SAND2022-16937C

# Investigating Methylamine Oxidation with Multiplexed Photoionization Mass Spectrometry: Insight into the Reactivity of C-centered and N-centered Radicals

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2. Laboratory of Physical Chemistry, Department of Chemistry, University of Helsinki, Helsinki, Finland

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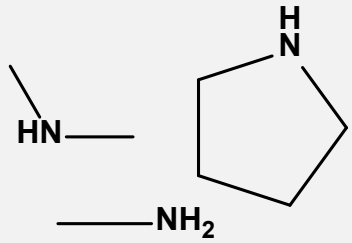
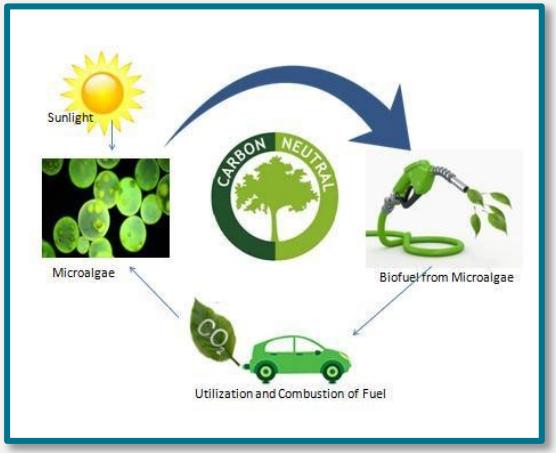
# Amines in the Atmosphere

Amines are released in combustion of biomass and industrial processes:

- Biofuels
- Agriculture
- Wildfires
- Carbon capture agents



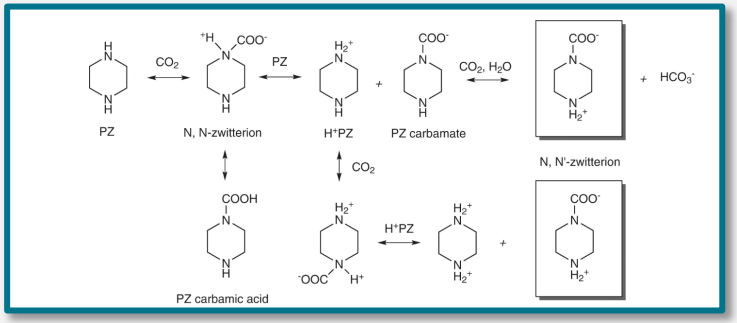




Image credit: https://www.usatoday.com/

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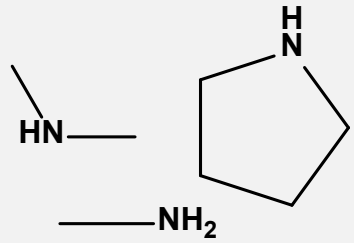


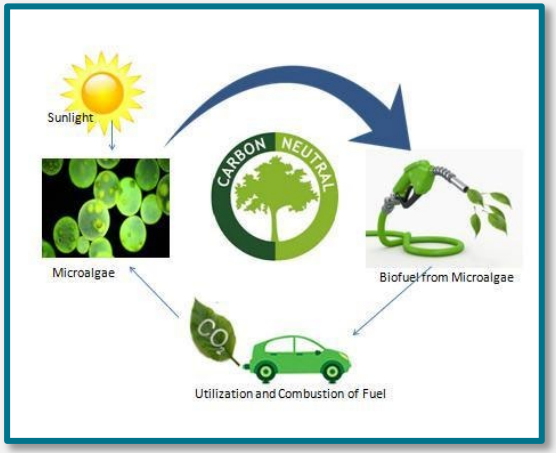


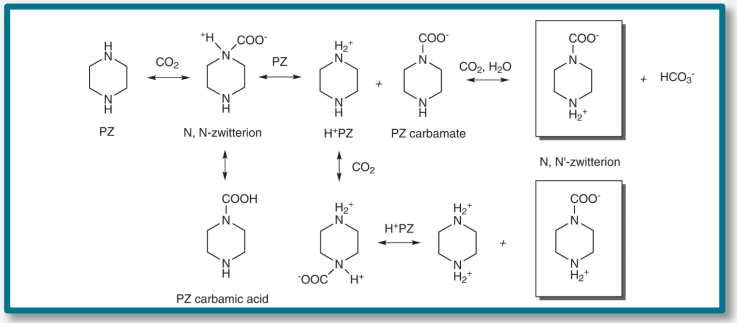


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# Methylamine Oxidation

- Methylamine is common degradation product of amines used for carbon capture *
- Byproduct of $NH_3$/methane combustion
- Limited work on oxidation pathways



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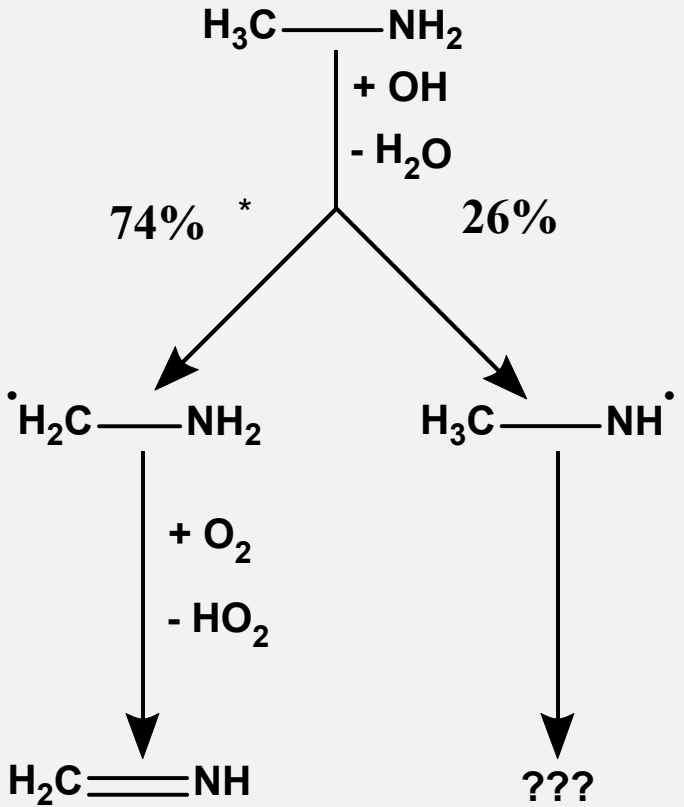


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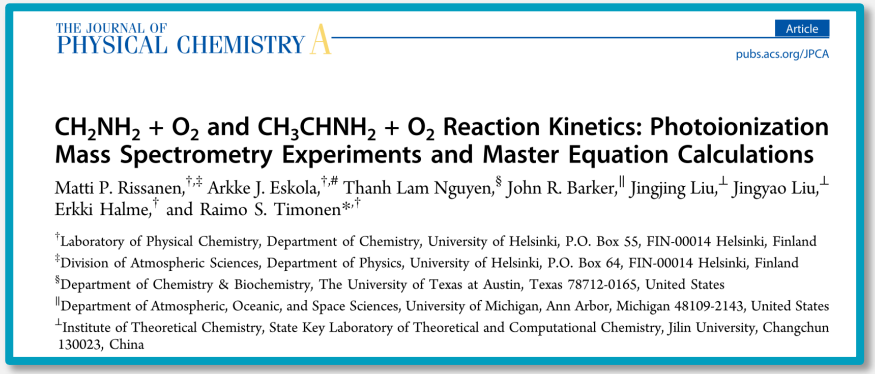

THE JOURNAL OF PHYSICAL CHEMISTRY A

Article

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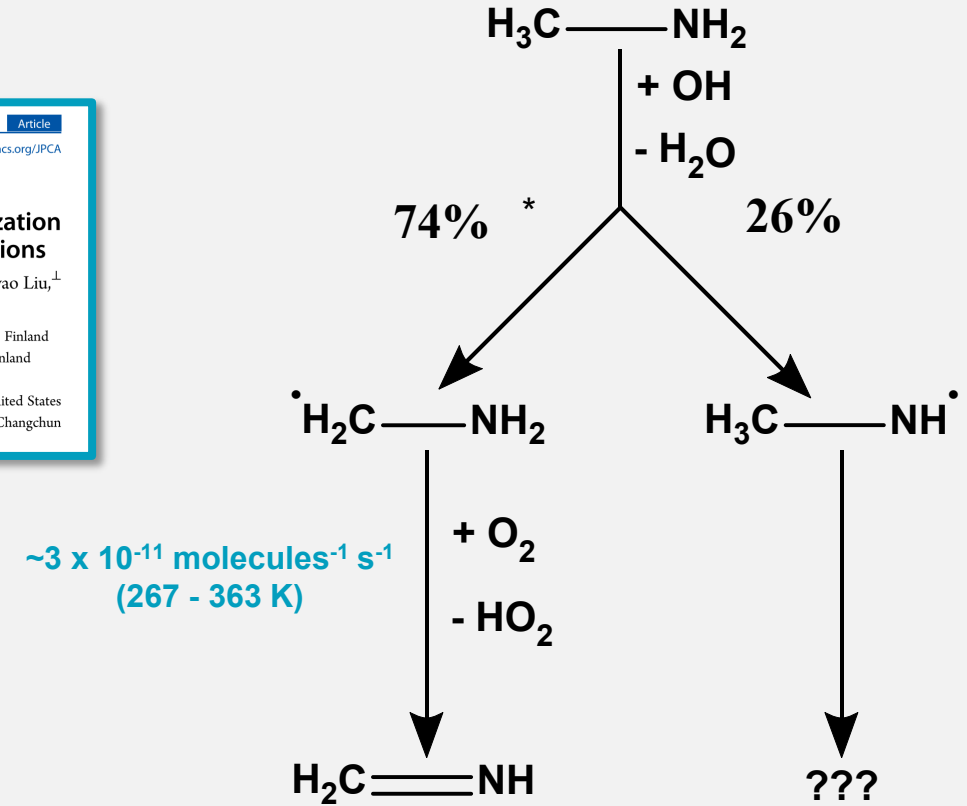
**$CH_2NH_2 + O_2$ and $CH_3CHNH_2 + O_2$ Reaction Kinetics: Photoionization Mass Spectrometry Experiments and Master Equation Calculations**


Matti P. Rissanen,[†,‡] Arkke J. Eskola,[†,#] Thanh Lam Nguyen,[§] John R. Barker,[∥] Jingjing Liu,[⊥] Jingyao Liu,[⊥] Erkki Halme,[†] and Raimo S. Timonen*[,†]

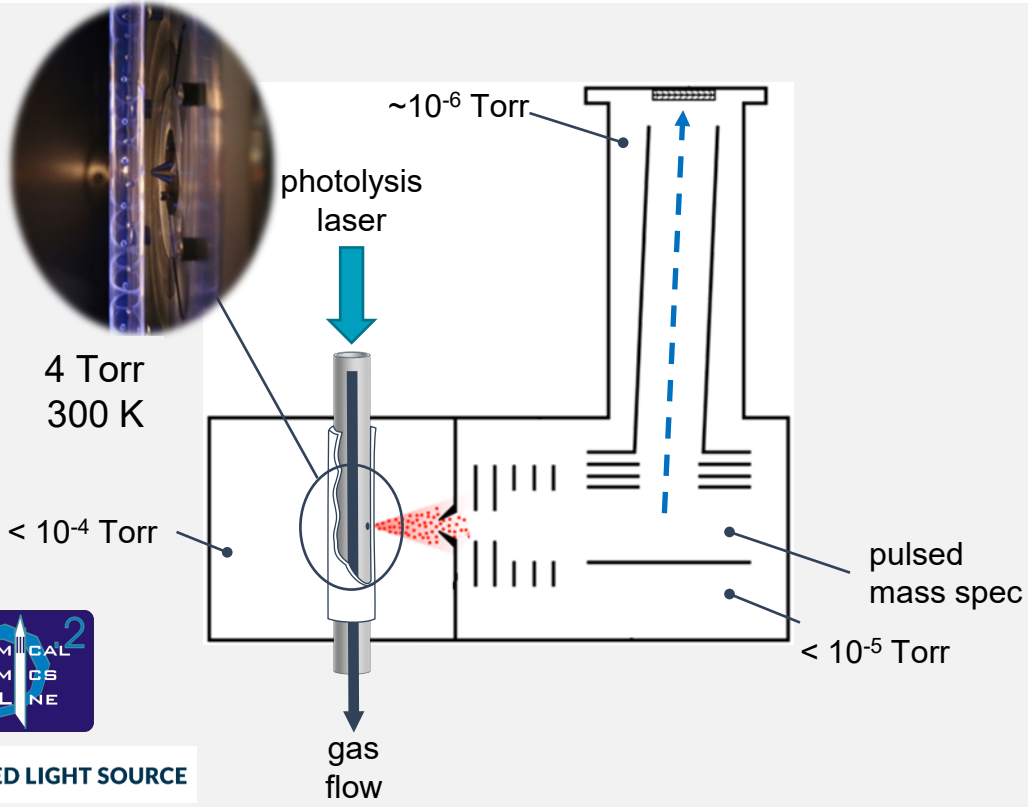
[†]Laboratory of Physical Chemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 Helsinki, Finland
[‡]Division of Atmospheric Sciences, Department of Physics, University of Helsinki, P.O. Box 64, FIN-00014 Helsinki, Finland
[§]Department of Chemistry & Biochemistry, The University of Texas at Austin, Texas 78712-0165, United States
[∥]Department of Atmospheric, Oceanic, and Space Sciences, University of Michigan, Ann Arbor, Michigan 48109-2143, United States
[⊥]Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun 130023, China



Rissanen, M. P., Eskola, A. J., Nguyen, T. L., Barker, J. R., Liu, J., Liu, J., Halme, E., & Timonen, R. S. (2014). CH 2 NH 2 + O 2 and CH 3 CHNH 2 + O 2 Reaction Kinetics: Photoionization Mass Spectrometry Experiments and Master Equation Calculations. *The Journal of Physical Chemistry A*, *118*(12), 2176–2186. https://doi.org/10.1021/jp411238e

# Methodology: Multiplexed VUV Photoionization Mass Spectrometer




Chemical Dynamics Beamline 9.0.2

ADVANCED LIGHT SOURCE

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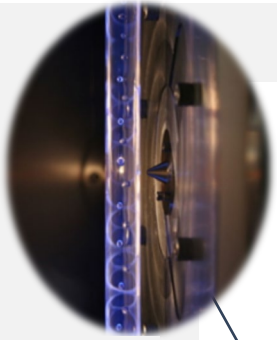

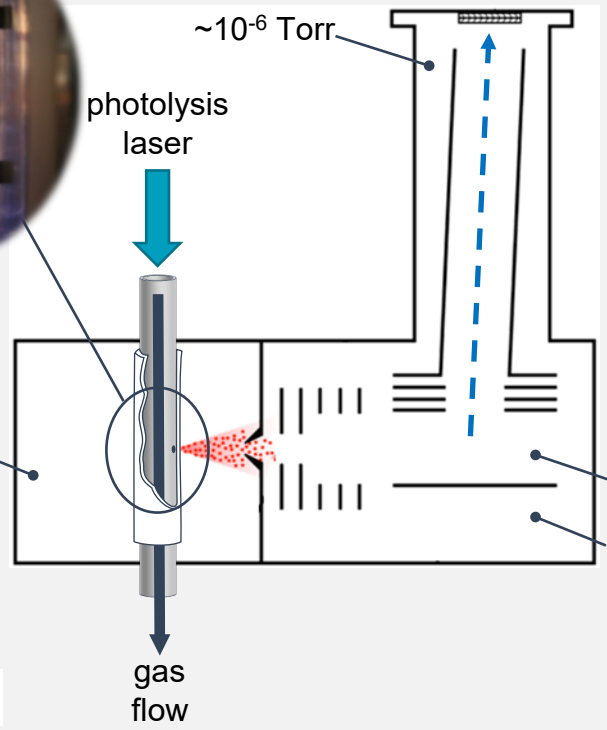


$$HO{-}OH + h\nu \rightarrow 2\ OH\bullet$$

$$RH + OH\bullet \rightarrow R\bullet + H_2O$$

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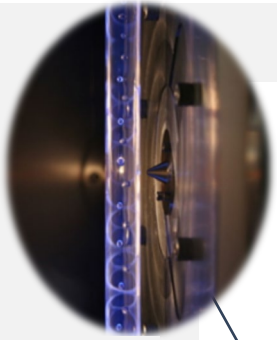

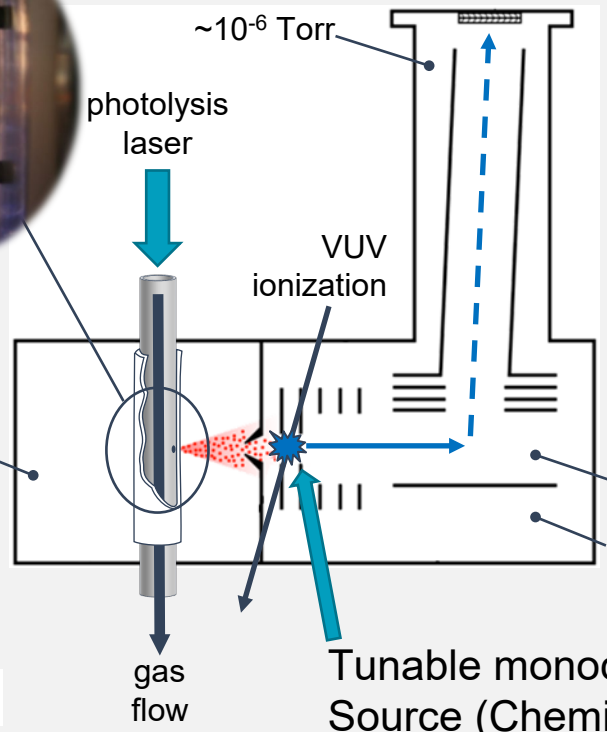


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Tunable monochromatic VUV radiation at the Advanced Light Source (Chemical Dynamics Beamline)

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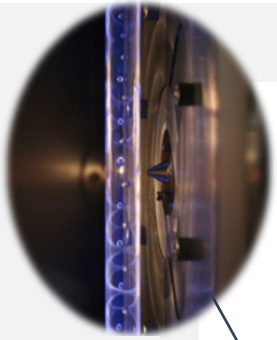

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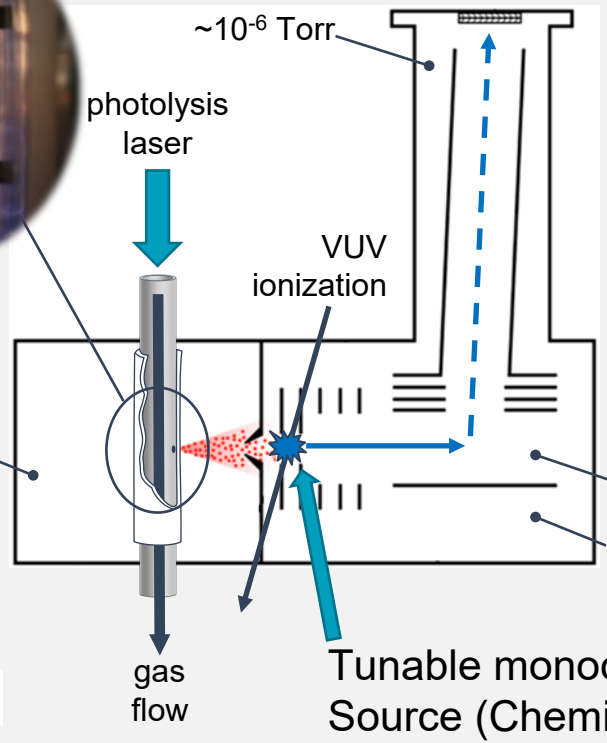
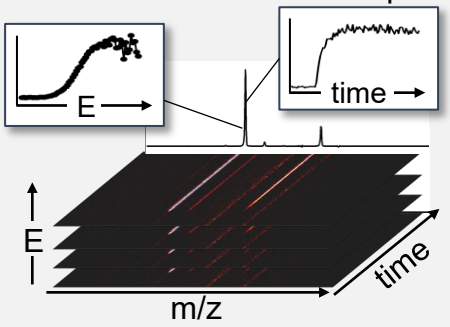



time- and E-resolved mass spectrum

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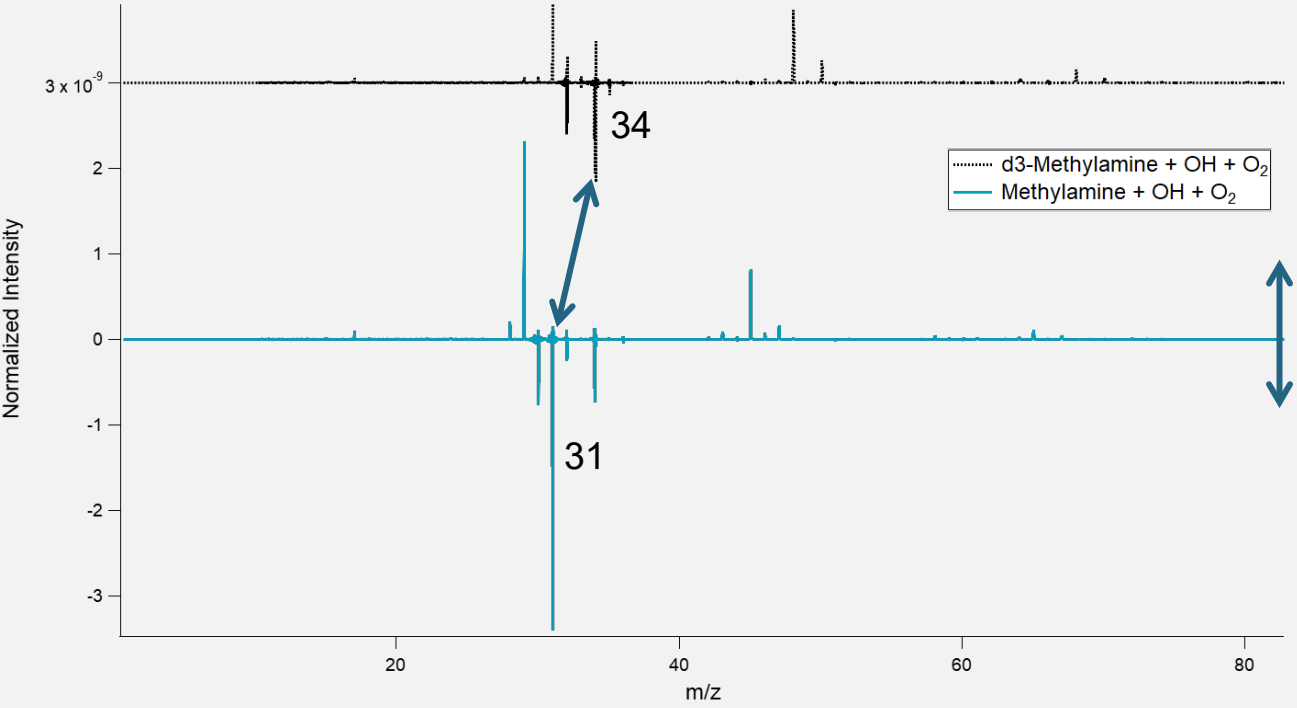
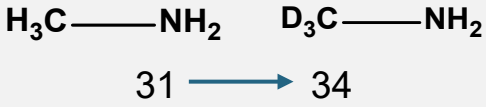


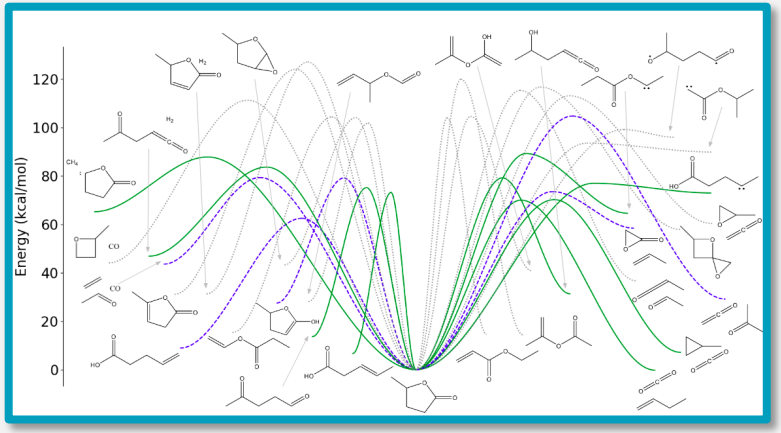

intermediates and products

reactants

# Methodology: KinBot

Automated reaction kinetics workflow tool for elementary gas-phase reactions.

- Searches for reaction paths starting from a parent compound, continuing over multiple wells
- Characterizes stationary points
- Assembles the chemical master equation
- Includes uncertainty quantification
- Open source




https://github.com/zadorlab/KinBot/



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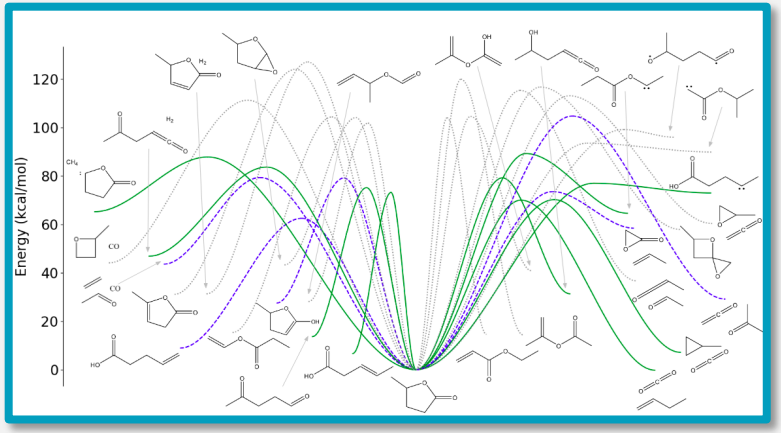


Great at finding new reaction pathways!

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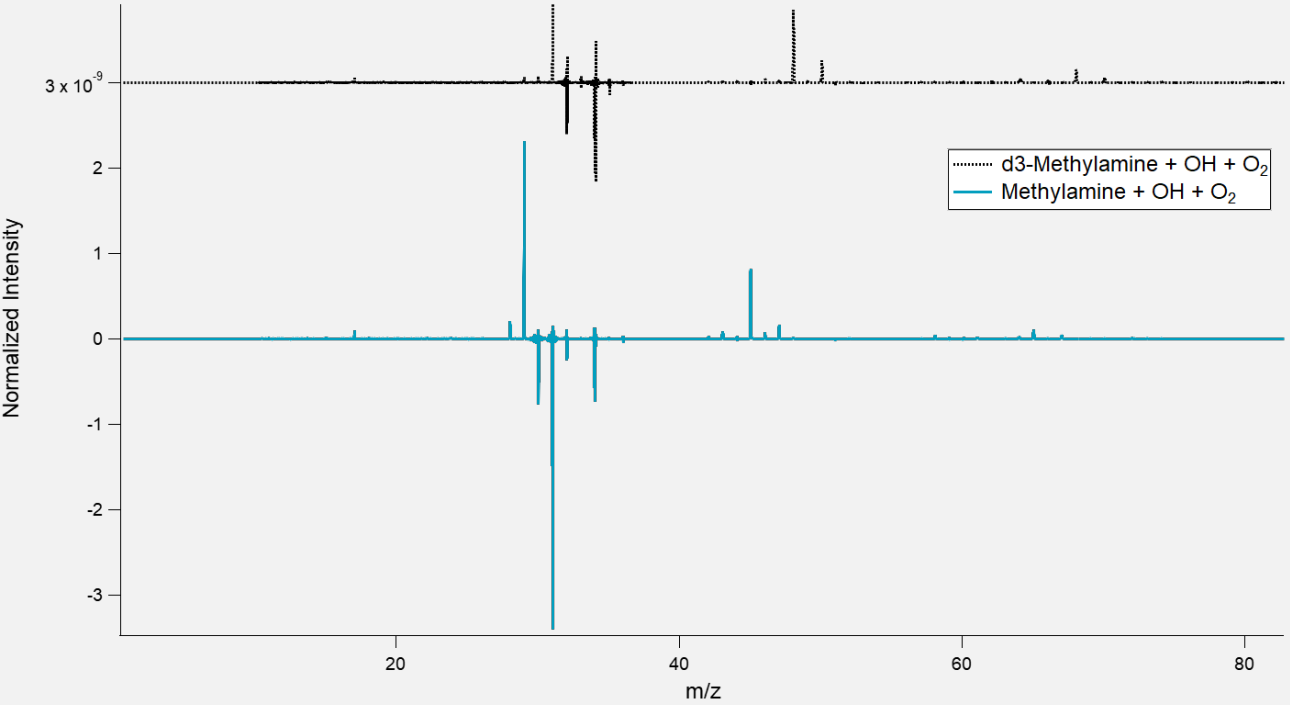
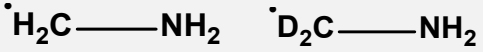
# Methylamine Oxidation: $CH_2NH_2 + O_2$

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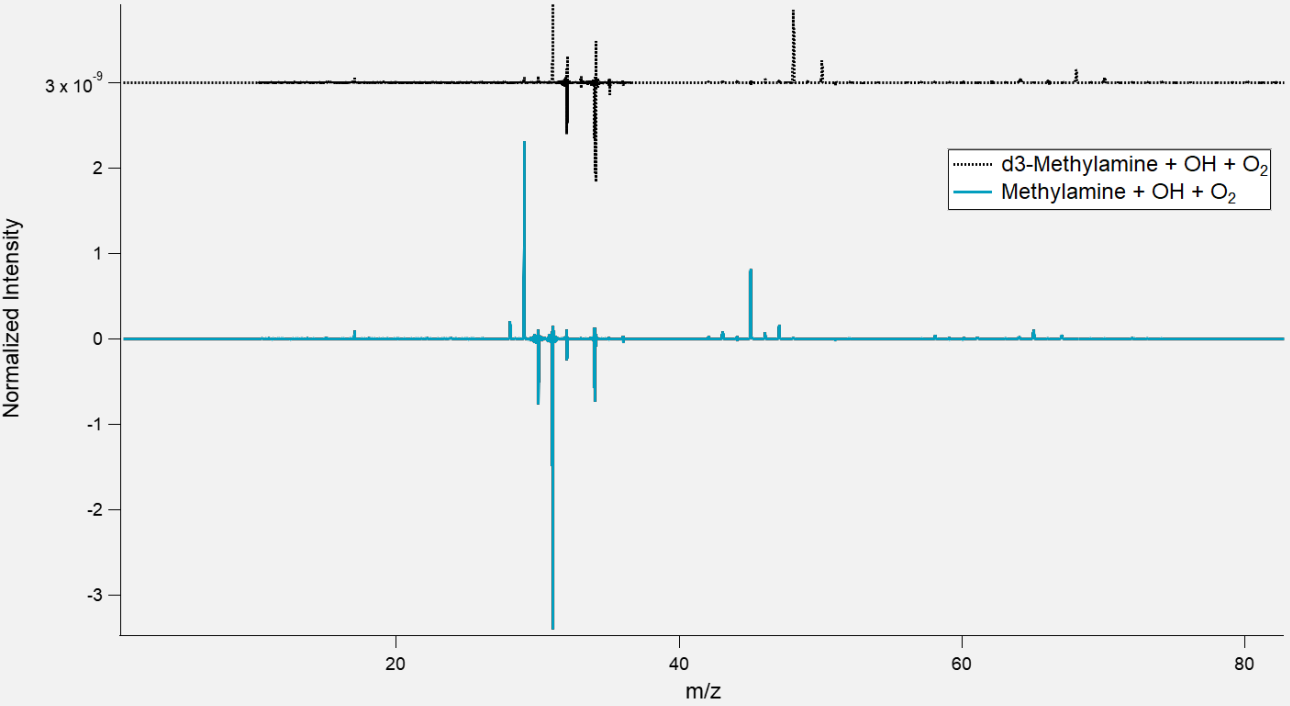


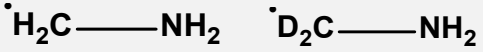


Too short-lived to see

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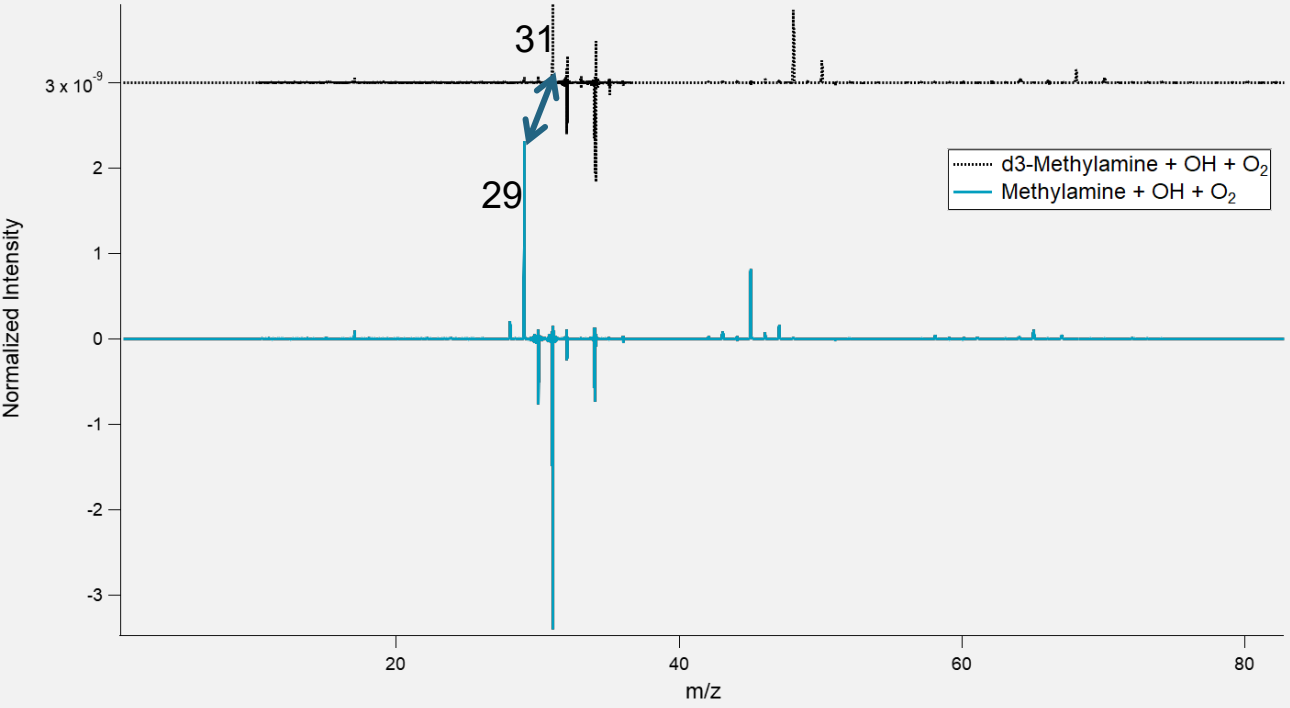


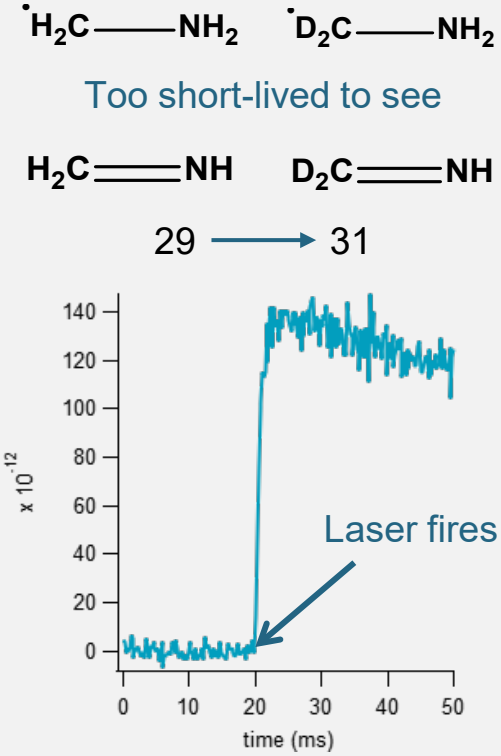


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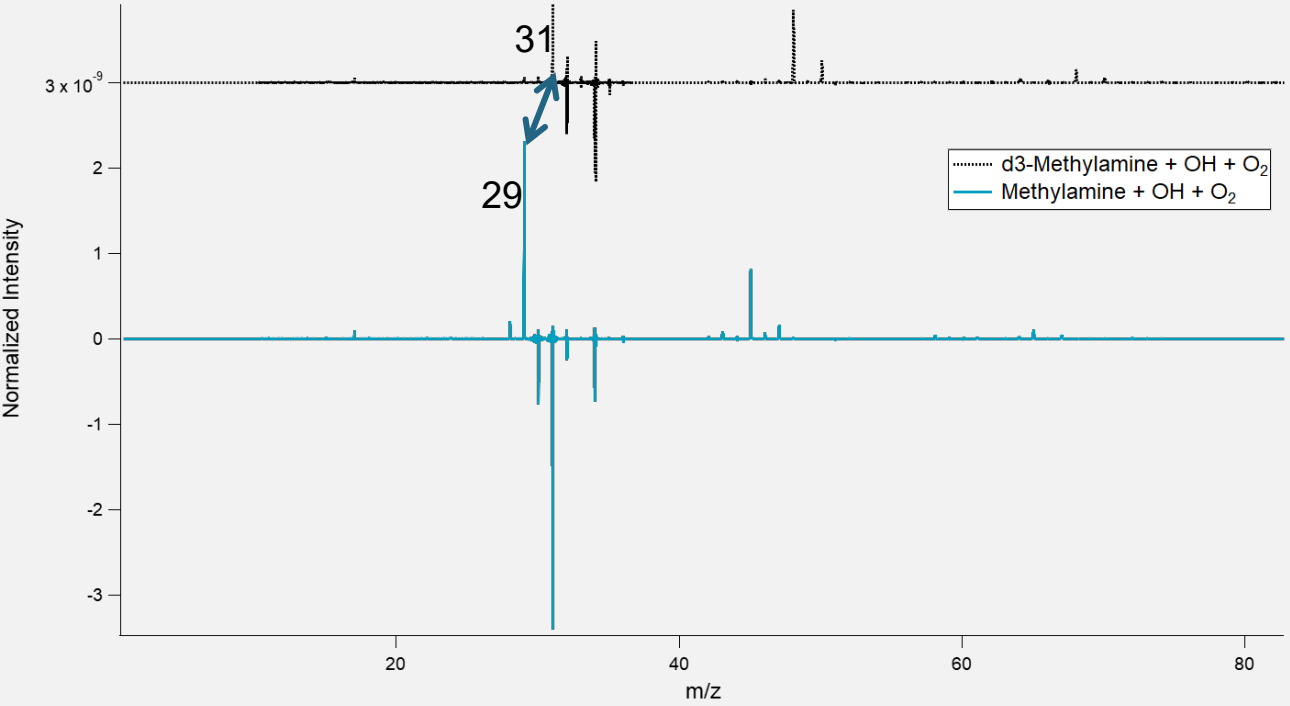
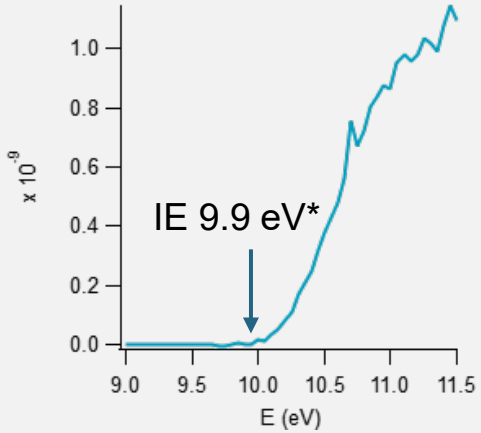



$\dot{H}_2C$—$NH_2$ $\dot{D}_2C$—$NH_2$

Too short-lived to see

$H_2C$=$NH$ $D_2C$=$NH$

29 → 31

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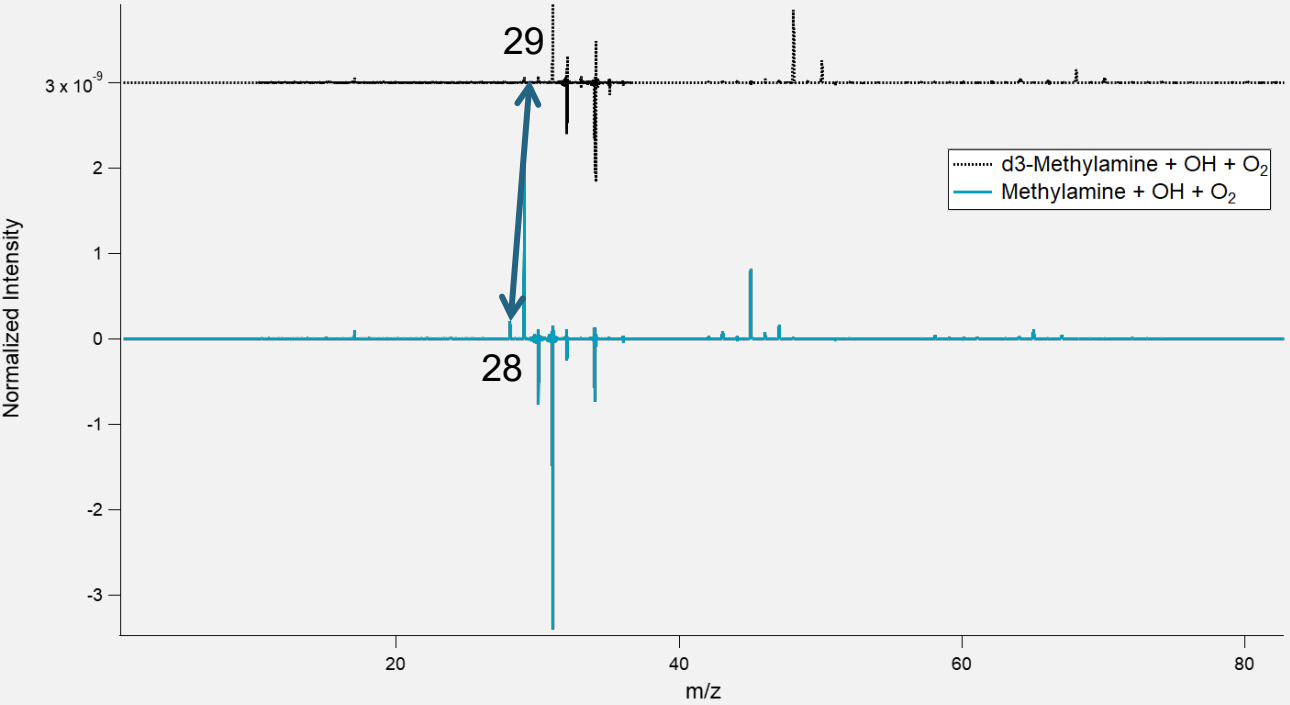


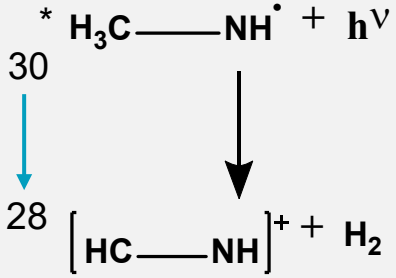


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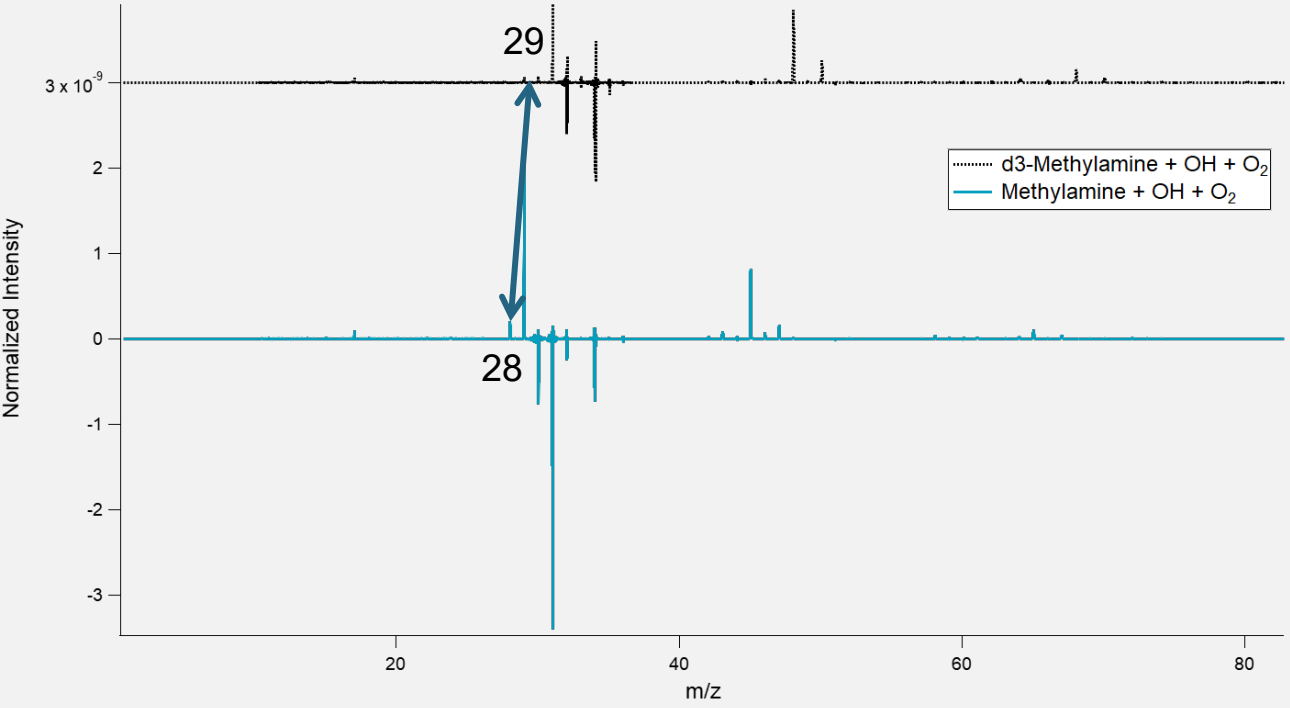


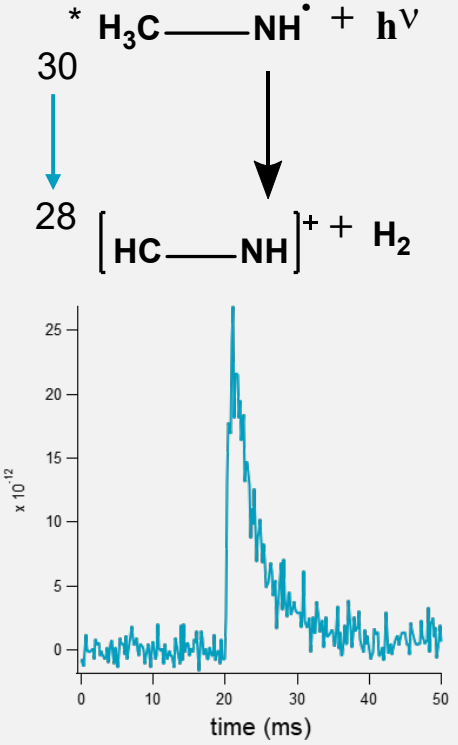


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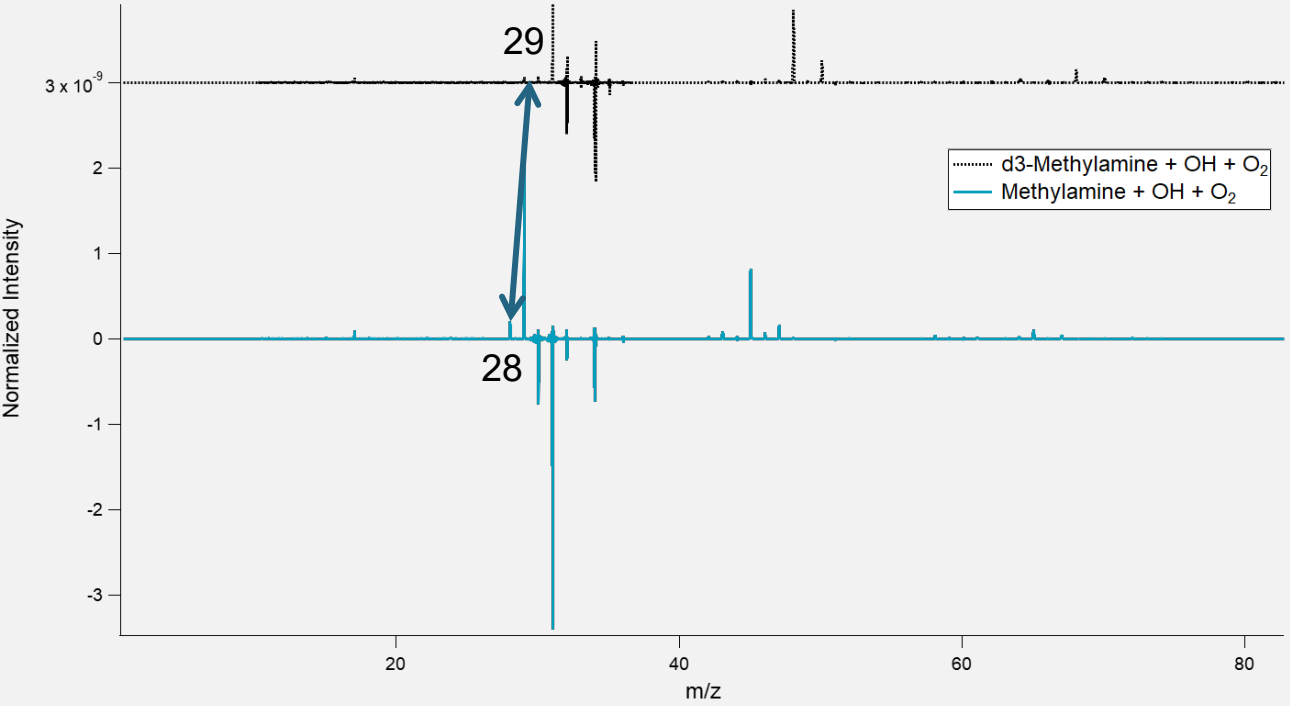


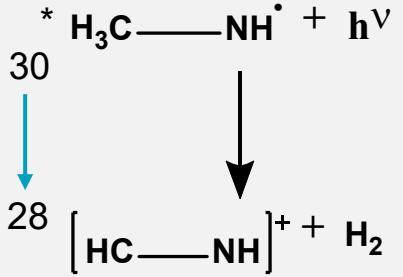


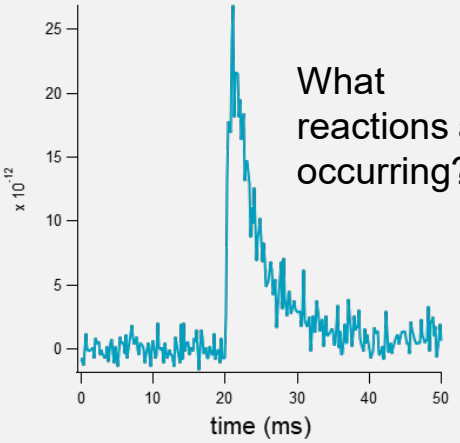


What reactions are occurring?

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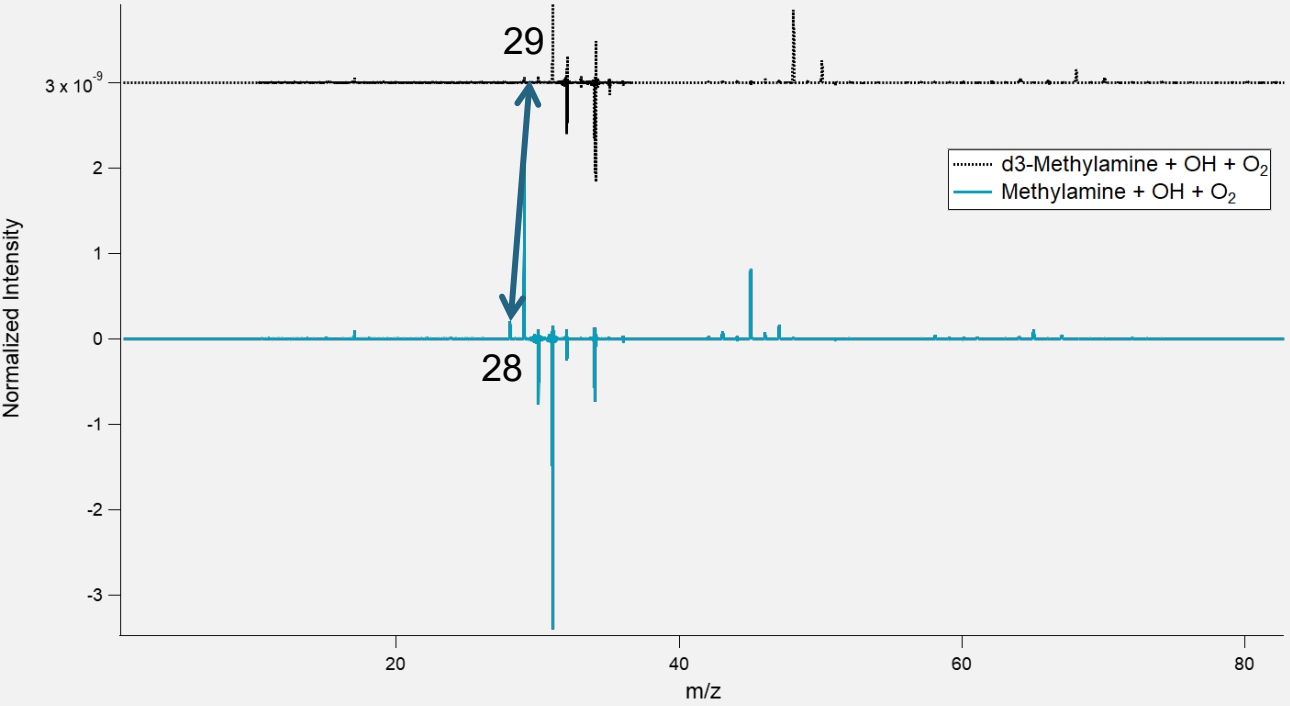


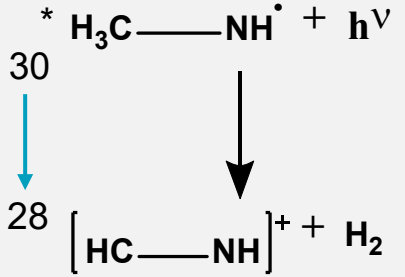


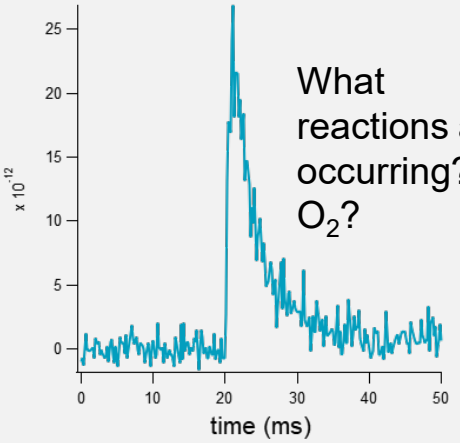


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# Methylamine Oxidation: $CH_3NH + O_2$



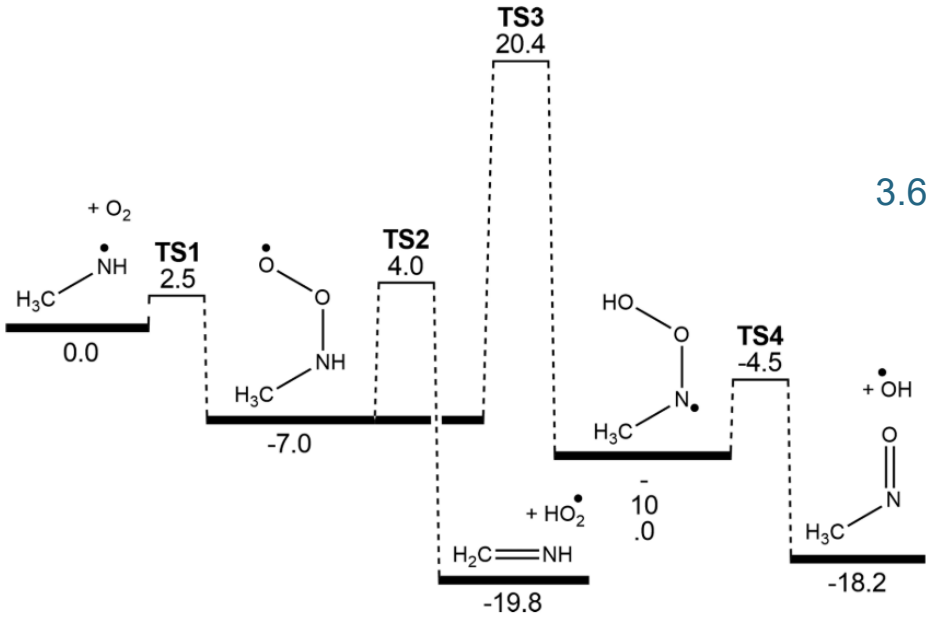


**FIGURE 1** Potential energy surface for the $CH_3N^{\bullet}H + O_2$ reaction. Energies are 0 K enthalpies in kcal $mol^{-1}$, at the G3X-K level of theory

$3.6 \times 10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

Alam, M. A., Ren, Z., & da Silva, G. (2019). Nitramine and nitrosamine formation is a minor pathway in the atmospheric oxidation of methylamine: A theoretical kinetic study of the CH 3 NH + O 2 reaction. *International Journal of Chemical Kinetics*, *51*(9), 723–728. https://doi.org/10.1002/kin.21303

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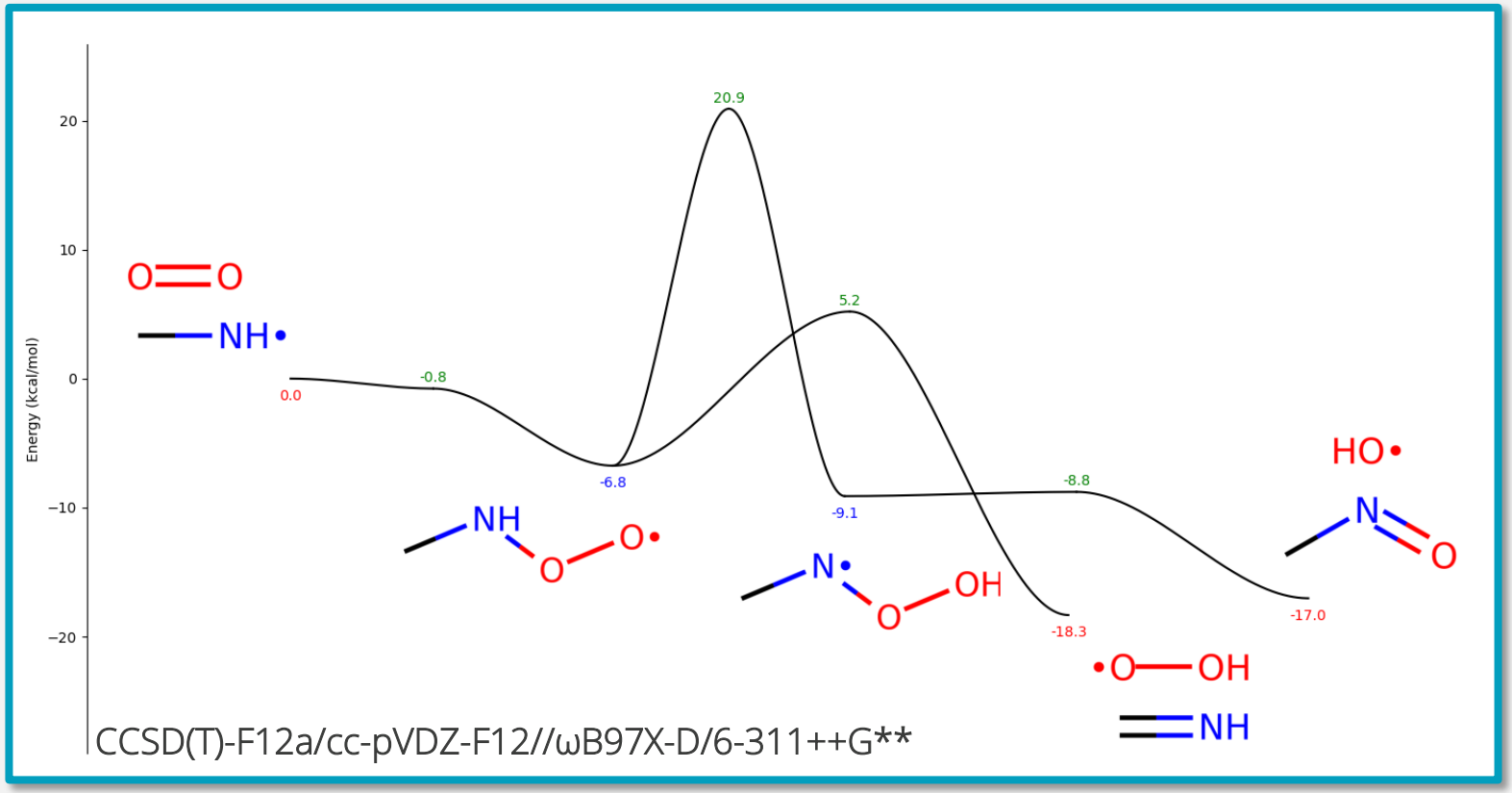

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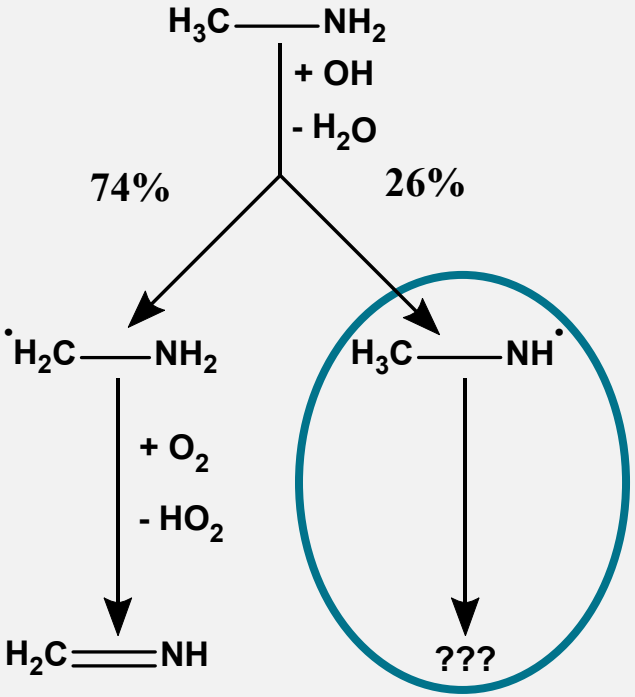


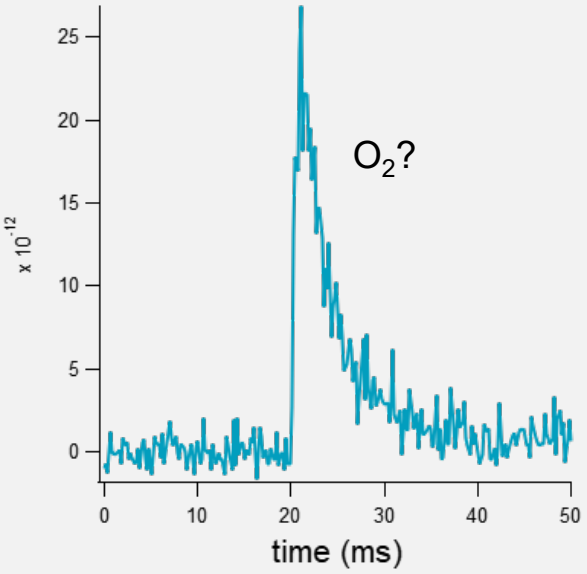


Rissanen, M. P., Eskola, A. J., Nguyen, T. L., Barker, J. R., Liu, J., Liu, J., Halme, E., & Timonen, R. S. (2014). CH 2 NH 2 + O 2 and CH 3 CHNH 2 + O 2 Reaction Kinetics: Photoionization Mass Spectrometry Experiments and Master Equation Calculations. *The Journal of Physical Chemistry A*, *118*(12), 2176–2186. https://doi.org/10.1021/jp411238e

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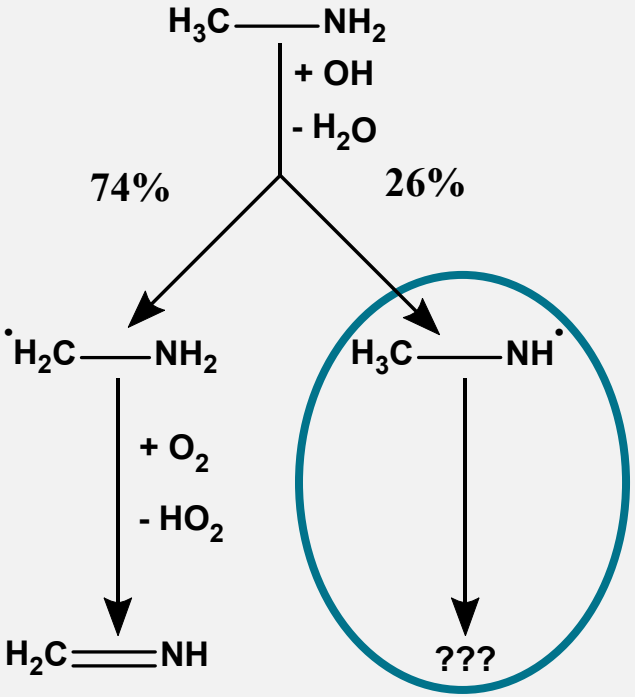


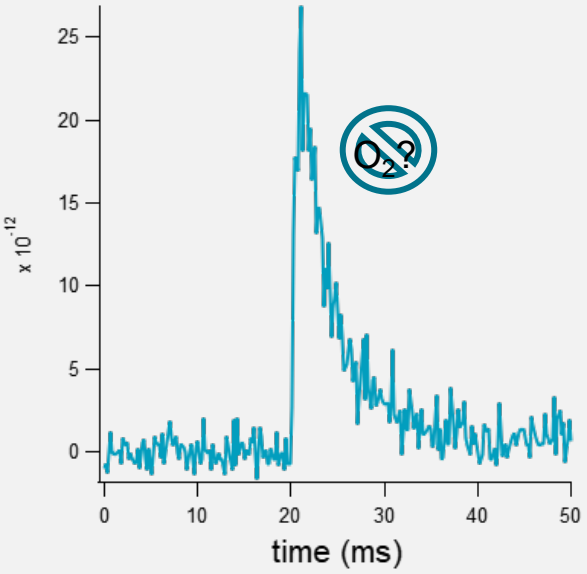


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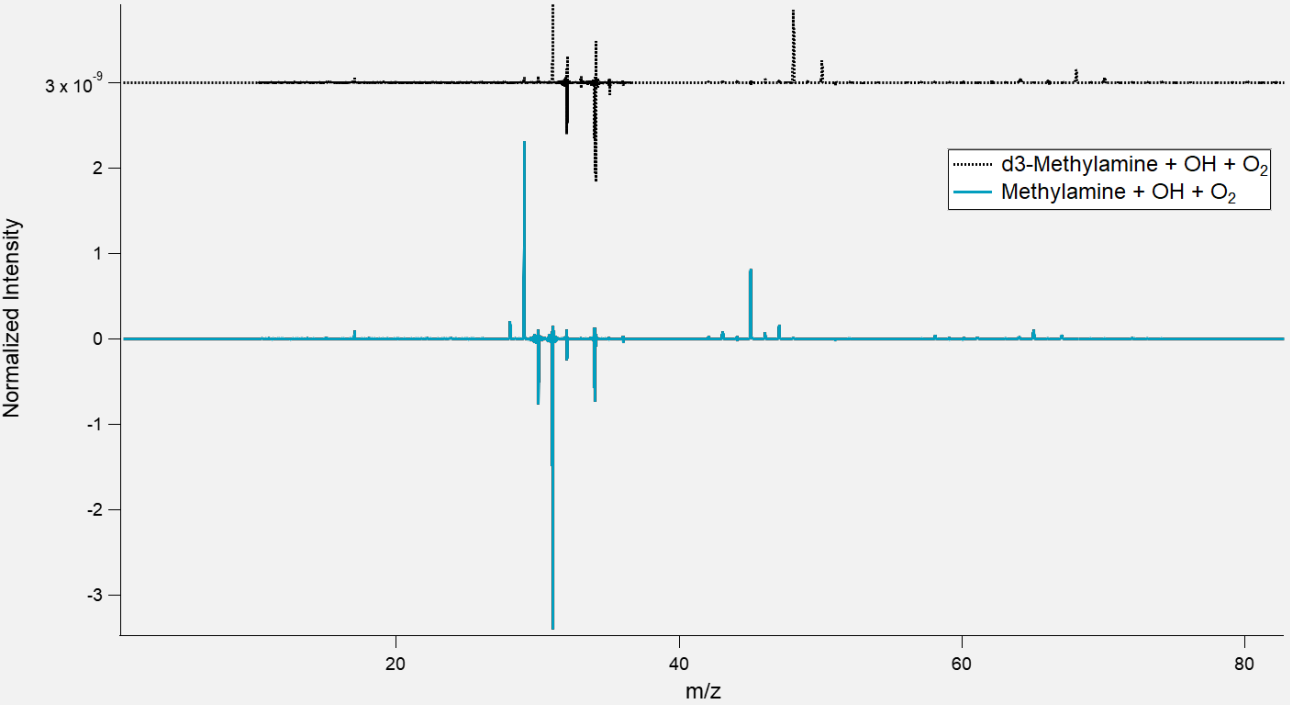
# Methylamine Oxidation: $CH_3NH$ + ?




What masses increase by 3 m/z in the d3-methylamine results?

$H_3C—NH_2$ $D_3C—NH_2$

31 → 34

* Forde, N. R., Butler, L. J., Ruscic, B., Sorkhabi, O., Qi, F., & Suits, A. (2000). Characterization of nitrogen-containing radical products from the photodissociation of trimethylamine using photoionization detection. *The Journal of Chemical Physics*, *113*(8), 3088–3097. https://doi.org/10.1063/1.1286973

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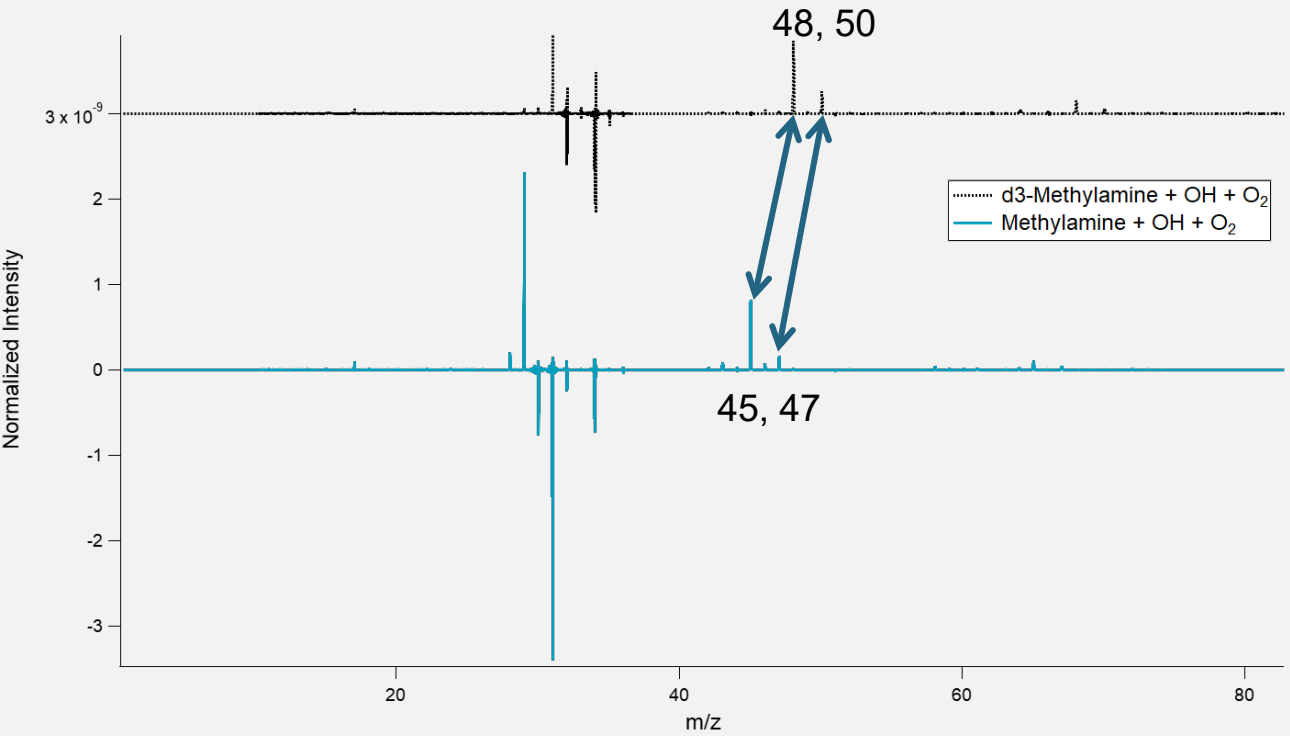



What masses increase by 3 m/z in the d3-methylamine results?

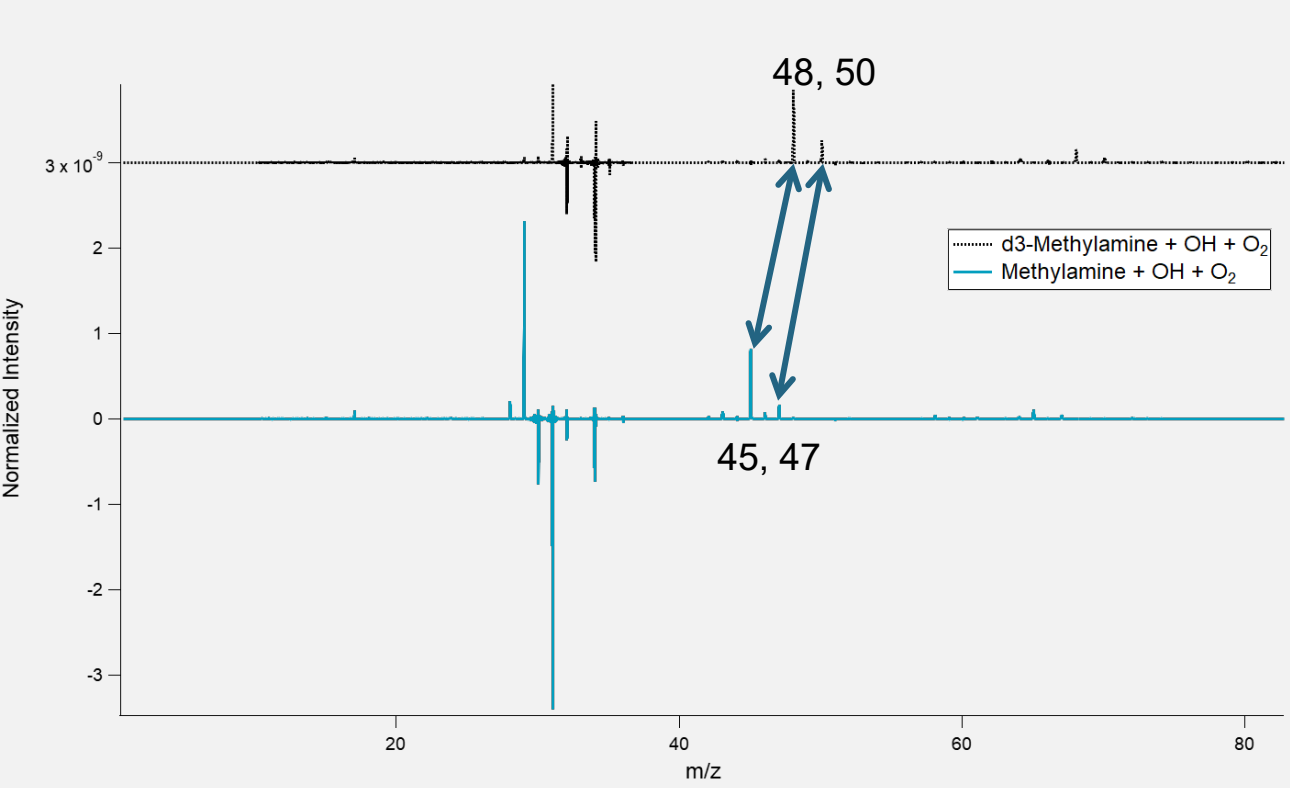
$H_3C—NH_2$ $D_3C—NH_2$

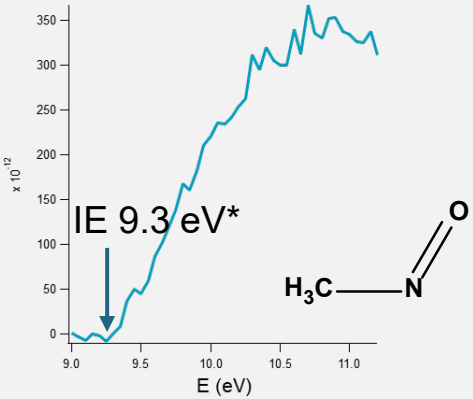
31 → 34

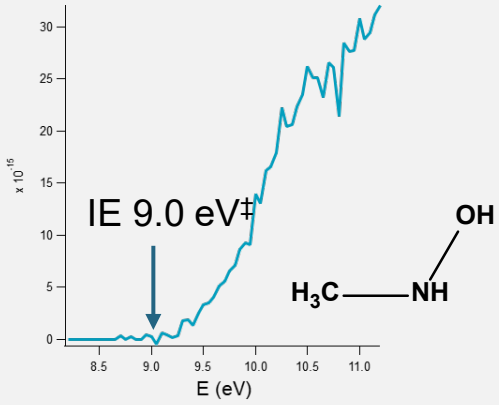
45 → 48

47 → 50

# Methylamine Oxidation: $CH_3NH$ + ?

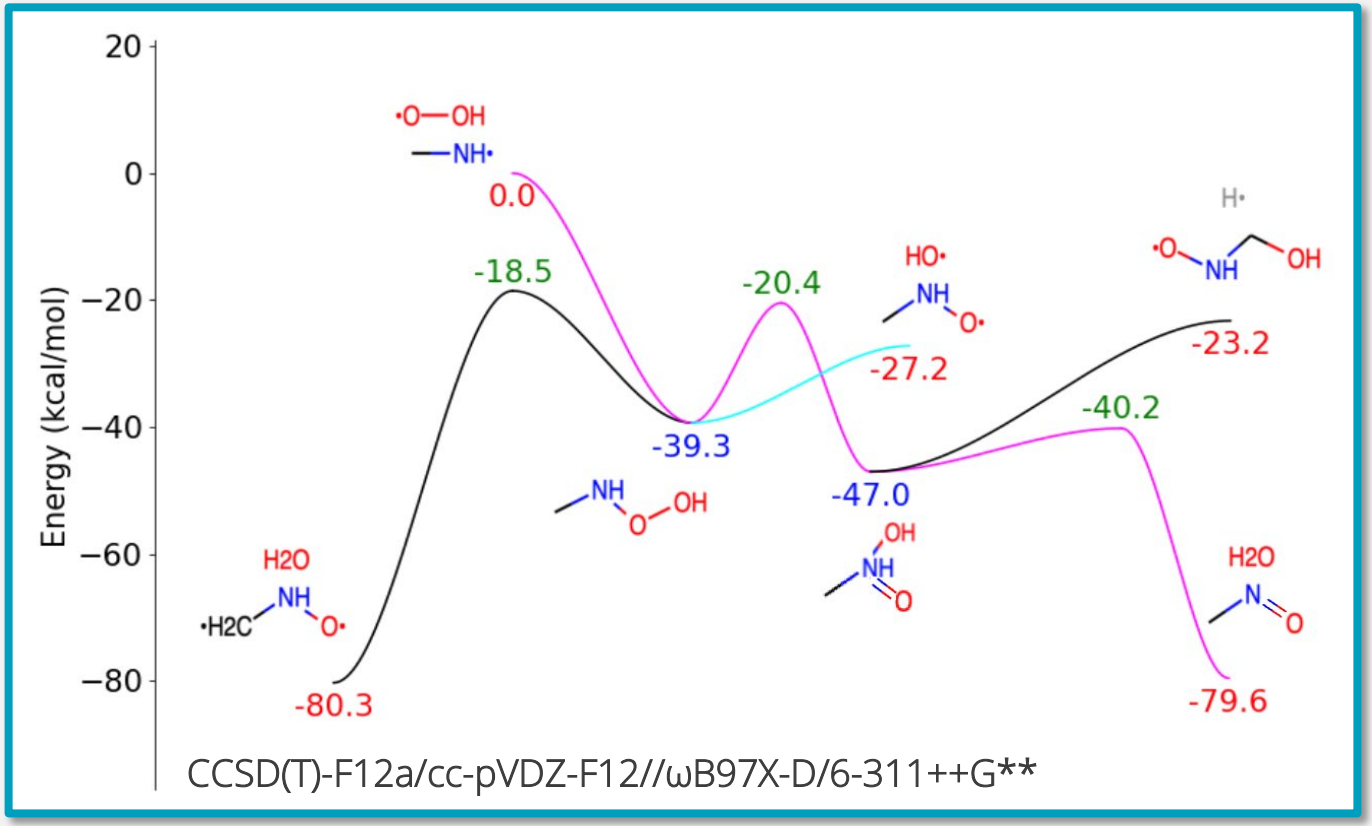



*Frost, D. C., Lau, W. M., McDowell, C. A., & Westwood, N. P. C. (1982). A study by He I photoelectron spectroscopy of monomeric nitrosomethane, the cis and trans dimers, and formaldoxime. *Journal of Physical Chemistry*, *86*(18), 3577–3581.
‡ Rademacher, P., & Freckmann, B. (1980). Photoelektronenspektren und konformationsverhalten von hydroxylamin und methylhydroxylaminen. *Journal of Electron Spectroscopy and Related Phenomena*, *19*(2), 251–259.

# Methylamine Oxidation: $CH_3NH + HO_2$



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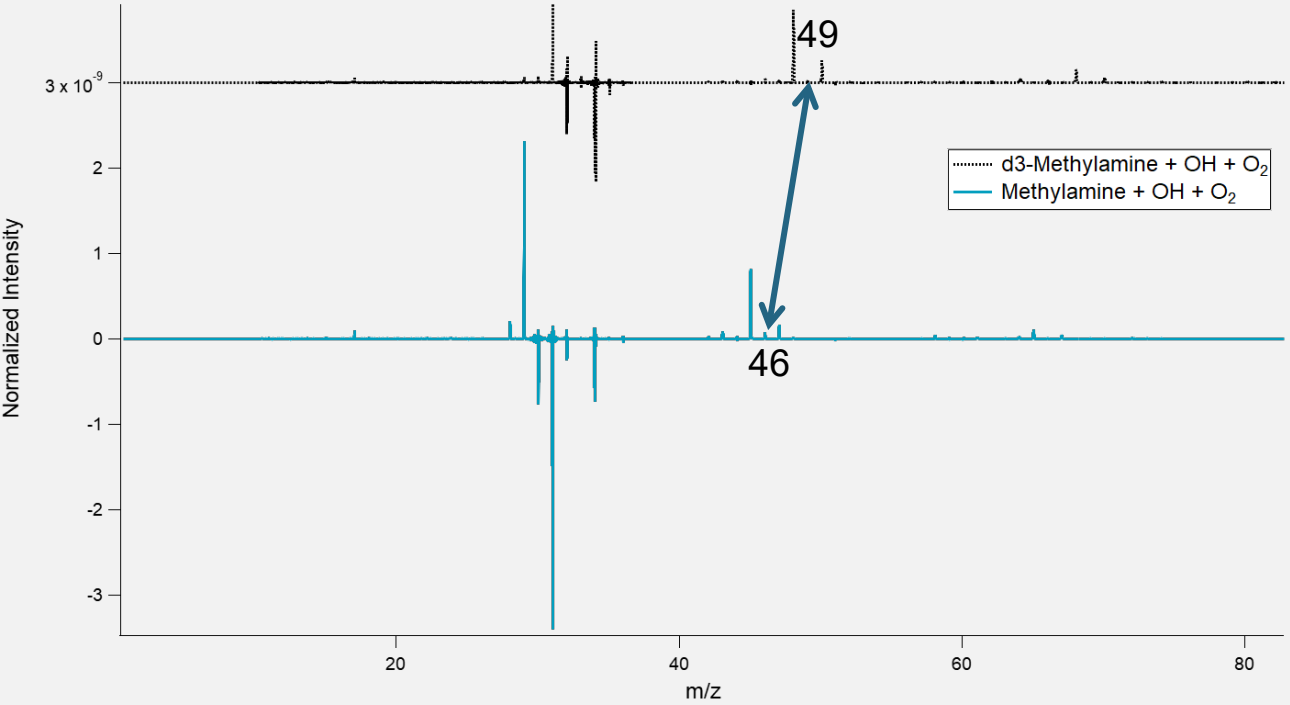


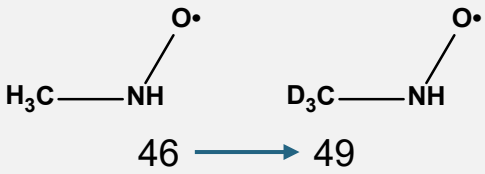

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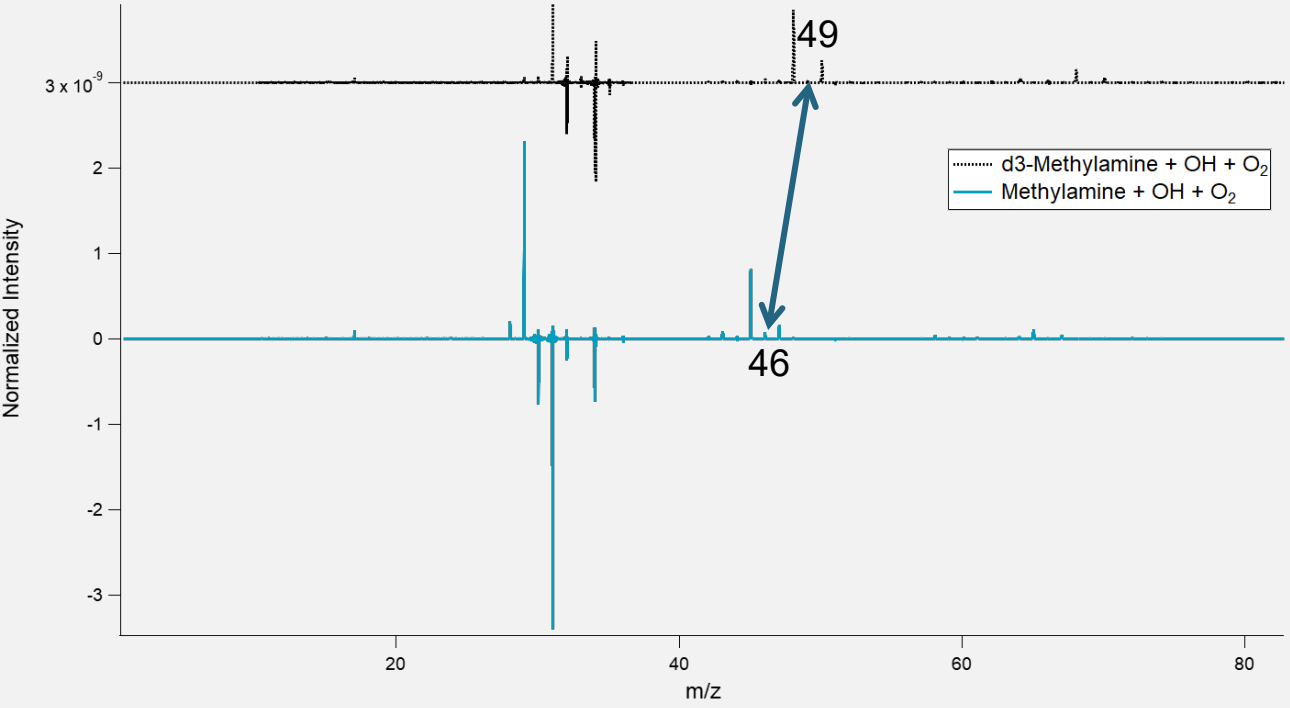


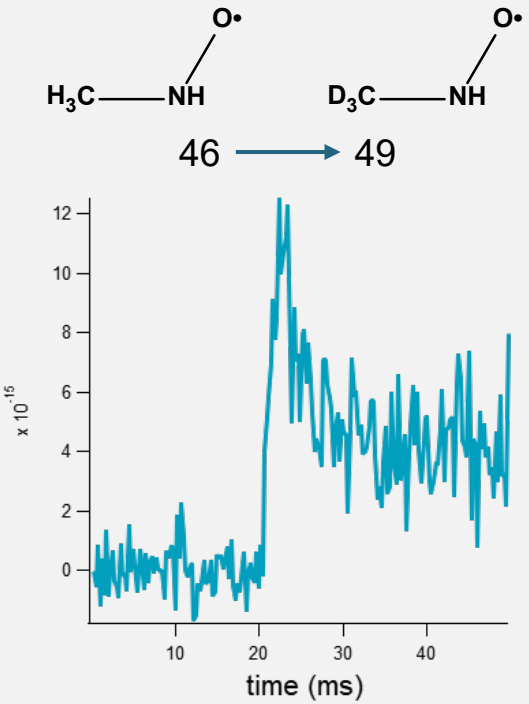

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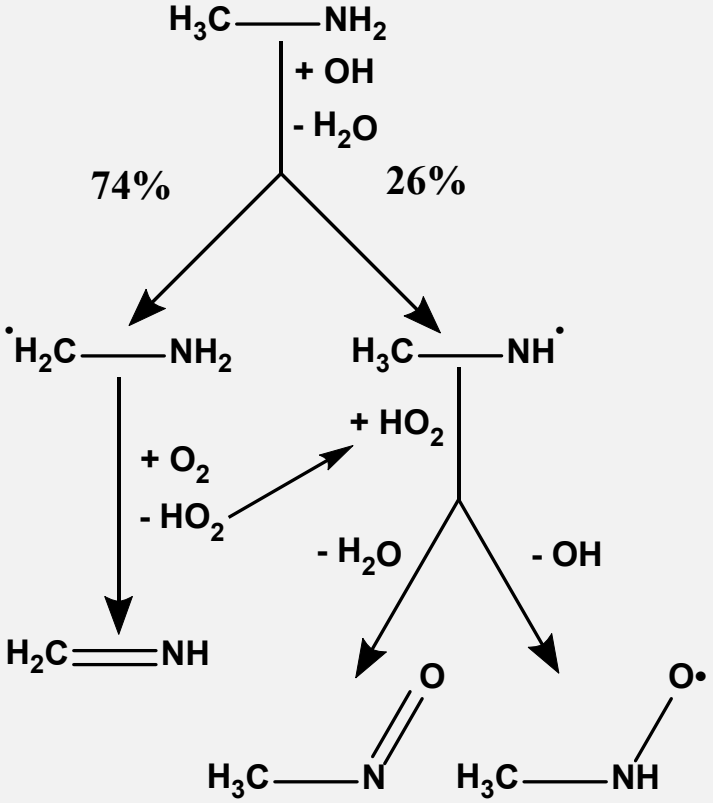


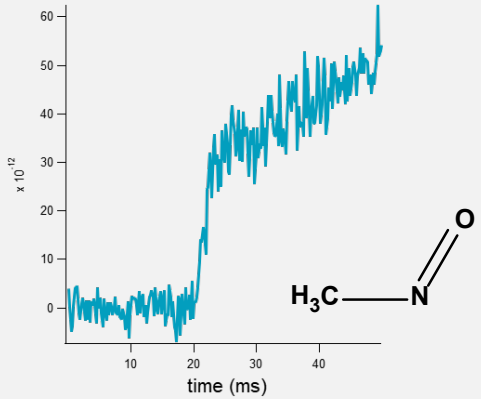


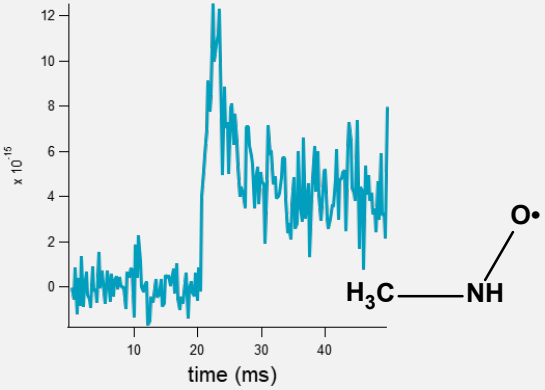

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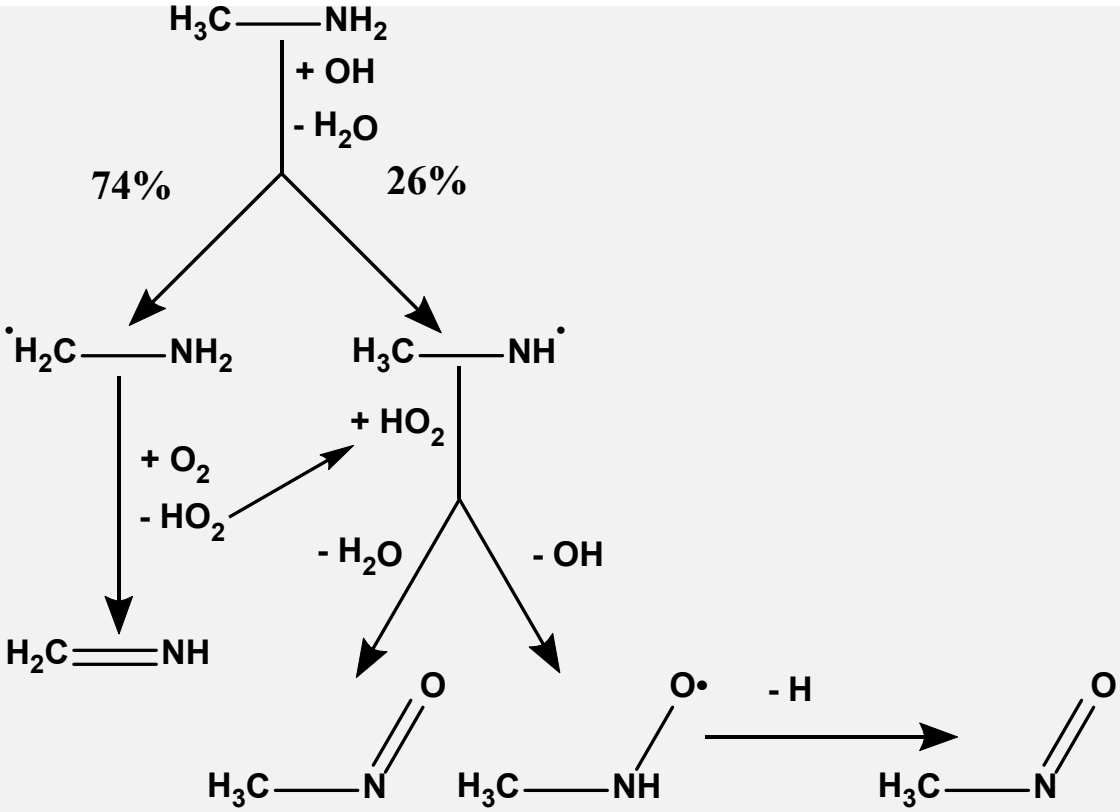


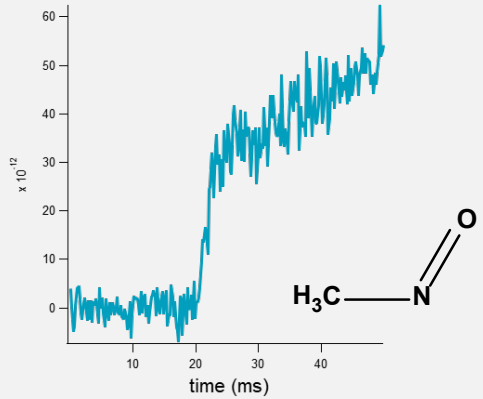


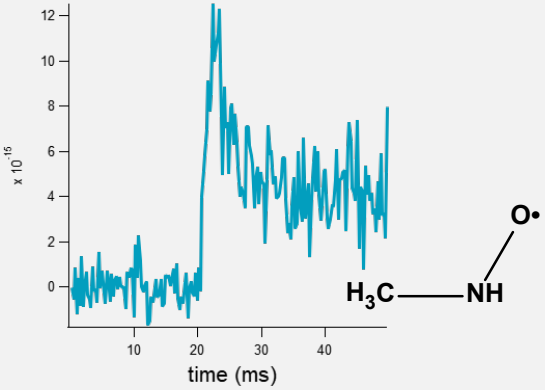

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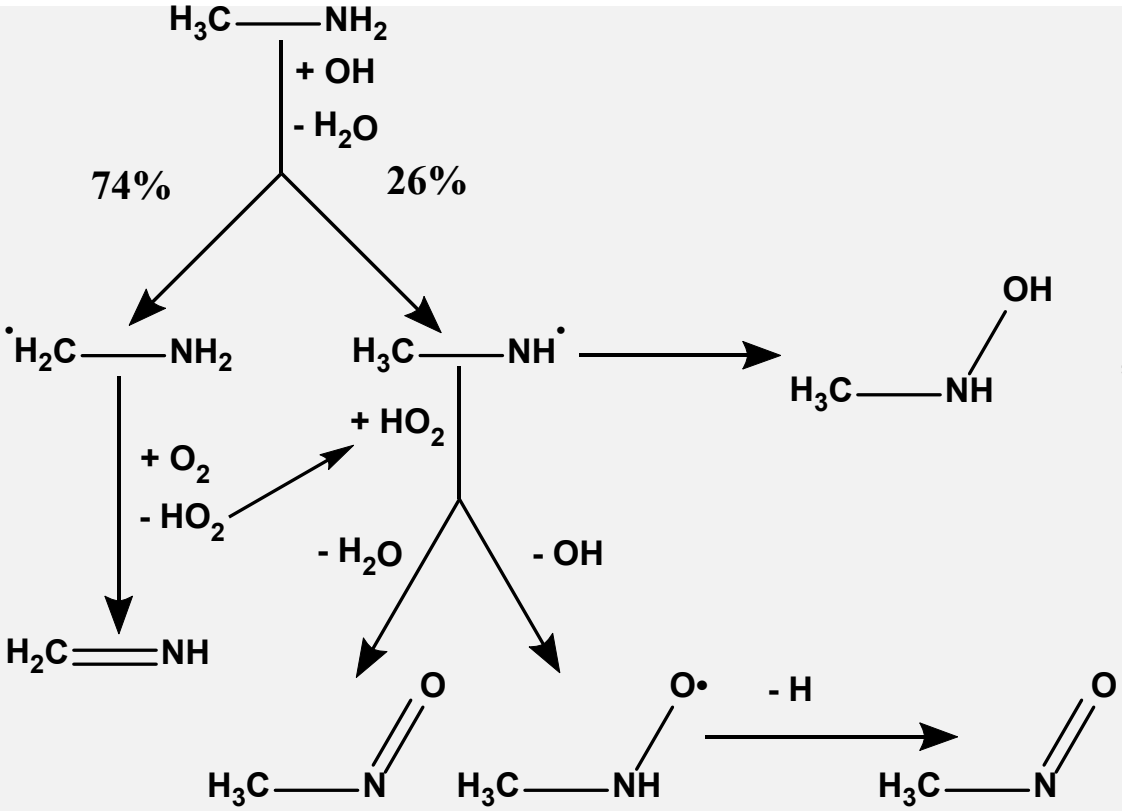


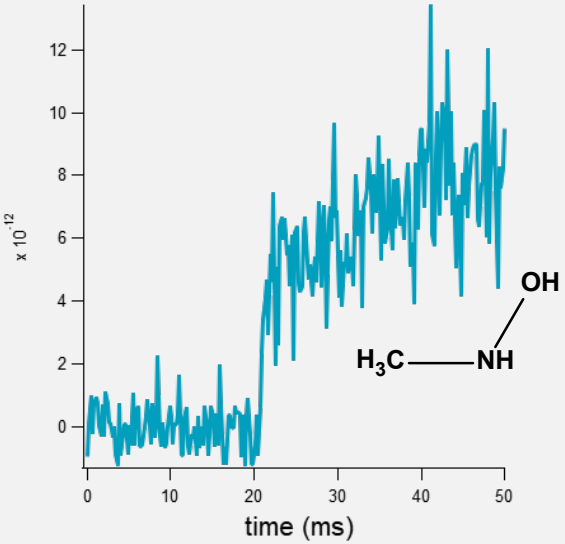

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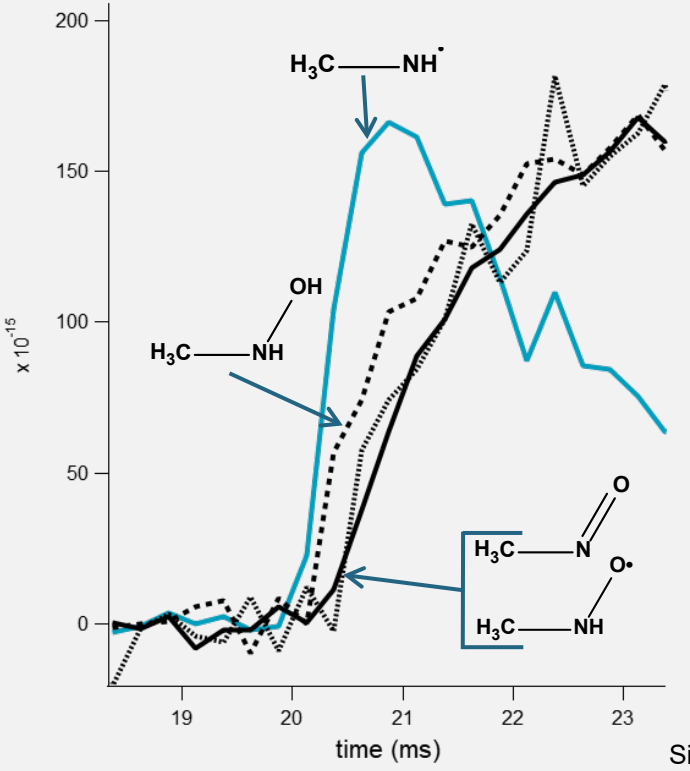
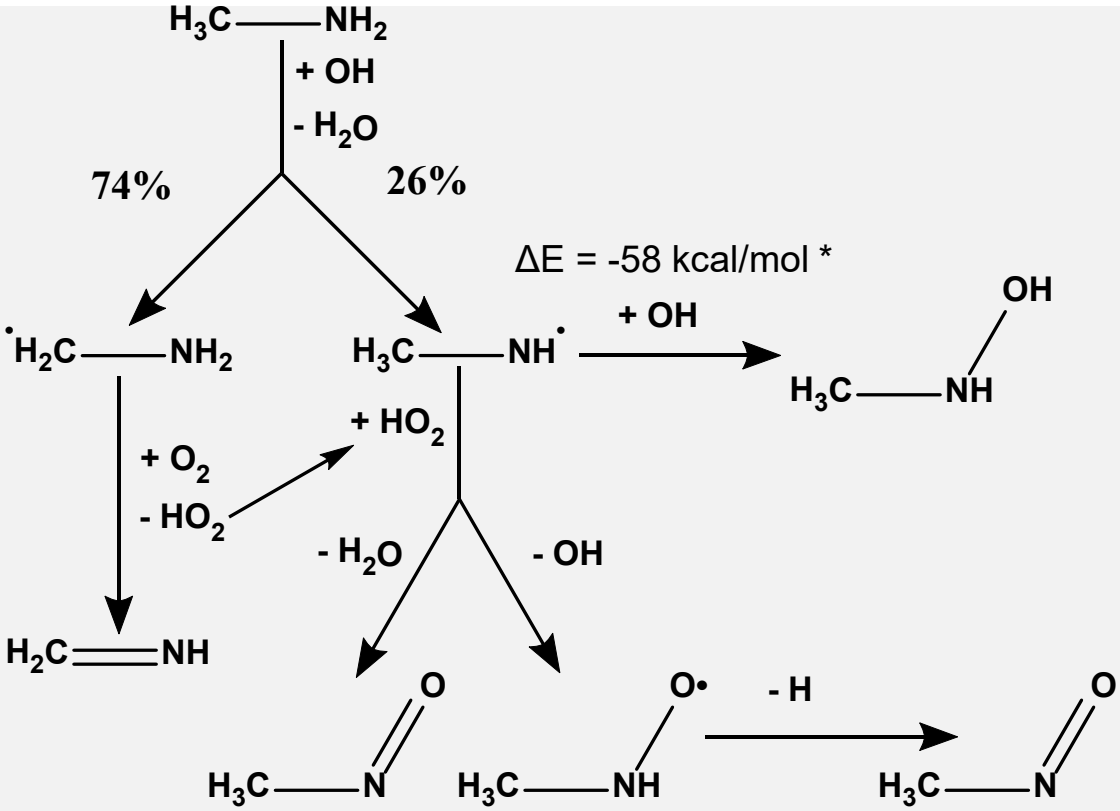
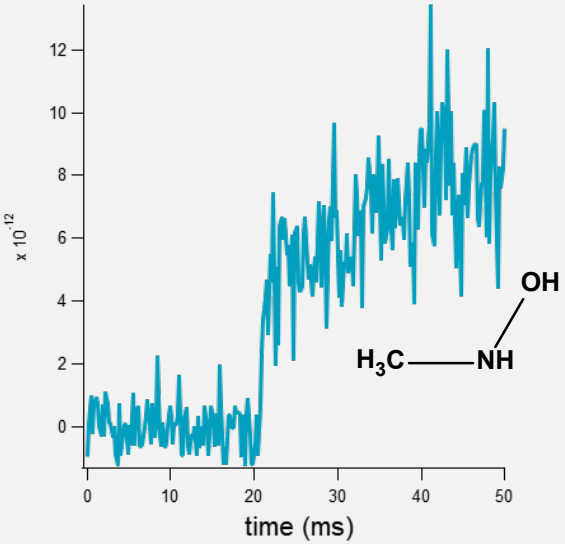



Signals normalized to height of CH3NH for comparison

# Methylamine Oxidation

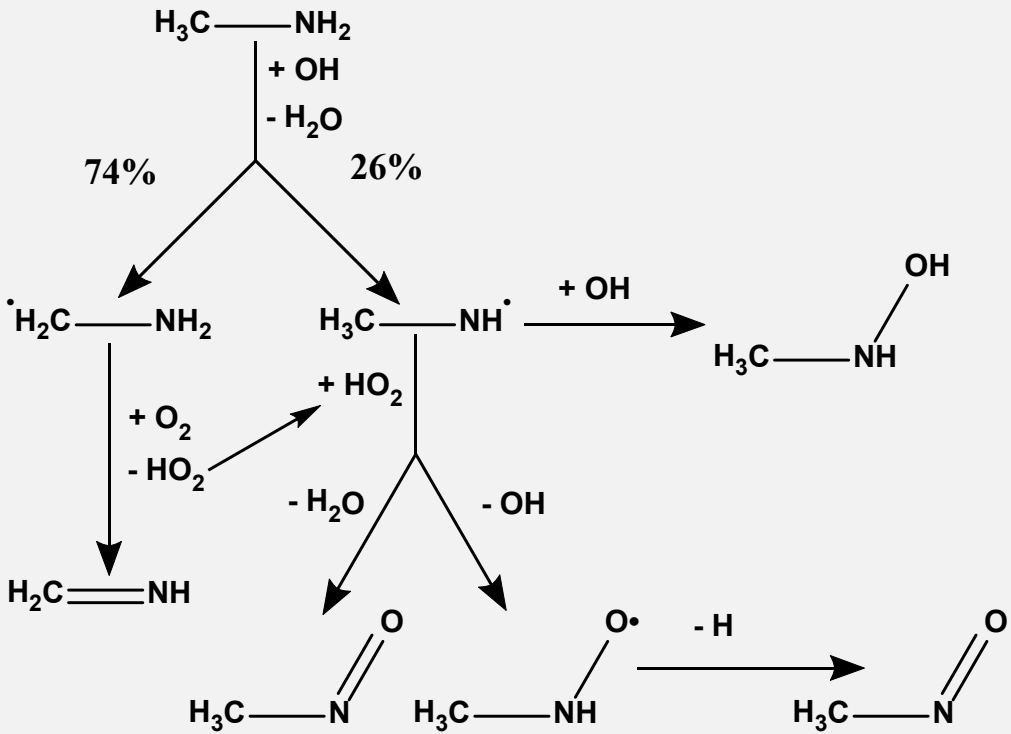



* ωB97X-D/6-311++G**

# Conclusions

- Can detect $CH_3NH$
- Unlikely to see products of $CH_3NH + O_2$
- $CH_3NH$ undergoes rapid reactions, potentially with $HO_2$ and OH

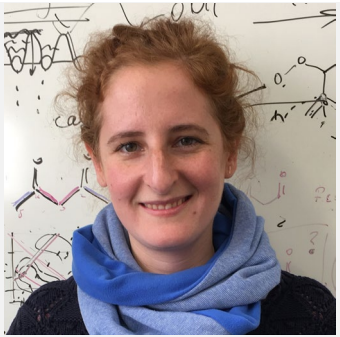


# Current/Future Work

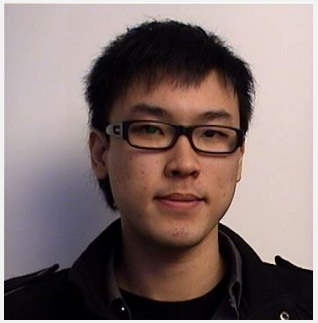
- Building comprehensive chemical kinetics model (Cantera)
- Theory to explore additional reactions of $CH_3NH$
  - Looking for graduate student intern!
- Atmospheric pressure experiments

# Acknowledgements

Lenny Sheps



Judit Zádor



Kendrew Au

Arkke Eskola

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

## Jill Hruby Fellowship

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# Methylamine Oxidation: $CH_3NH + O_2$