SAND2022-11149C

Investigating Amine Oxidation with Computational Chemistry and Photoionization Mass Spectrometry: Insight into the Reactivity of C-centered and N-centered Radicals

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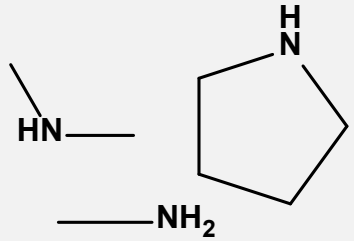
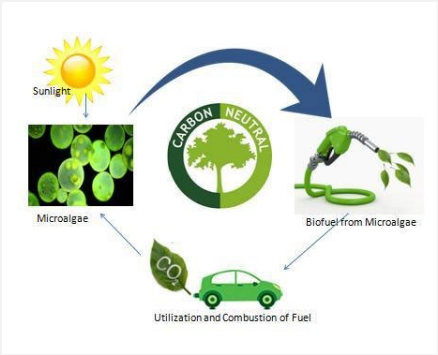
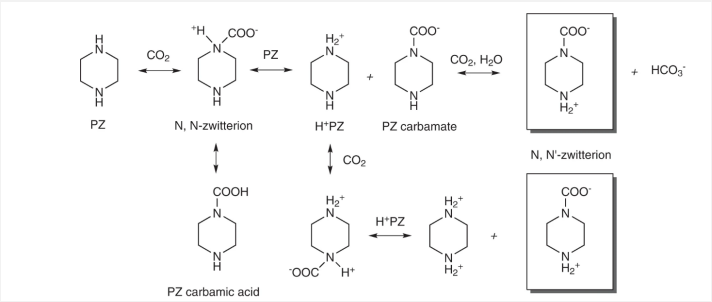
Atmospheric and Combustion Chemistry

Amines are released in combustion of biomass and industrial processes:

- Biofuels
- Wildfires
- Carbon capture agents



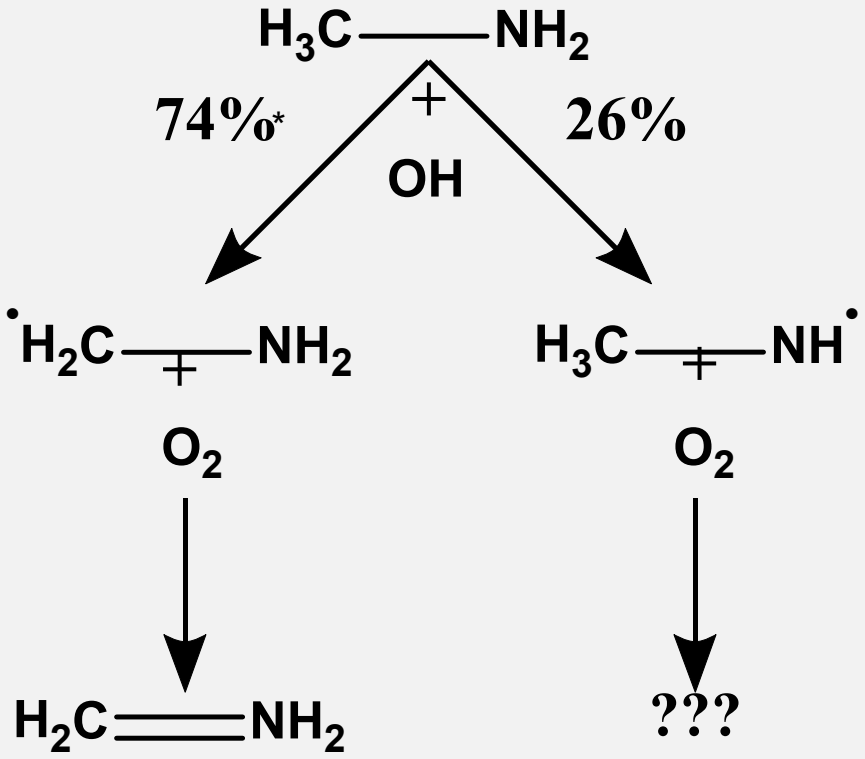




Katiyar, Richa & Kumar, Amit & Gurjar, Bhola. (2017). Microalgae Based Biofuel: Challenges and Opportunities. 10.1007/978-981-10-3791-7_9.
Yamada, H. (2021). Amine-based capture of CO2 for utilization and storage. *Polymer Journal*, *53*(1), 93–102. https://doi.org/10.1038/s41428-020-00400-y

Methylamine Oxidation

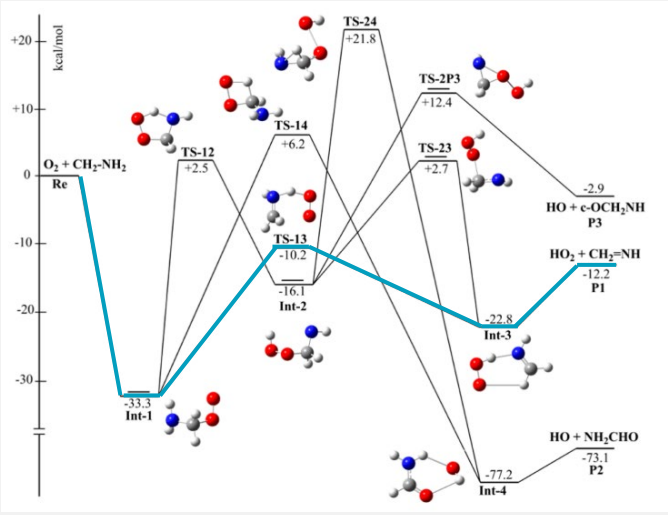
- Methylamine is common degradation product of amines used for CCS
- Byproduct of NH_3/methane combustion
- Limited experimental work on reactions of radicals with O_2



*Butkovskaya, N. I., & Setser, D. W. (2016). Branching Ratios and Vibrational Distributions in Water-Forming Reactions of OH and OD Radicals with Methylamines. *Journal of Physical Chemistry A*, *120*(34), 6698–6711.
* Onel, L., Blitz, M., Dryden, M., Thonger, L., & Seakins, P. (2014). Branching ratios in reactions of oh radicals with methylamine, dimethylamine, and ethylamine. *Environmental Science and Technology*, *48*(16), 9935–9942.

Methylamine Oxidation

- Previous work has produced rate constant for $CH_2NH_2 + O_2$
- CH_2NH_2 produced in $NH_2CH_2CH_2NH_2$ photolysis



THE JOURNAL OF PHYSICAL CHEMISTRY A
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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*[,†]

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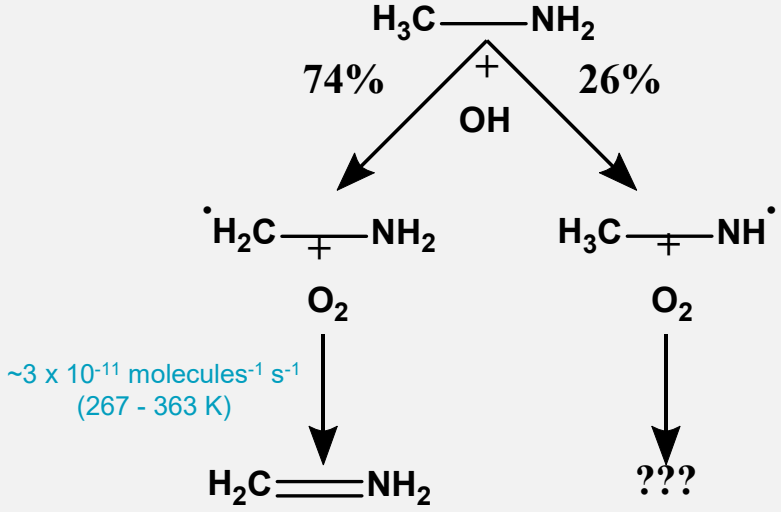
[⊥]Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun 130023, China

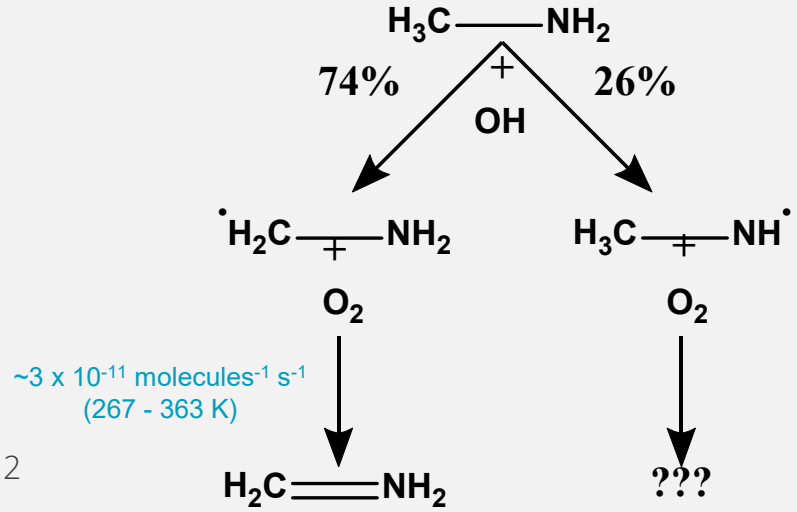


Rissanen, M. P., Eskola, A. J., Nguyen, T. L., Barker, J. R., Liu, J., Liu, J., Halme, E., & Timonen, R. S. (2014). CH 2 NH 2 + O 2 and CH 3 CHNH 2 + O 2 Reaction Kinetics: Photoionization Mass Spectrometry Experiments and Master Equation Calculations. *The Journal of Physical Chemistry A*, *118*(12),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

Methylamine Oxidation

Objectives:

- Remeasure k for $CH_2NH_2 + O_2$
- Determine products of $CH_3NH + O_2$
- Measure k for $CH_3NH + O_2$
  - First experimental study of $CH_3NH + O_2$



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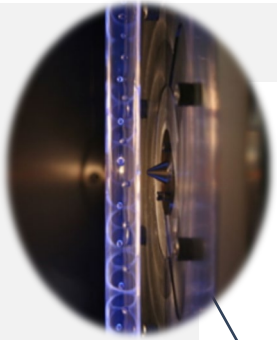
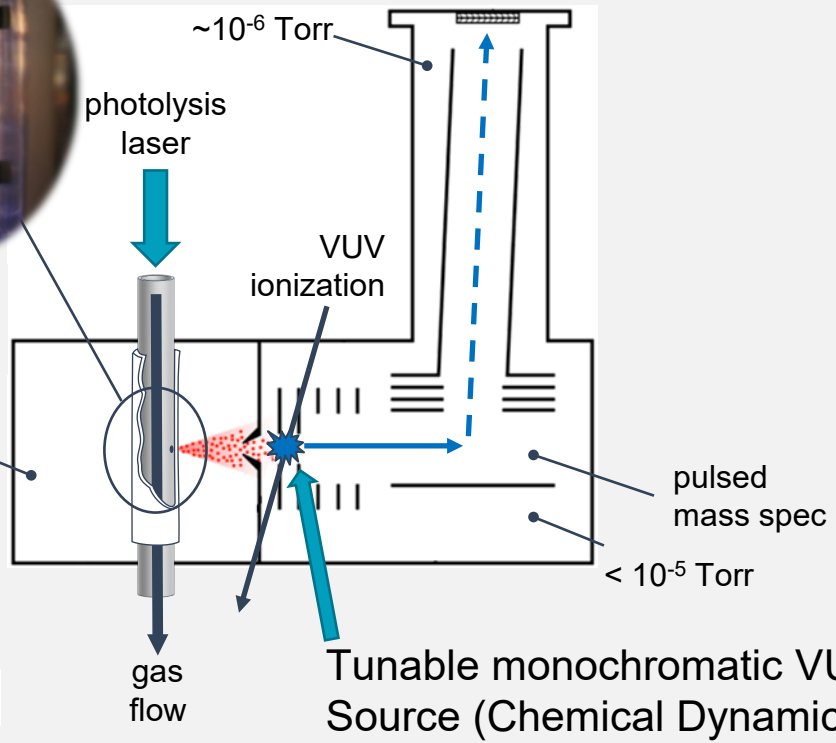
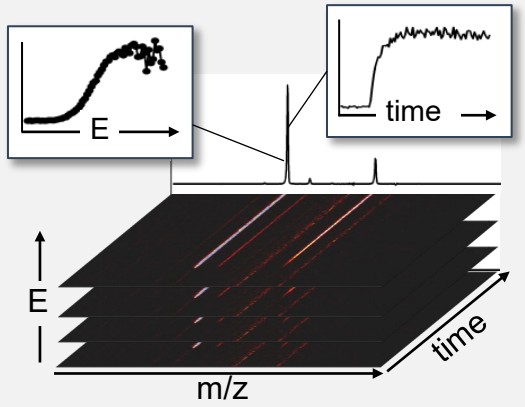
Methodology: Multiplexed VUV Photoionization Mass Spectrometer



1 – 50 Torr
300 – 1000 K



time- and E-resolved mass spectrum

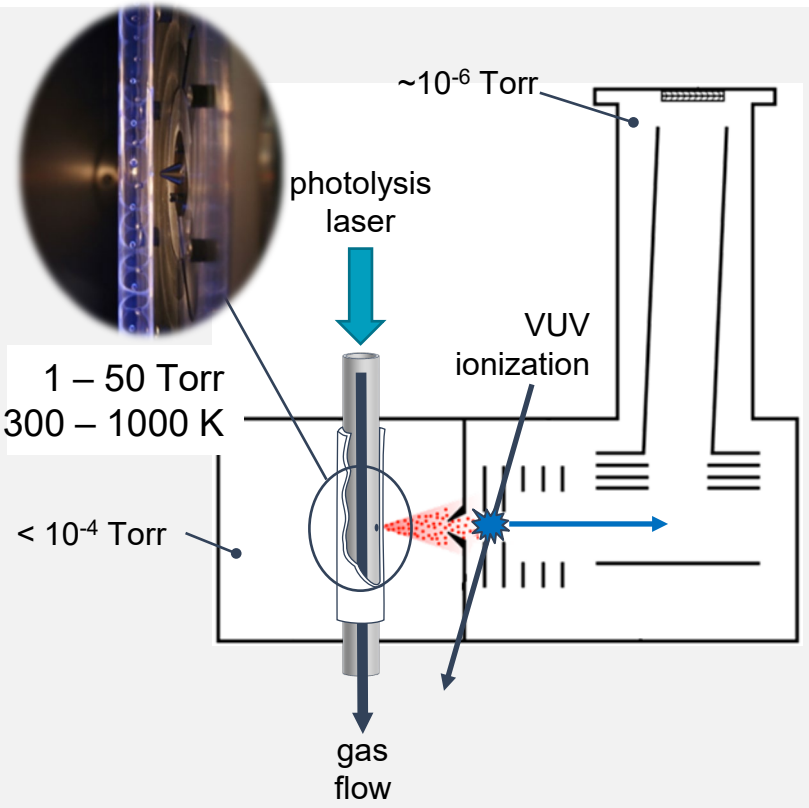


Tunable monochromatic VUV radiation at the Advanced Light Source (Chemical Dynamics Beamline)

Methodology: Multiplexed VUV Photoionization Mass Spectrometer

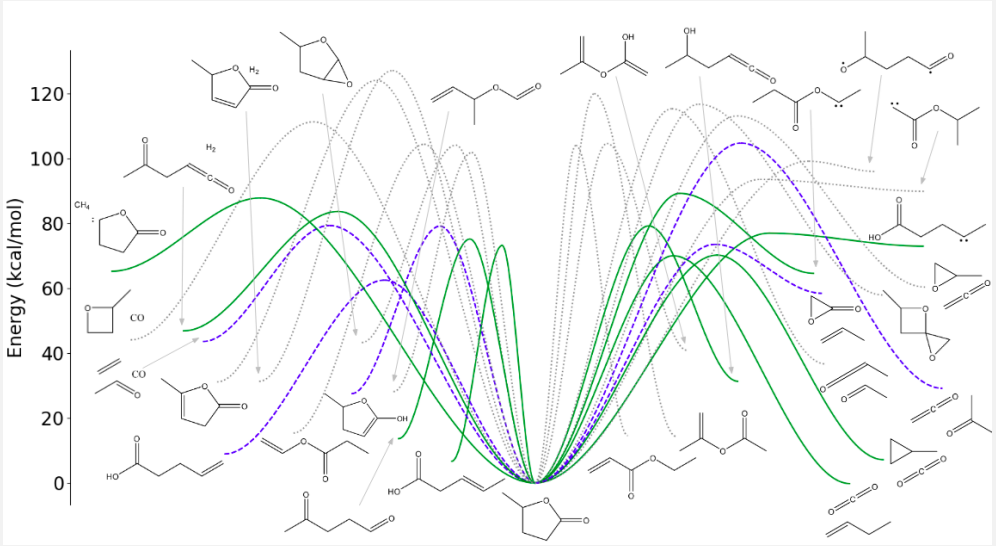
- 300 K, 4 Torr
- Methylamine + H_2O_2 + O_2
- d3-Methylamine + H_2O_2 + O_2

$$HOOH + h\nu \longrightarrow 2 \cdot OH$$



Methodology: KinBot

Automatically searches for reaction paths starting from a parent compound, continuing over multiple wells.



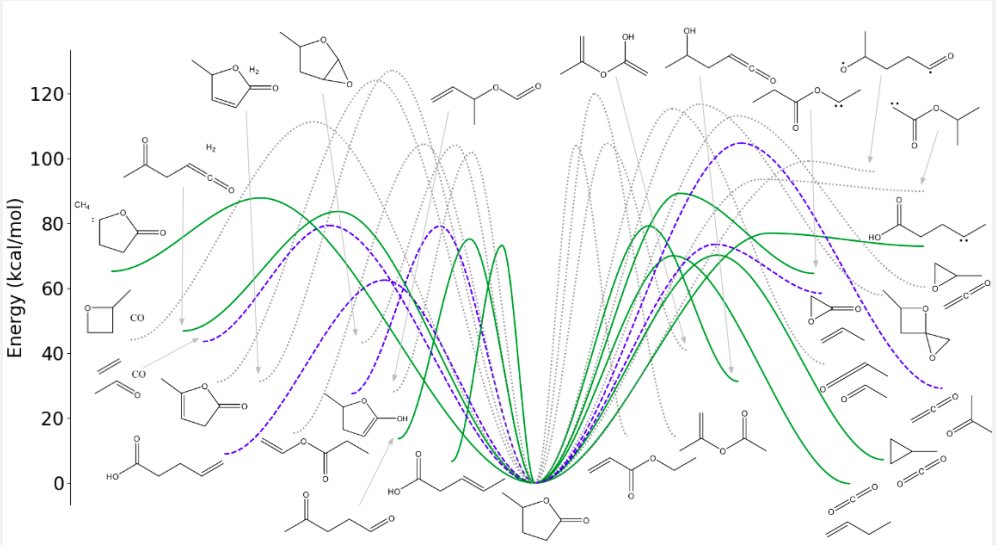
https://github.com/zadorlab/KinBot/

Van de Vijver R, Zádor J. KinBot: Automated stationary point search on potential energy surfaces. *Comput Phys Commun*. 2020;248:106947. doi:10.1016/j.cpc.2019.106947

Methodology: KinBot

Automatically searches for reaction paths starting from a parent compound, continuing over multiple wells.

Reaction templates are used to find transitions states, intermediates, and products.



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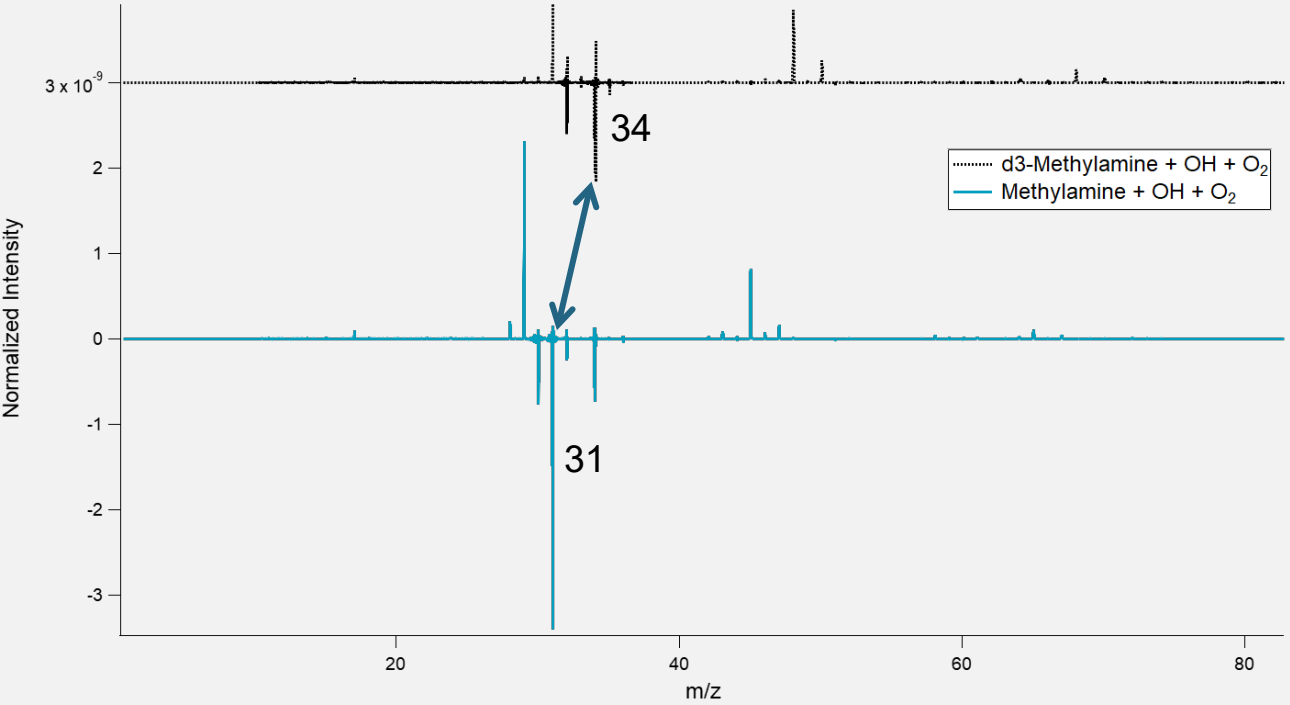
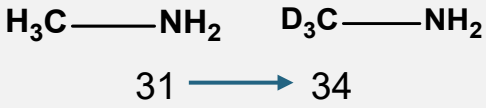
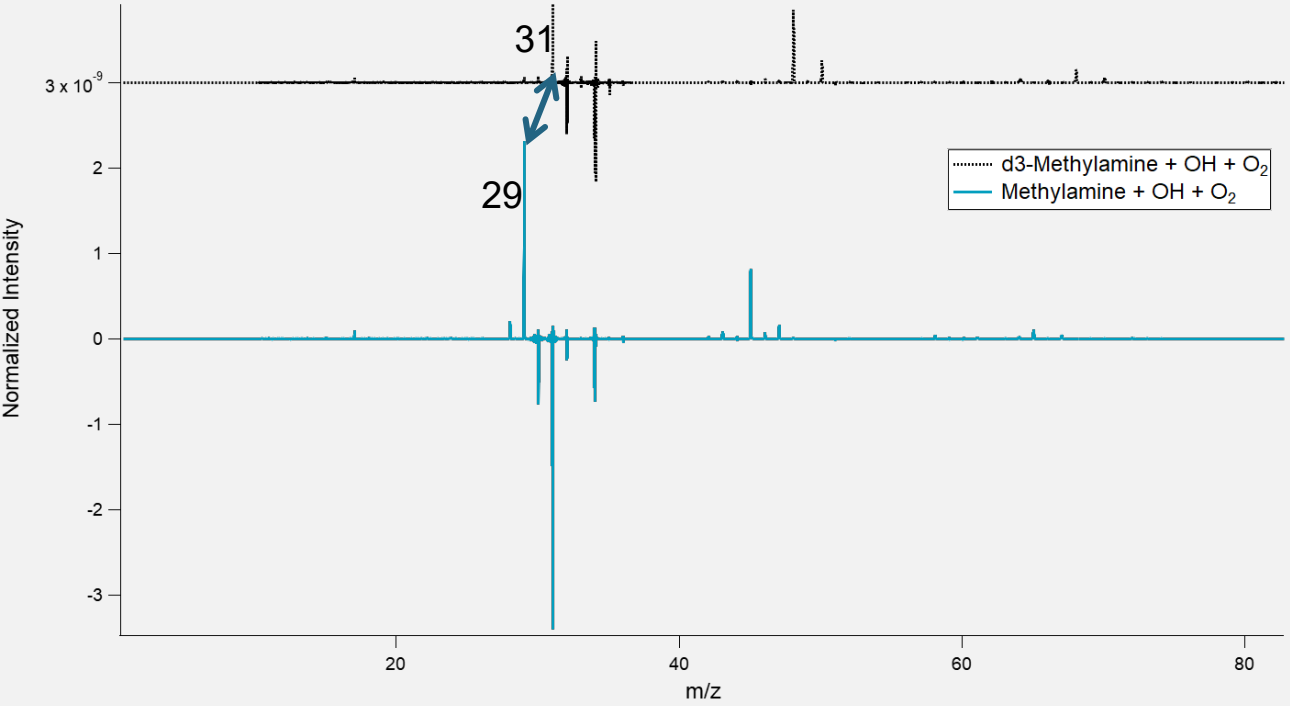
Methylamine Oxidation

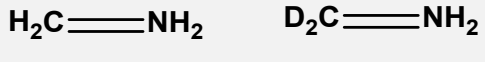




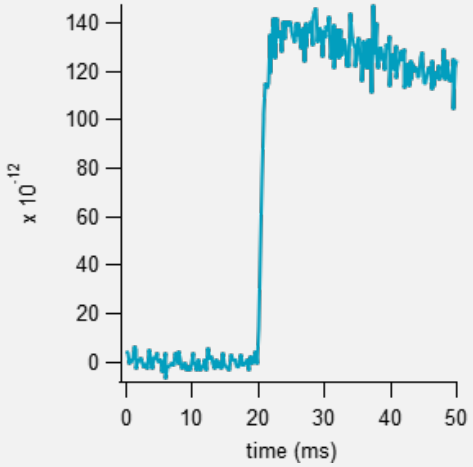
Methylamine Oxidation: $CH_2NH_2 + O_2$



Too short-lived to see

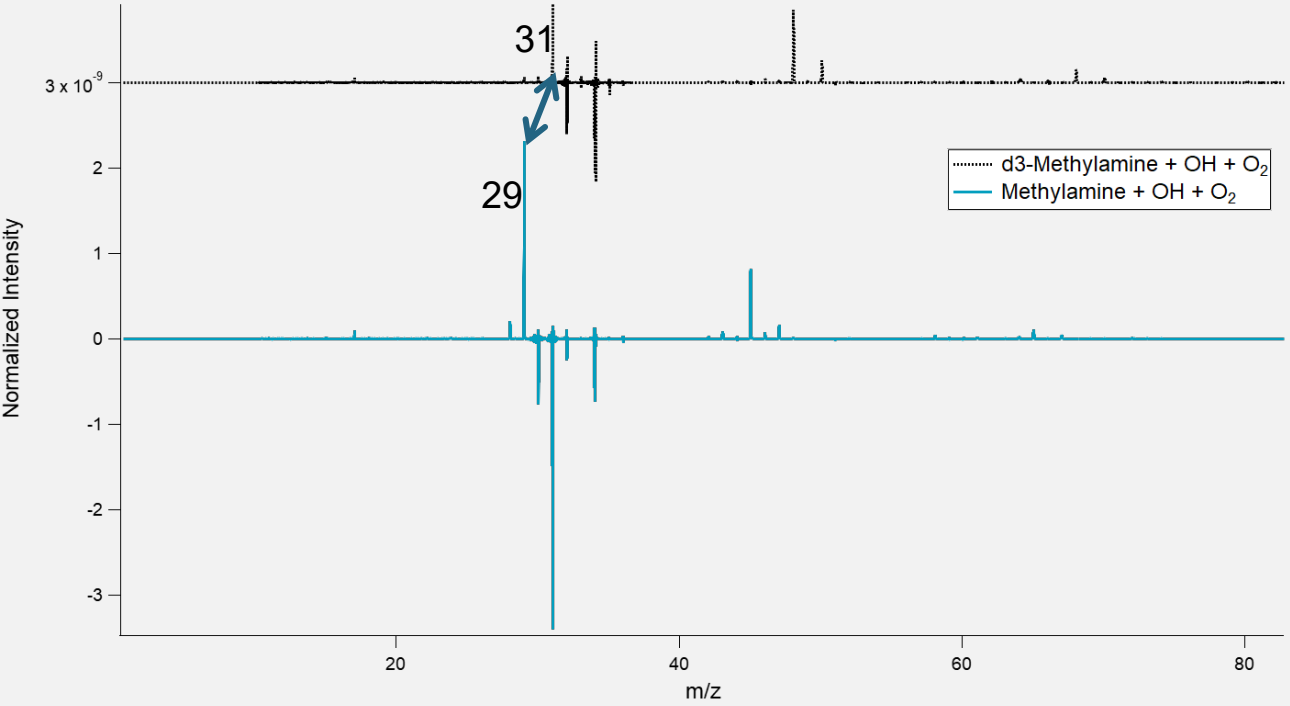


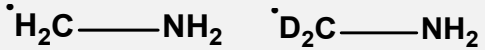
29 → 31



*Holzmeier, F., Lang, M., Hader, K., Hemberger, P., & Fischer, I. (2013). H 2 CN + and H 2 CNH + : New insight into the structure and dynamics from mass-selected threshold photoelectron spectra. *The Journal of Chemical Physics*, *138*(21), 214310. https://doi.org/10.1063/1.4808050

Methylamine Oxidation: $CH_2NH_2 + O_2$





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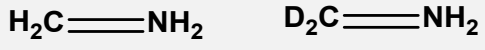

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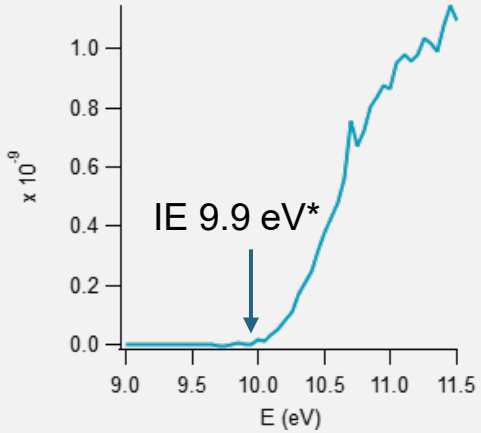

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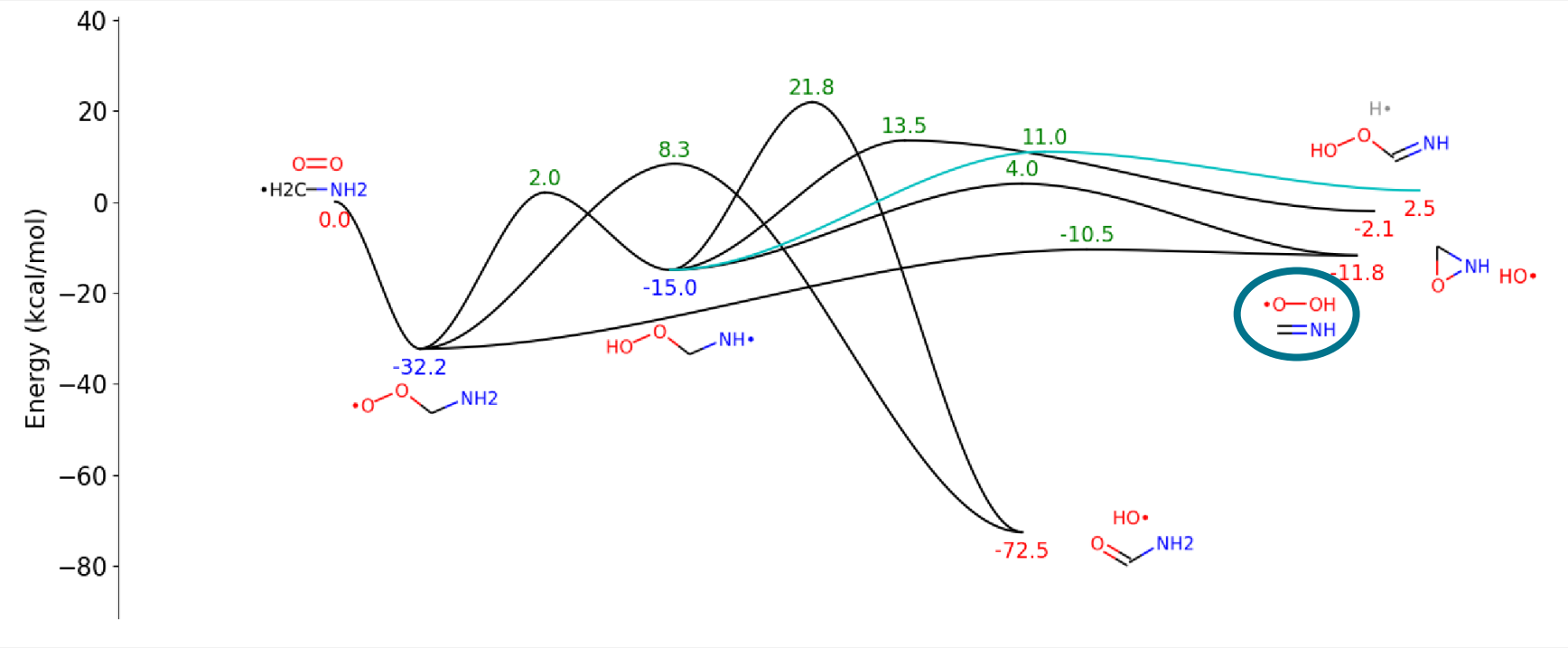
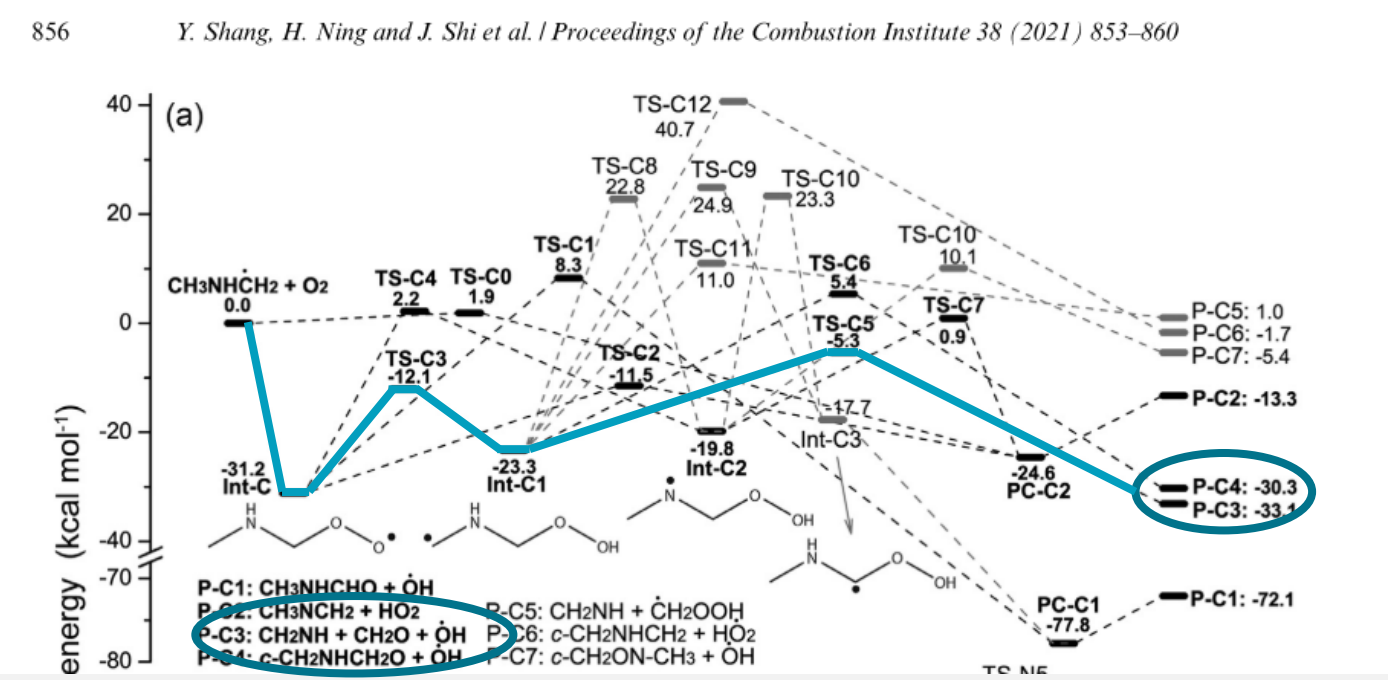
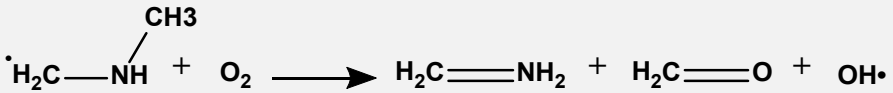
Methylamine Oxidation: CH2NH2 + O2



CCSD(T)-F12/cc-pVDZ-f12a// wB97X-D/6-311++G**

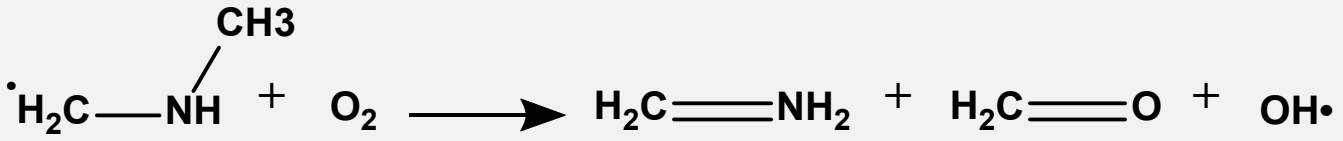
Methylamine Oxidation: CH2NH XS from DMA





Shang, Y., Ning, H., Shi, J., & Luo, S.-N. (2021). Insight into the low-temperature oxidation of dimethylamine radicals. *Proceedings of the Combustion Institute*, *38*(1), 853–860. https://doi.org/10.1016/j.proci.2020.06.286

Methylamine Oxidation: CH2NH XS from DMA



- CH_2NH is produced in 1:1 ratio with CH_2O
- CH_2O has known photoionization cross section

$$S_M \frac{\sigma_F}{S_F} = \sigma_M$$

Shang, Y., Ning, H., Shi, J., & Luo, S.-N. (2021). Insight into the low-temperature oxidation of dimethylamine radicals. *Proceedings of the Combustion Institute*, *38*(1), 853–860. https://doi.org/10.1016/j.proci.2020.06.286

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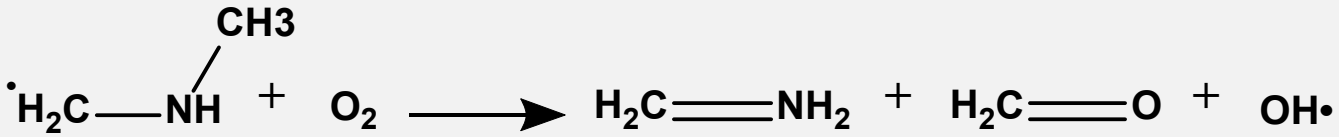
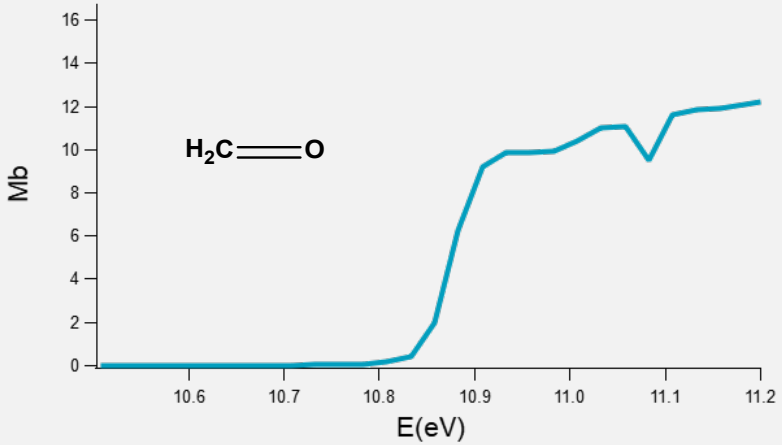
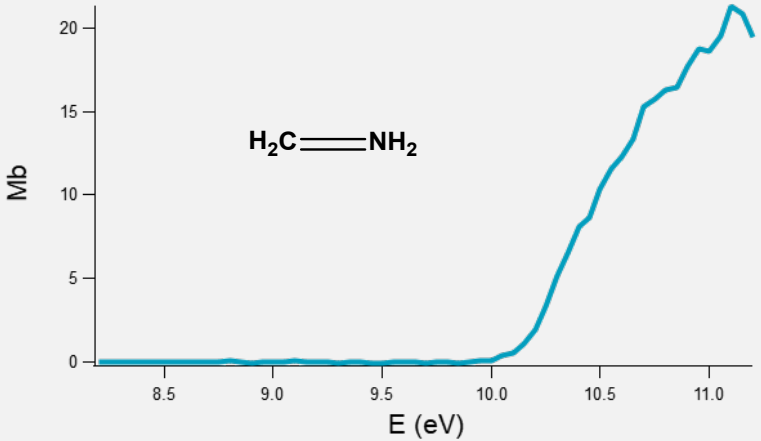


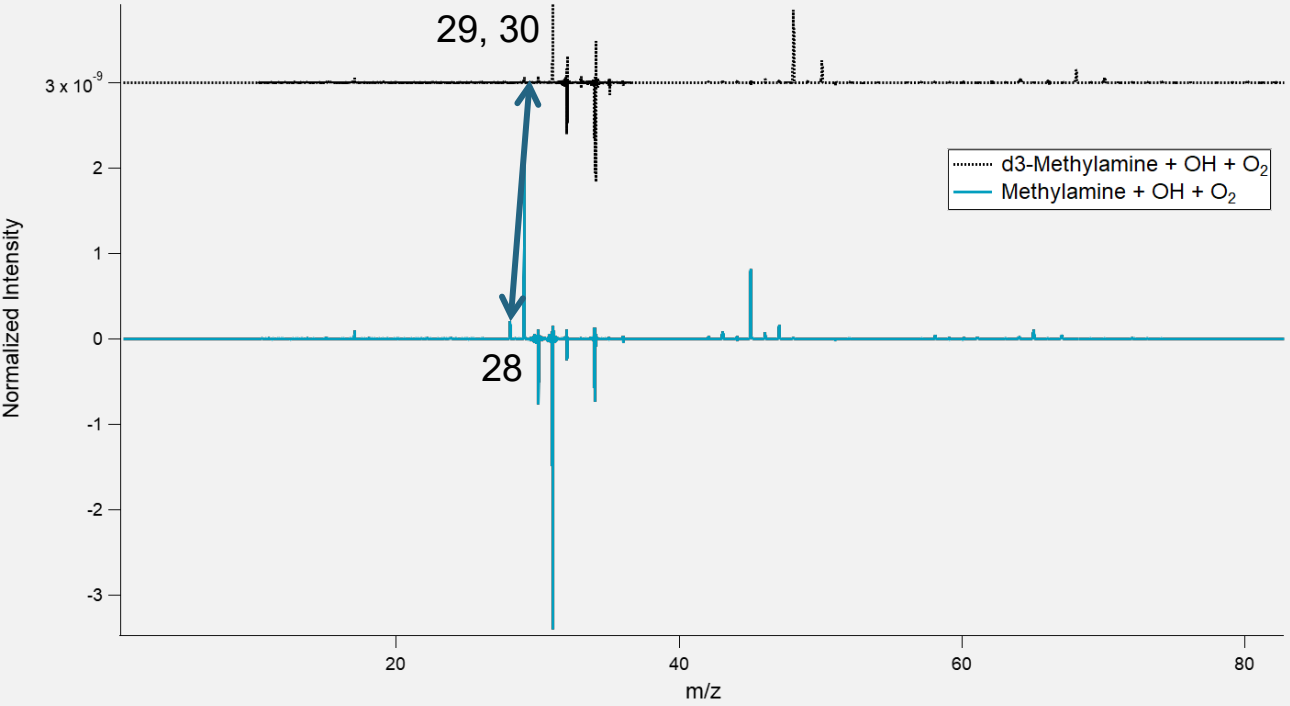


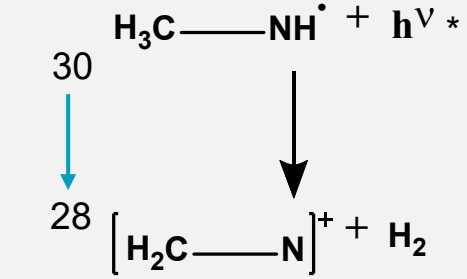


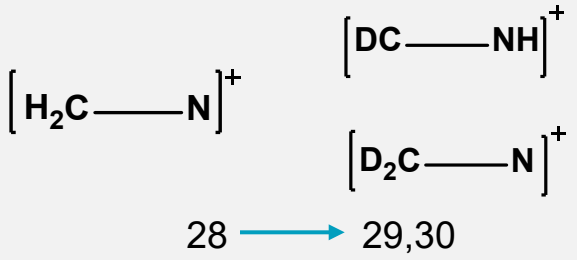
$$S_M \frac{\sigma_F}{S_F} = \sigma_M$$

Dodson, L. G., Shen, L., Savee, J. D., Eddingsaas, N. C., Welz, O., Taatjes, C. A., Osborn, D. L., Sander, S. P., & Okumura, M. (2015). VUV Photoionization Cross Sections of HO 2 , H 2 O 2 , and H 2 CO. *The Journal of Physical Chemistry A*, *119*(8), 1279–1291. https://doi.org/10.1021/jp508942a

Methylamine Oxidation: $CH_3NH + O_2$







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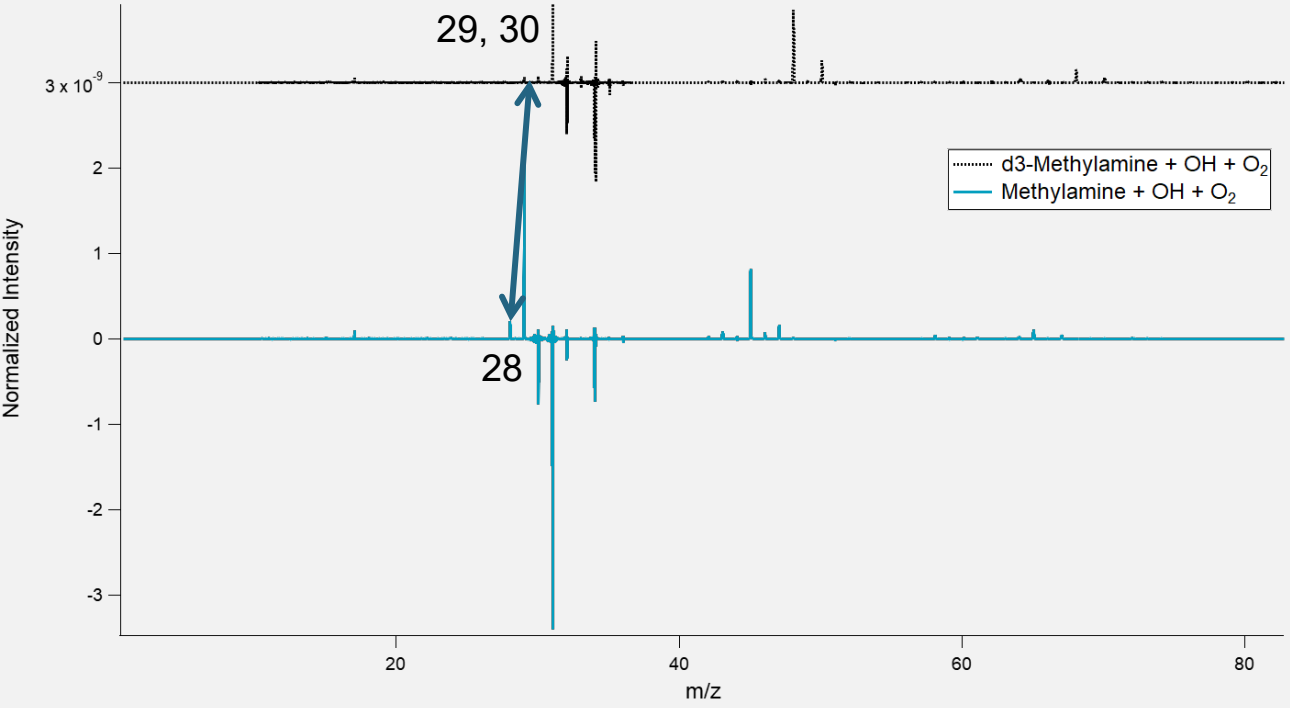
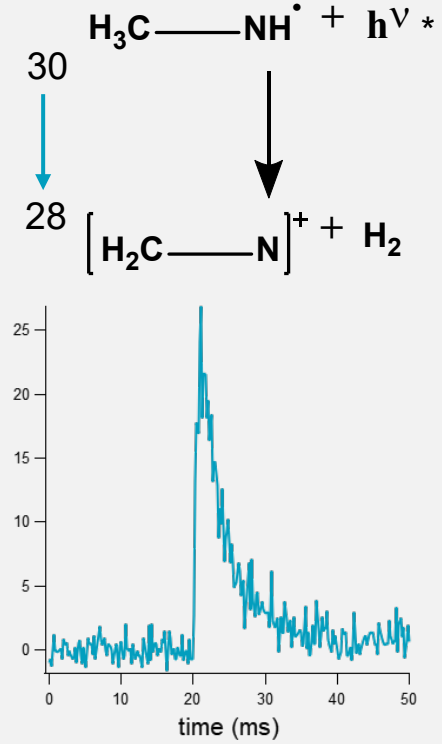
Methylamine Oxidation: $CH_3NH + O_2$





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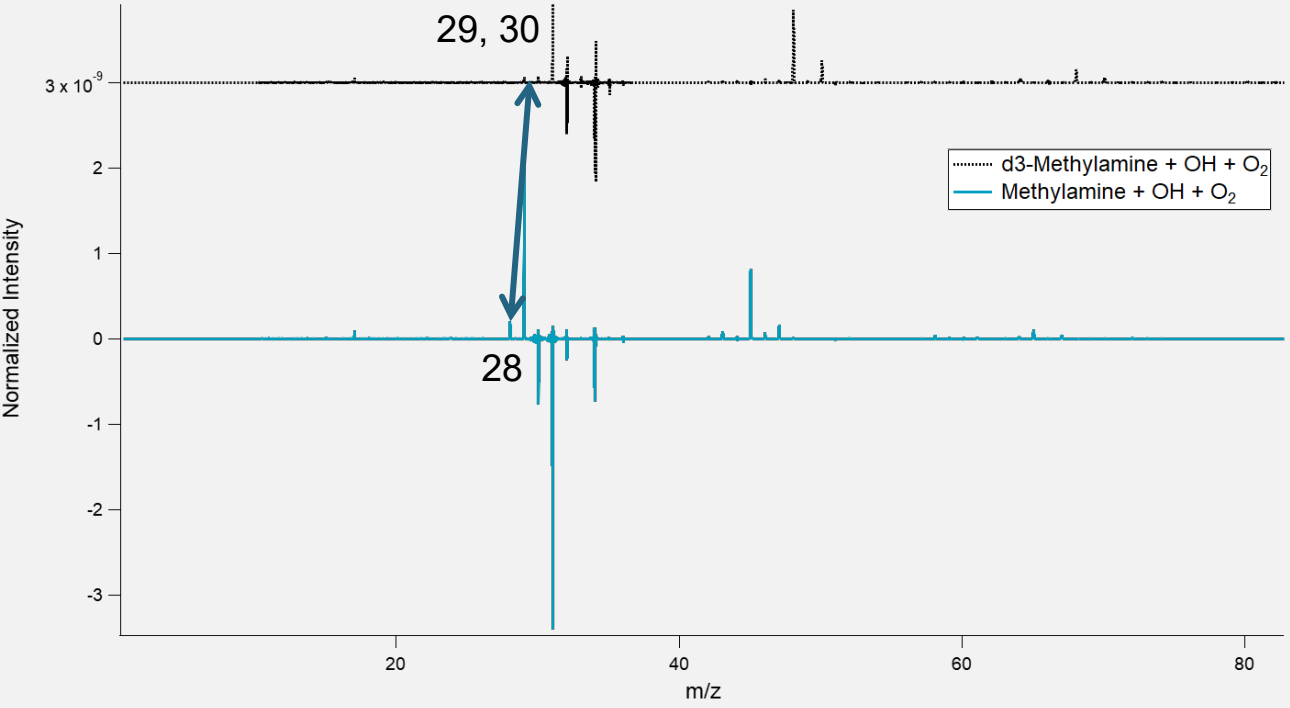
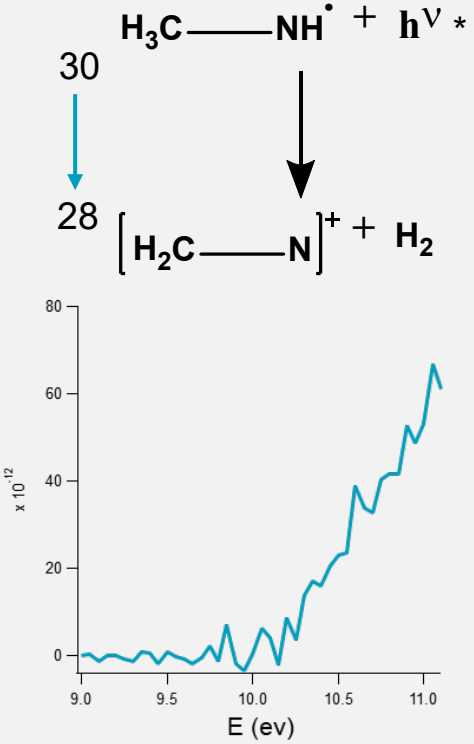
Methylamine Oxidation: $CH_3NH + O_2$





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Methylamine Oxidation: $CH_3NH + O_2$

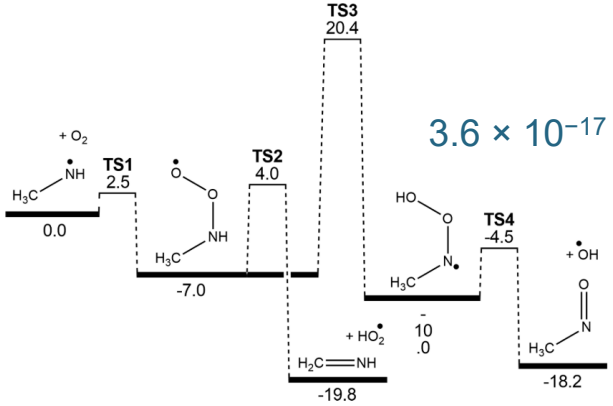
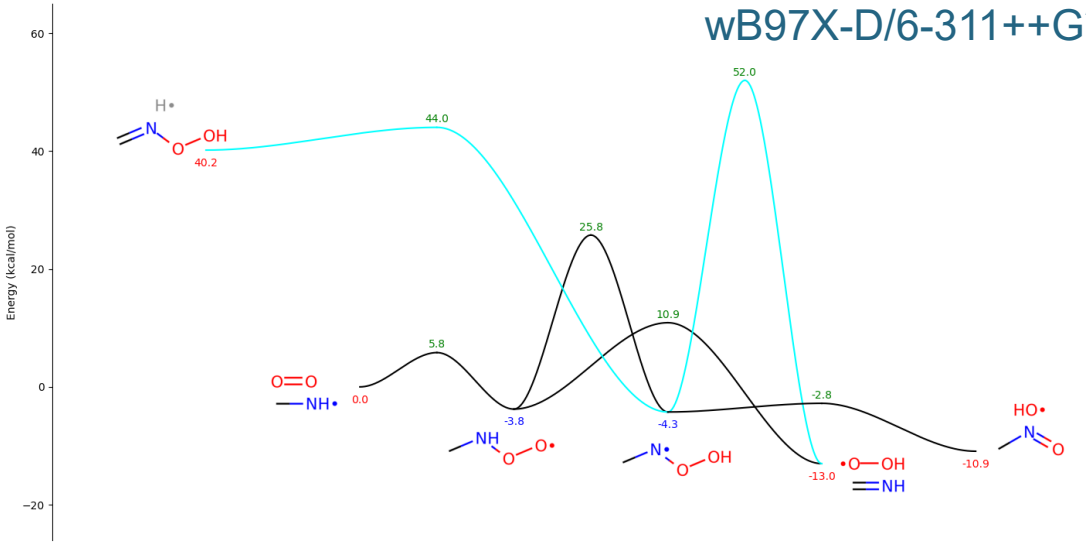


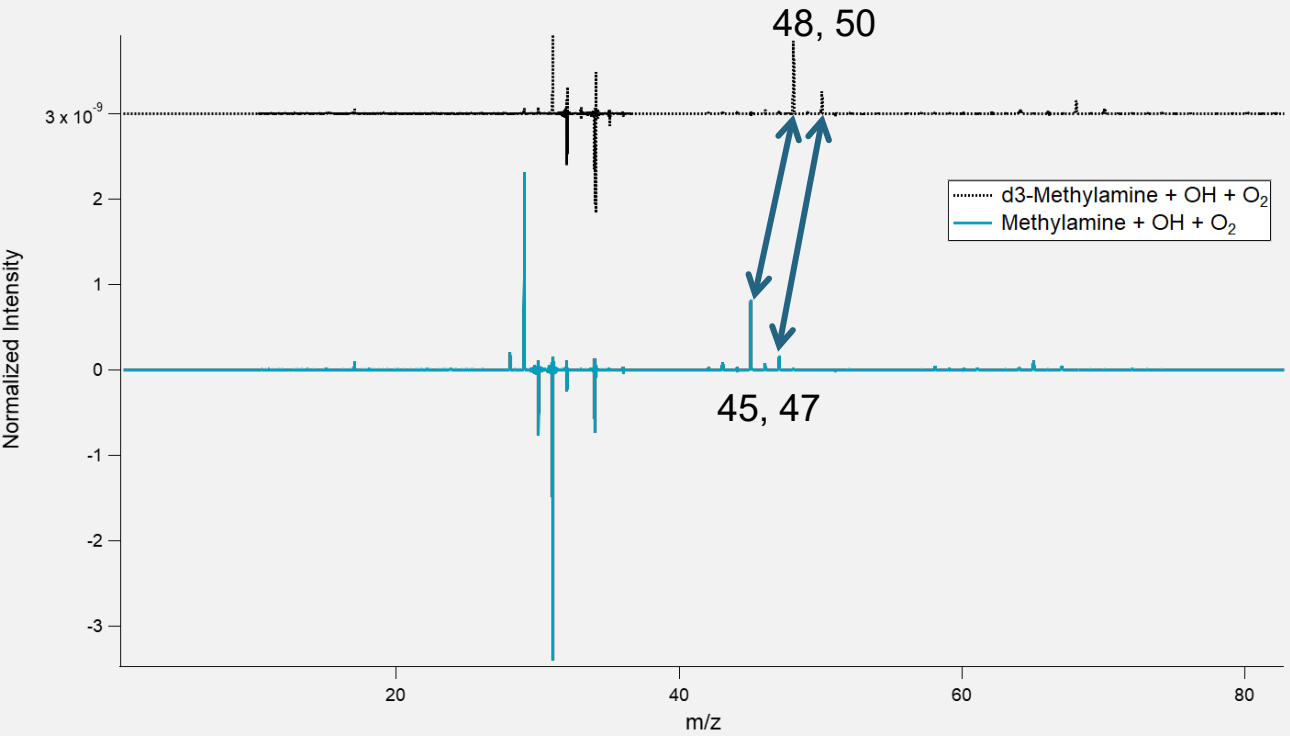
FIGURE 1 Potential energy surface for the $CH_3N^{\bullet}H + O_2$ reaction. Energies are 0 K enthalpies in kcal mol^{-1}, at the G3X-K level of theory

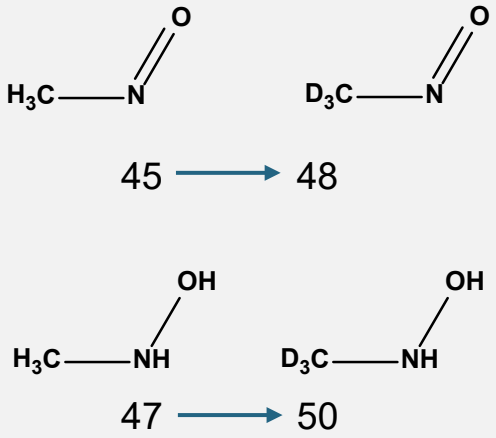
3.6×10^{-17} cm^3 $molecule^{-1}$ s^{-1}



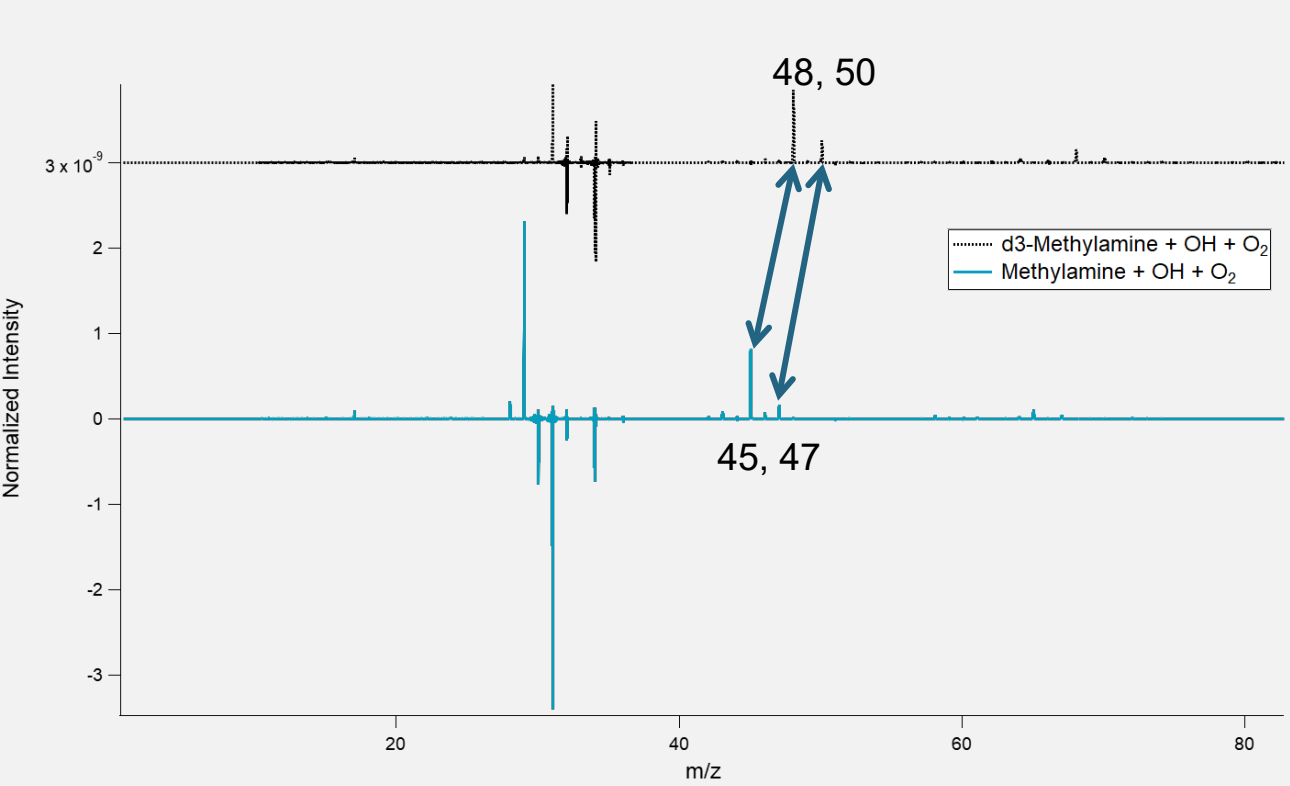
Alam, M. A., Ren, Z., & da Silva, G. (2019). Nitramine and nitrosamine formation is a minor pathway in the atmospheric oxidation of methylamine: A theoretical kinetic study of the CH 3 NH + O 2 reaction. *International Journal of Chemical Kinetics*, *51*(9), 723–728. https://doi.org/10.1002/kin.21303

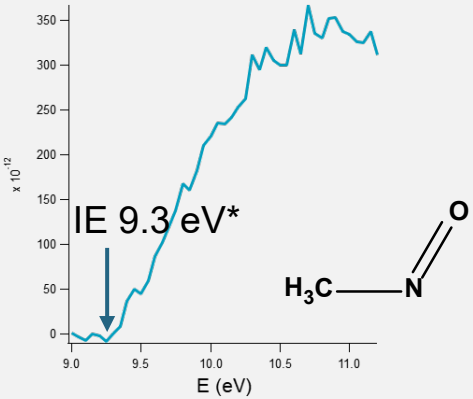
Methylamine Oxidation: $CH_3NH + O_2$

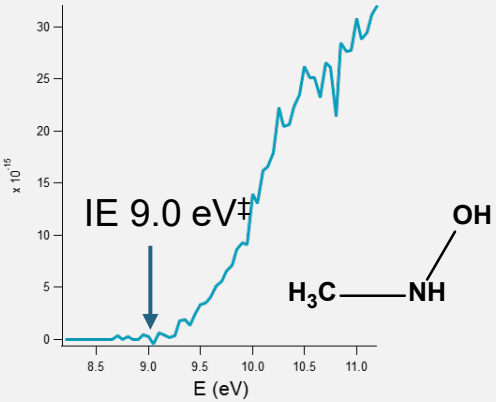




Methylamine Oxidation: $CH_3NH + O_2$







*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.

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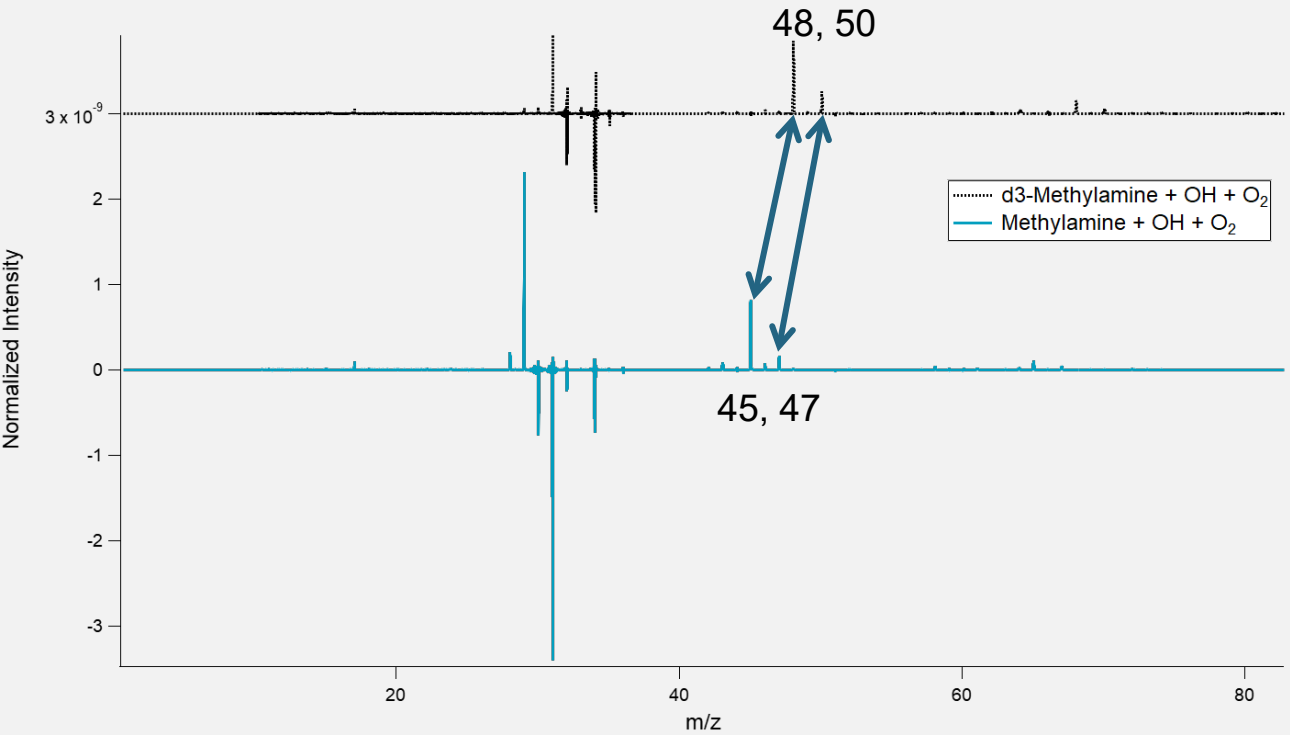
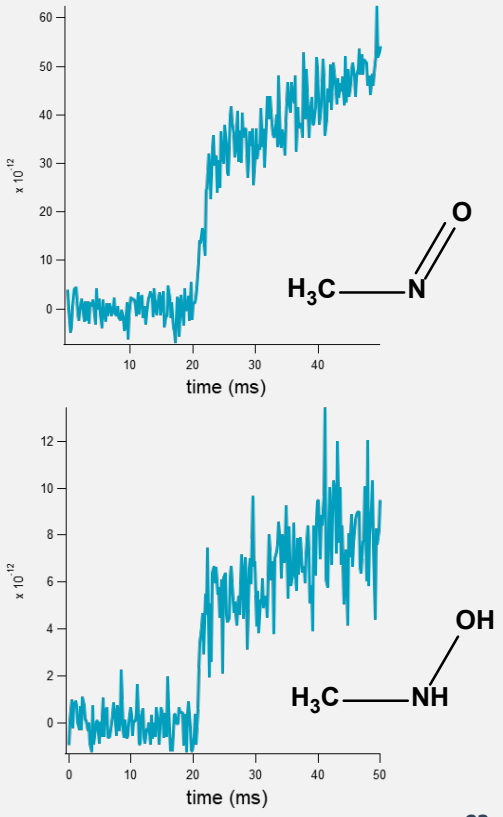
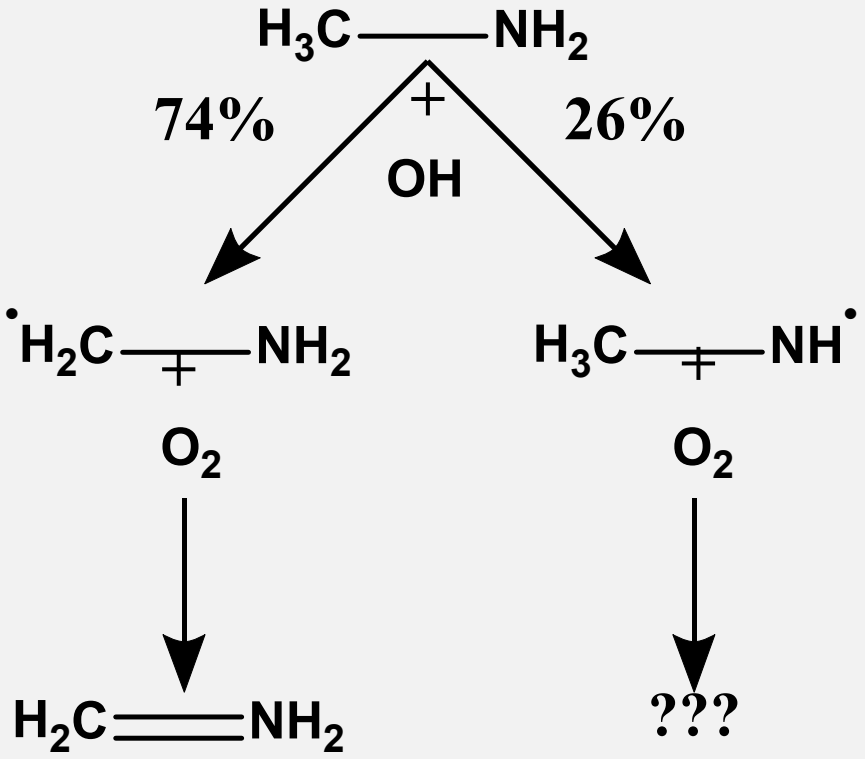




[OH] variation shows these species have faster rise time than methanimine, suggesting bimolecular pathways

Conclusions

- $CH_2NH_2 + O_2$ rapidly forms CH_2NH
- Measured CH_2NH photoionization cross section
- First experimental detection of CH_3NH
- CH_3NH undergoes bimolecular reactions



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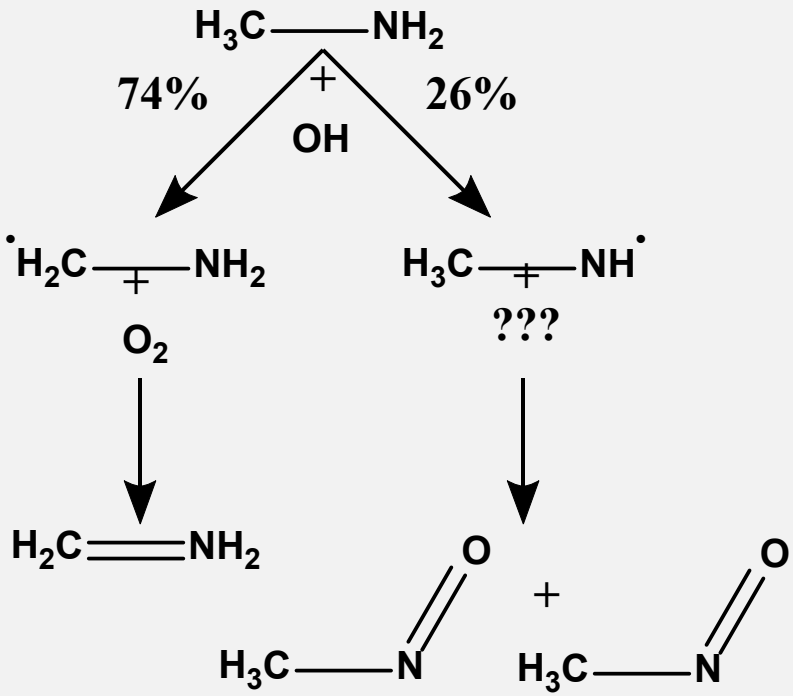
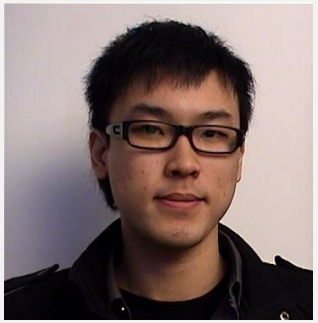


Future Work

- Theory – what is CH3NH reacting with?
- High pressure experiments
- Temperature scans
- Cl initiated chemistry, change CH_2NH_2:CH_3NH ratio

Acknowledgements

Lenny Sheps



Kendrew Au

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Jill Hruby Fellowship

This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

This research used resources of the Advanced Light Source, a U.S. DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.

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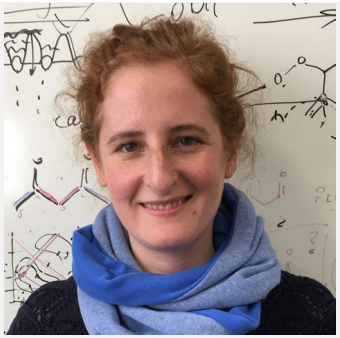
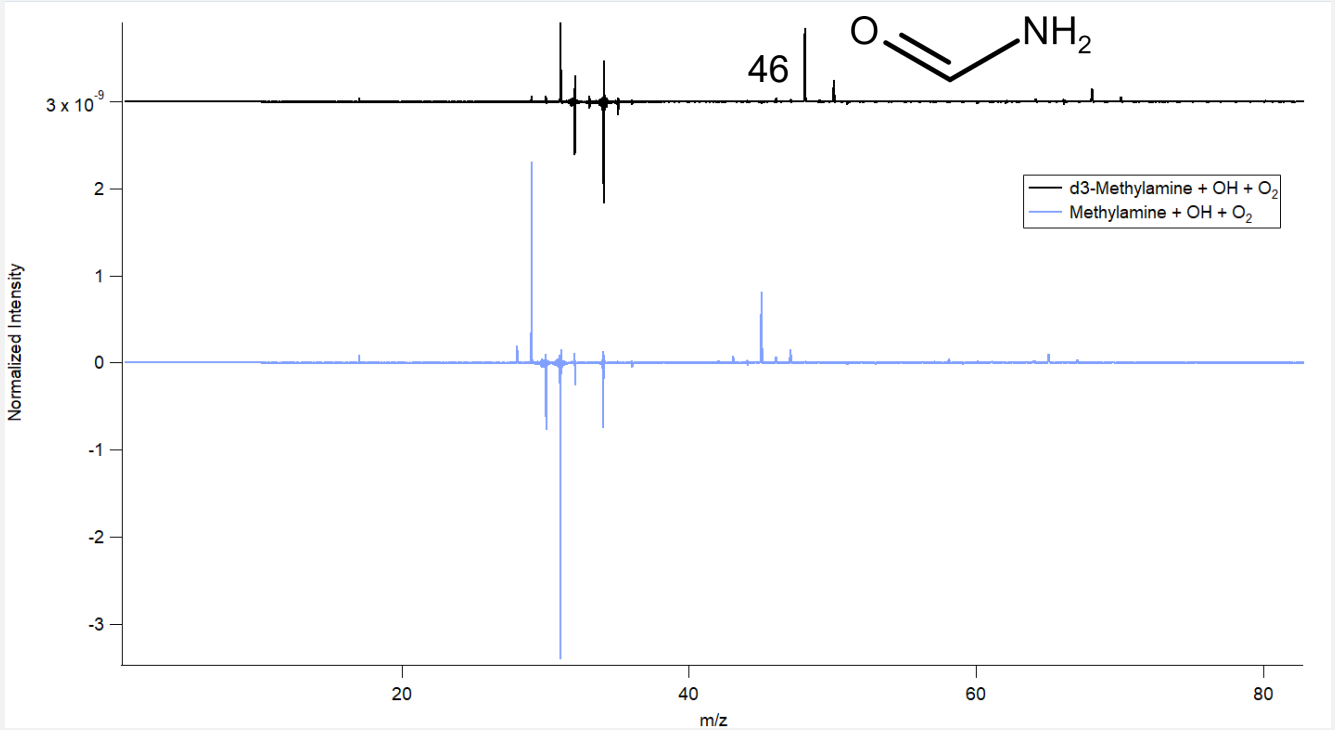


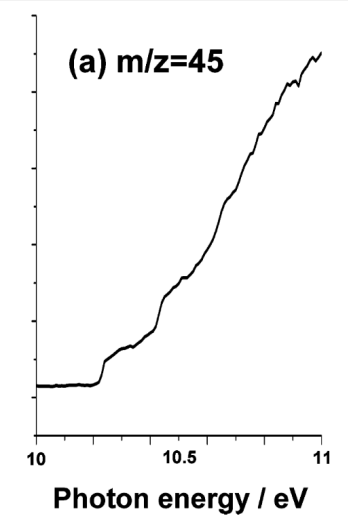
Judit Zádor

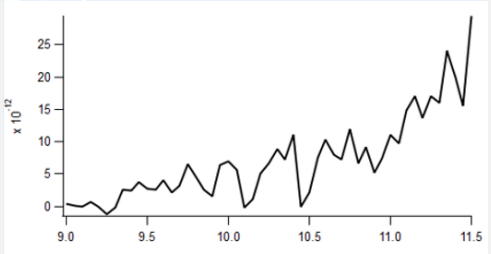
Arkke Eskola

Bonus Material

Methylamine Oxidation: CH2NH2 + O2

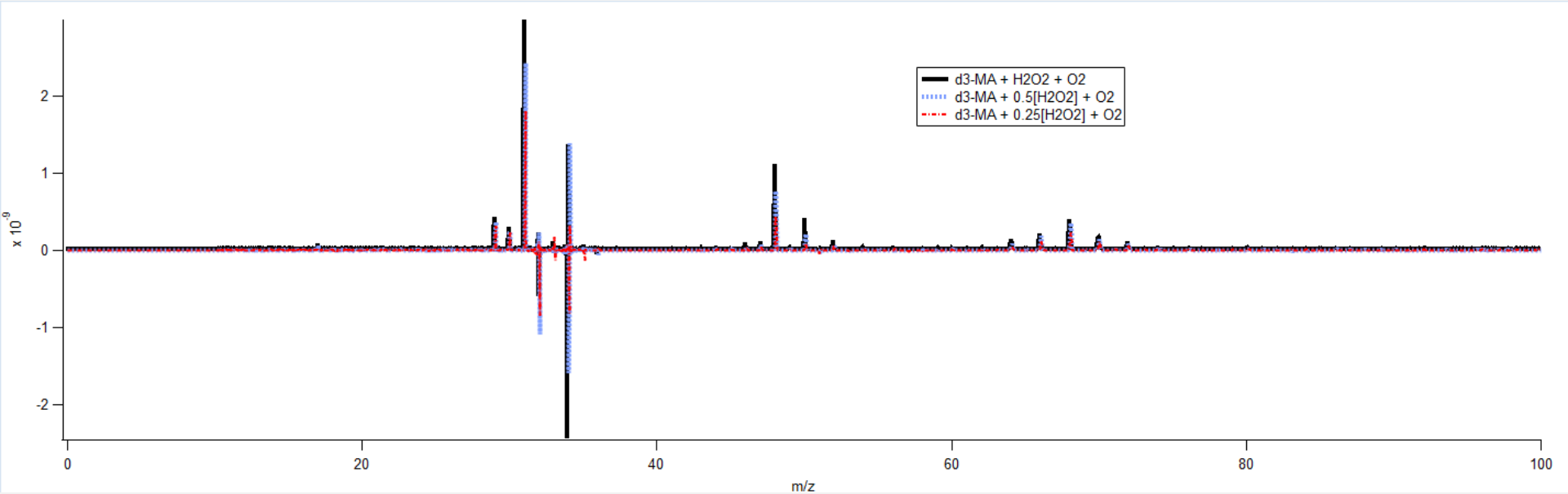




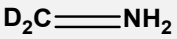


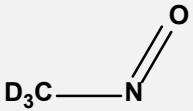
Leach, S., Jochims, H.-W., & Baumgärtel, H. (2010). Photoionization Mass Spectrometric Study of the Prebiotic Species Formamide in the 10−20 eV Photon Energy Range. *The Journal of Physical Chemistry A*, *114*(14), 4847–4856. https://doi.org/10.1021/jp9098182

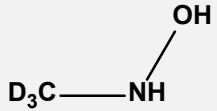
Methylamine Oxidation

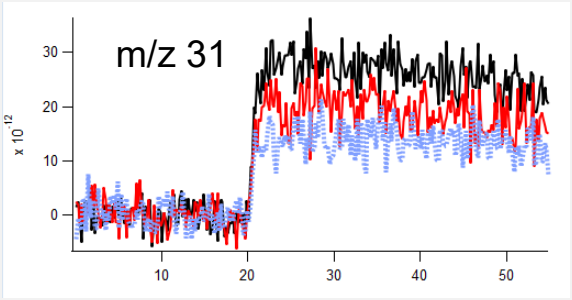


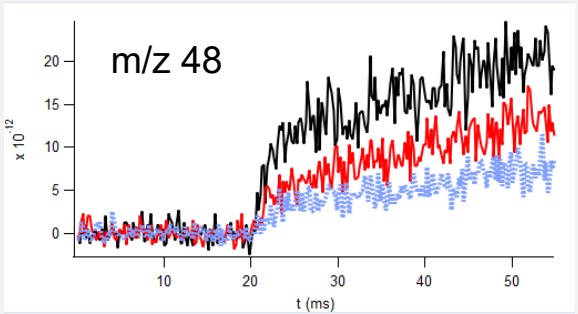
Methylamine Oxidation

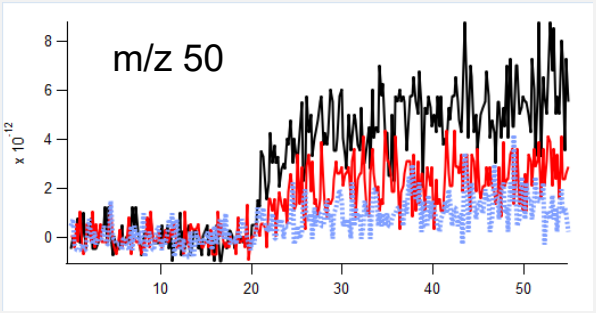


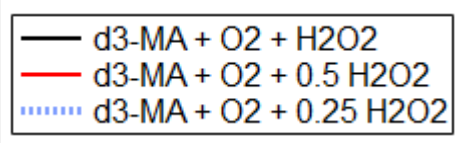




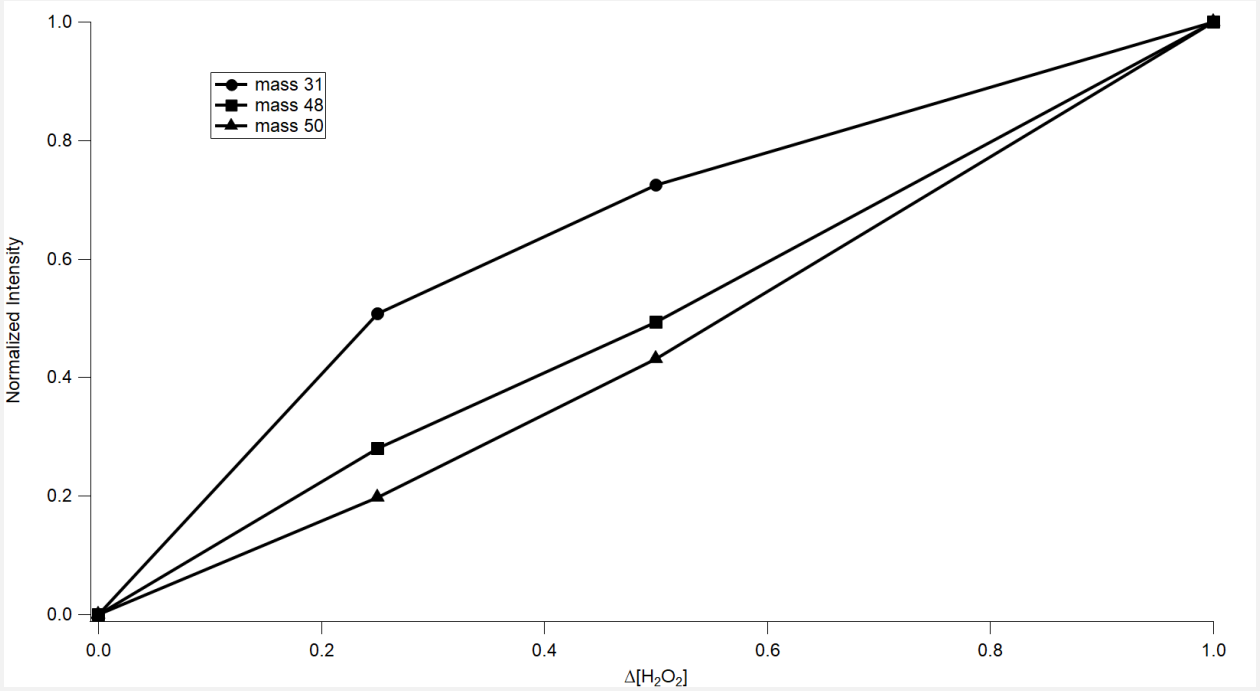


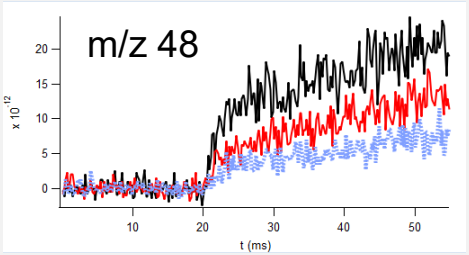


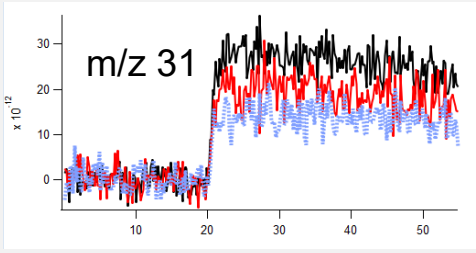


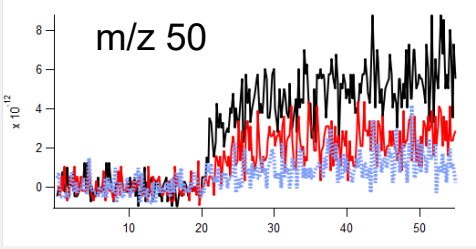


Methylamine Oxidation

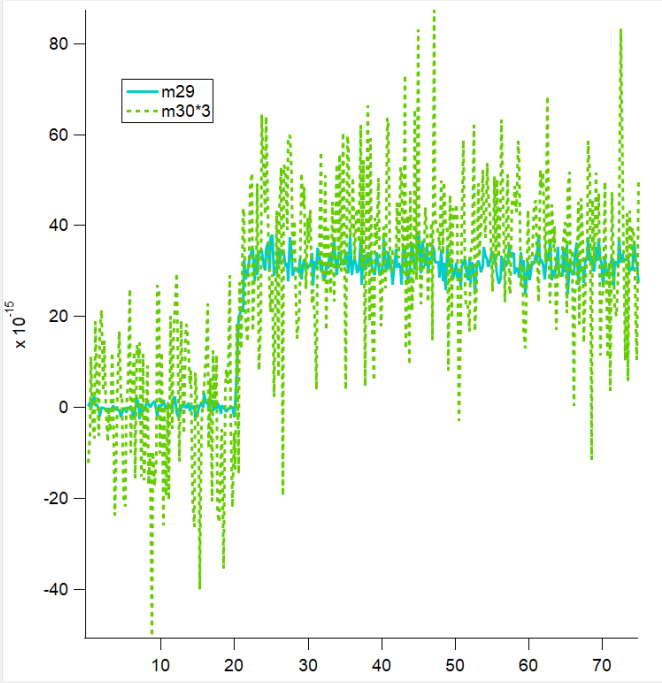








DMA Oxidation



CH3NH + O2

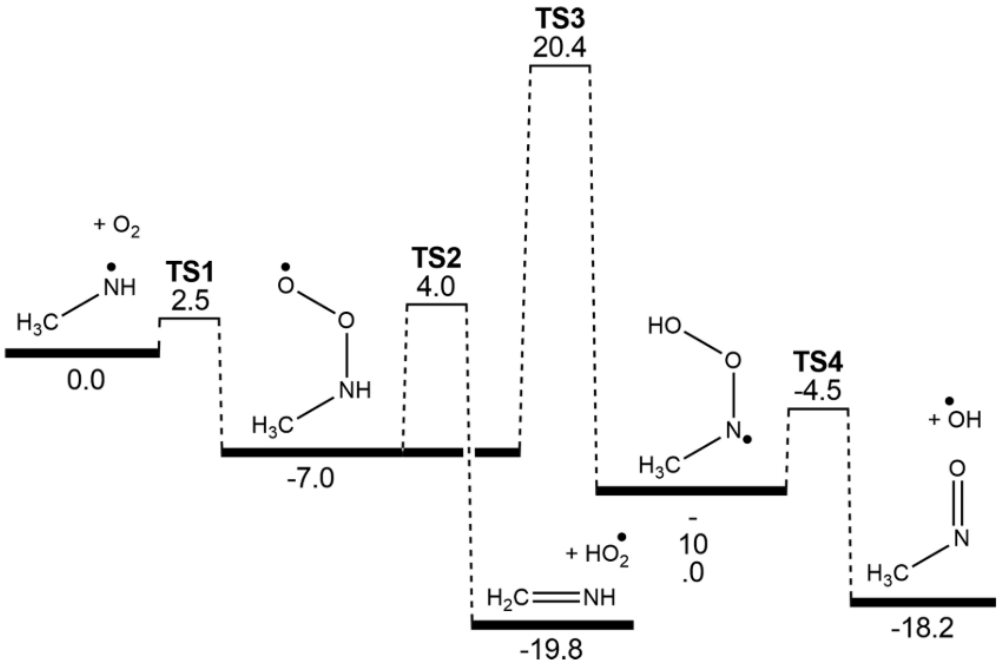


FIGURE 1 Potential energy surface for the $CH_3N^{\bullet}H + O_2$ reaction. Energies are 0 K enthalpies in kcal mol^{-1}, at the G3X-K level of theory

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