch at 949.4 cm$^{-1}$ < 1% deep and therefore not discernable on this plot.
$\text{C$_2$H}_4$ Q-branch (red) peaks at 949.4 cm$^{-1}$. It is typically less than 1% deep even at JPL. It lies under a 60%-deep T-dependent CO$_2$ line centered at 949.5 cm$^{-1}$, the wing of a saturated H$_2$O line centered at 948.3 cm$^{-1}$, and the SF$_6$ R-branch.
Retrieved MkIV C$_2$H$_4$ columns from 12 sites

Points color-coded by altitude.
- JPL (green) and Ames (purple) are only sites with non-zero C$_2$H$_4$
- Ft Sumner (lime), occasionally measures high C$_3$H$_8$, but always measures zero C$_2$H$_4$
- At JPL (green) C$_2$H$_6$ is highly variable without an obvious seasonal cycle.

JPL C$_2$H$_4$ (green) has decreased by a factor 2-3 over the past 25 years.
MkIV \( C_2H_4 / CO \) correlation

Plot color-coded by altitude, as in previous plot.

CO also shows a large decrease over the past 25 years, such that the \( C_2H_4 / CO \) correlation is very good at JPL.

Implies common sources for \( C_2H_4 \) and CO, i.e. urban pollution.
$\text{C}_2\text{H}_4$ correlations with $\text{C}_2\text{H}_6$ and $\text{C}_2\text{H}_2$ are positive, but not as good as those with CO.
Comparison with surface in-situ obs

Washenfelder [2011] measured 2.16 ppb of $\text{C}_2\text{H}_4$ (Ethene) at ground level in Pasadena, CA. Assuming that this was uniformly distributed throughout the PBL of 150 mbar thickness, the column would be $6 \times 10^{15}$ molecules/cm$^2$. MkIV $\text{C}_2\text{H}_4$ columns at JPL in the 2010 timeframe range from 0 to $6 \times 10^{15}$ and so are consistent.

<table>
<thead>
<tr>
<th>VOC</th>
<th>Initial Concentration (ppbv)</th>
<th>Residual BL Concentration$^a$ (ppbv)</th>
<th>Emission Ratio VOC/$\text{C}_2\text{H}_4$</th>
<th>Measured Concentration$^b$ (ppbv)</th>
<th>Modeled Concentration$^c$ (ppbv)</th>
<th>Model-Measured Difference$^d$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyene</td>
<td>0.12$^a$</td>
<td>0.24</td>
<td>$1.00^f$</td>
<td>1.78</td>
<td>1.78</td>
<td>0</td>
</tr>
<tr>
<td>Ethene</td>
<td>0.065$^e$</td>
<td>0.065</td>
<td>$1.36^f$</td>
<td>2.16</td>
<td>1.88</td>
<td>$-13$</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.039$^g$</td>
<td>0.040</td>
<td>$0.19^f$</td>
<td>0.36</td>
<td>0.34</td>
<td>$-4$</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.017$^e$</td>
<td>0.028</td>
<td>$0.83^f$</td>
<td>1.19</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>m,p-Xylene</td>
<td>0$^g$</td>
<td>0</td>
<td>$0.32^f$</td>
<td>0.40</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>α-Xylene</td>
<td>0$^g$</td>
<td>0</td>
<td>$0.14^f$</td>
<td>0.17</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>1-Ethylbenzene</td>
<td>0$^g$</td>
<td>0.003</td>
<td>$0.14^f$</td>
<td>0.17</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>n-Propylbenzene</td>
<td>0$^g$</td>
<td>0</td>
<td>$0.028^f$</td>
<td>0.04</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Isopropylbenzene</td>
<td>0$^g$</td>
<td>0</td>
<td>$0.007$</td>
<td>0.04</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>1,2,3-Trimethylbenzene</td>
<td>0$^g$</td>
<td>0</td>
<td>$0.027^f$</td>
<td>0.22</td>
<td>$-24$</td>
<td></td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>0$^g$</td>
<td>0</td>
<td>$0.12^f$</td>
<td>0.10</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.26$^i$</td>
<td>0.5$^i$</td>
<td>$0.5^f$</td>
<td>3.39</td>
<td>2.19</td>
<td>$-35$</td>
</tr>
</tbody>
</table>

$^a$ Measured concentration at ground level in Pasadena, CA.

$^b$ Measured concentration in the PBL.

$^c$ Modeled concentration based on the initial concentration and emission ratio.

$^d$ Percentage difference between measured and modeled concentrations.
Measuring C$_2$H$_4$ in the 3000 cm$^{-1}$ region will be difficult. The strongest feature, the nu$_{11}$ Q-branch at 2988.5 cm$^{-1}$, is 7 times weaker than the 949 cm$^{-1}$ feature. Even worse, it coincides with a saturated H$_2$O line. Perhaps one or two of the Q-branches in the 3060 to 3140 cm$^{-1}$ region are usable, but these are 15 times weaker than the one at 949 cm$^{-1}$.
C₂H₄ Summary/Conclusions

C₂H₄ can be measured from sea-level when columns exceed ~2E+15 molec./cm²

I was skeptical at first that C₂H₄ could be retrieved, since its Q-branch is less than 1% deep and is hidden behind a 60% deep CO₂ line that is strongly T-dependent.

But the results are convincing: Under clear, unpolluted conditions C₂H₄ is always zero, whereas in big cities it is highly variable, correlating with CO.

The fact that the fitted window contains 7 other CO₂ lines of similar E” (on average) seems to lessen the impact of CO₂ and T uncertainties on the C₂H₄ retrievals.

C₂H₄ has a strong correlation with CO, implying similar sources (urban pollution). But C₂H₄’s lifetime is much shorter and so it quickly falls to zero away from sources.

When fitting SF₆ from polluted site, C₂H₄ must be included as an interferent.

No chance of retrieving C₂H₄ from the 3000 cm⁻¹ region, e.g., with a TCCON instrument equipped with an InSb detector.
Aliso Canyon gas leak

From Wikipedia, the free encyclopedia

The Aliso Canyon gas leak (also called Porter Ranch gas leak[1] and Porter Ranch gas blowout[2]) was a massive natural gas leak that was discovered by SoCalGas employees on October 23, 2015.[3] Gas was released from a well within the Aliso Canyon's underground storage facility in the Santa Susana Mountains near Porter Ranch, Los Angeles.[4] The second-largest gas storage facility of its kind in the United States, it belongs to the Southern California Gas Company, a subsidiary of Sempra Energy. On January 6, 2016, Governor Jerry Brown issued a state of emergency.[5] The Aliso gas leak carbon footprint is said to be larger than the Deepwater Horizon leak in the Gulf of Mexico. On February 11, 2016 the gas company reported that it had the leak under control.[6]

On February 18, 2016, state officials announced that the leak was permanently plugged. An estimated 97,100 tonnes (95,600 long tons; 107,000 short tons) of methane and 7,300 tonnes (7,200 long tons; 8,000 short tons) of ethane was released into the atmosphere,[7] making it the worst natural gas leak in U.S. history in terms of its environmental impact.[8][9][10]

Aliso Canyon Underground Storage Facility is located 40 km from JPL. Jan 4 LA Times states that NG leak began Oct 23, 2015 and peaked on Nov 28 at 60 Tons of CH₄ per hour. By Dec 22 leak rate had decreased to 30 Tons per hour as the underground storage pressure dropped from the initial 2700 psi.
MkIV 2015 $\text{C}_2\text{H}_6$ and $\text{CH}_4$ Time Series from JPL

Plots color-coded by $\text{C}_2\text{H}_6$ (blue=low; red=high). NG leak began on Oct 23 (red arrow)

Only one day with large $\text{C}_2\text{H}_6$ enhancement: by 1.8 ppb (factor 3) on Nov 10

$\text{CH}_4$ was also slightly high on this day, but enhancement hard to quantify due to natural variations of 1-2%
Back-trajectories for Nov 10, 2015

Yellow pin indicates location of Aliso Canyon Underground Storage Facility. Green ball denotes JPL. Within trajectory uncertainties, this represents confirmation that $C_2H_6$ enhancement on Nov 10 was from Aliso Canyon NG leak.
C$_2$H$_2$, C$_2$H$_4$, C$_3$H$_8$ and CO all slightly high on Nov 10, but probably unrelated to NG leak. Plots color-coded by C$_2$H$_6$ (blue=low; red=high)
If no $N_2O$ present in leaked NG, then $N_2O$ can be used to account for dynamics. $CH_4$-$N_2O$ correlation shows 0.04 ppm (2.5%) enhancement in $CH_4$ on Nov 10 (red). 1.8 ppb enhancement of $C_2H_6$. Implies NG is 1.8 ppb / 40 ppb = 4.5% $C_2H_6$

Wikipedia article claims 97,100 tons of $CH_4$ and 7,300 tons of $C_2H_6$, implying leaked NG was 7.0% $C_2H_6$ by weight or 3.7% by mole fraction.
Spectral fit to C$_2$H$_6$ Q-branch on Nov 10

C$_2$H$_6$ absorption (red) is under-broadened due to plume being near the surface, not uniformly mixed throughout lower troposphere.
NG Leak -- Summary/Conclusions

Factor 3 enhancement of \( \text{XC}_2\text{H}_6 \) (1.8 ppb) observed from JPL on Nov 10, 2015.

A 2.5% enhancement of \( \text{XCH}_4 \) (40 ppb) is also seen on this date.

Back-trajectories reveal airmasses passed close to Aliso Canyon, an hour or two before arriving at JPL on Nov 10, 2015.

\( \text{C}_2\text{H}_6 \) mole fractions inferred from MkIV columns (4.5%) are not inconsistent with composition of leaked NG (3.7%)

Due to the geography, airmasses arriving at JPL from Aliso Canyon have also traversed the densely populated Northern San Fernando Valley. Small enhancements of \( \text{C}_3\text{H}_8 \), \( \text{C}_2\text{H}_4 \), \( \text{C}_2\text{H}_2 \) and CO are seen on Nov 10, but are within natural variability.

LA is a large source of \( \text{C}_3\text{H}_8 \) from LPG. In the US in winter, LPG is approximately 90% propane and 10% butane. NG is only ~1% propane.
MkIV column data access

The MkIV data shown in previous slides is available from NDACC-IRWG archive and from the website below.

A single file contains 30 years of data for 28 gases from 12 different sites (mainly Barcroft and JPL).

Ground-Based Observations

Between balloon and aircraft campaigns, the MkIV instrument is used to make ground-based observations. Although these measurements lack the vertical resolution that is a platforms, ground-based observations can nevertheless be made much more frequently - MkIV has averaged over 50 days of observation per year recently. Ground-base accurate method of ascertaining whether the composition of the Earth's atmosphere is changing, which is the main purpose of NDACC.

MkIV Ground-based Vertical Column Abundances 1985-2015

| Individual Column Abundances: (89 columns, 4229 rows) | m4_avg_1985_2015.vav |
| Individual Column Abundances: (Ames-1001 format) | m4_avg_1985_2015.vav.ames |
| Daily Average Column Abundances: (89 cols, 1090 rows) | m4_avg_1985_2015.vad |
| List of windows: (265 rows) | all_mols_mir_1985_2015.gnd |
| Window-to-window biases: | m4_avg_1985_2015.vav.cew |
Distributions and seasonal variations of tropospheric ethene (C$_2$H$_4$) from Atmospheric Chemistry Experiment (ACE-FTS) solar occultation spectra

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Received 14 October 2008; accepted 8 January 2009; published 17 February 2009.

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Figure 1. Example of ethene spectral signatures in an ACE-FTS spectrum around 9 km tangent altitude, measured at 26.96°N, 101.79°E on April 28, 2005. The black line represents the measured spectrum and the coloured lines the molecule-by-molecule simulations in the spectral window. The dark blue rectangle identifies the spectral micro-window used for the retrievals and the dotted arrows the position of the dominant ethene lines in it.

Figure 4. (left) Example of retrieved C$_2$H$_4$ profiles from the same occultation as in Figure 1 and comparison with other carbon tracers. (right) Relationship between the C$_2$H$_4$ and C$_2$H$_2$ vmrs around 6 km in the troposphere, considering all measured data points. The red curve is obtained by fitting a line through the data points, weighted by their respective uncertainties. The equation of the linear regression, the number of points (N), and the corresponding correlation coefficient R are given in the upper left corner.
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