

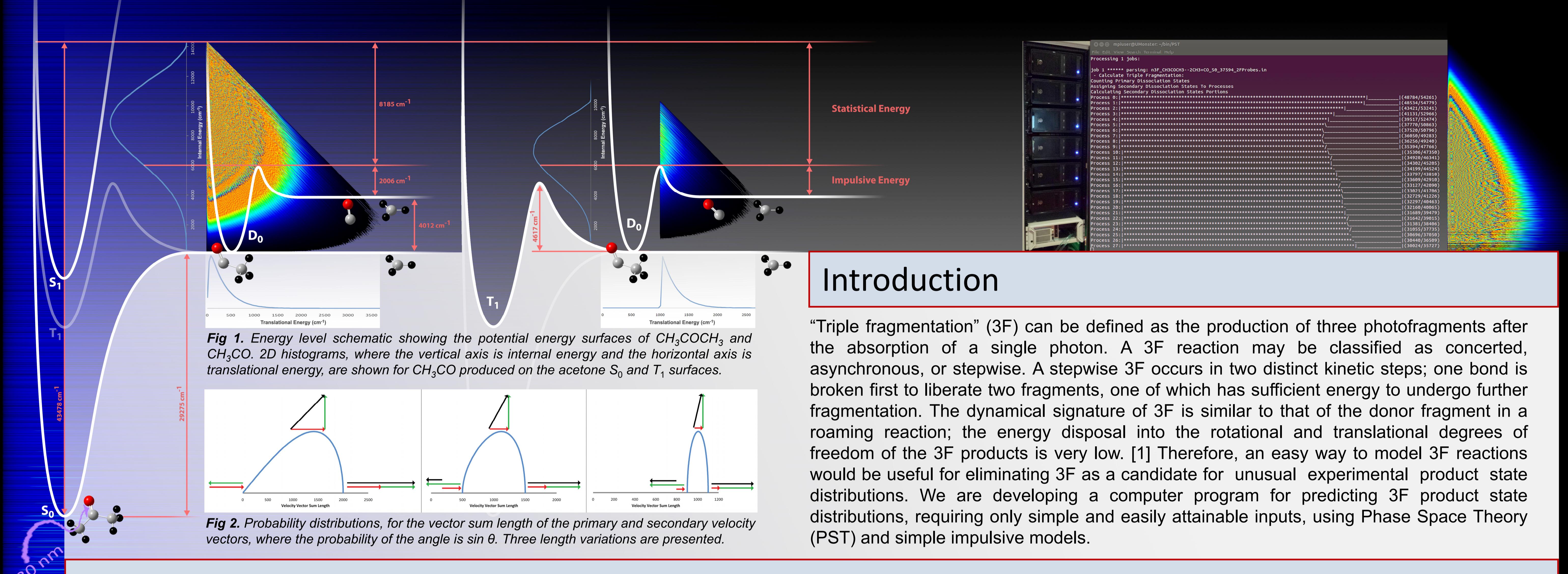


# A Phase Space Theory for Stepwise Triple Fragmentation

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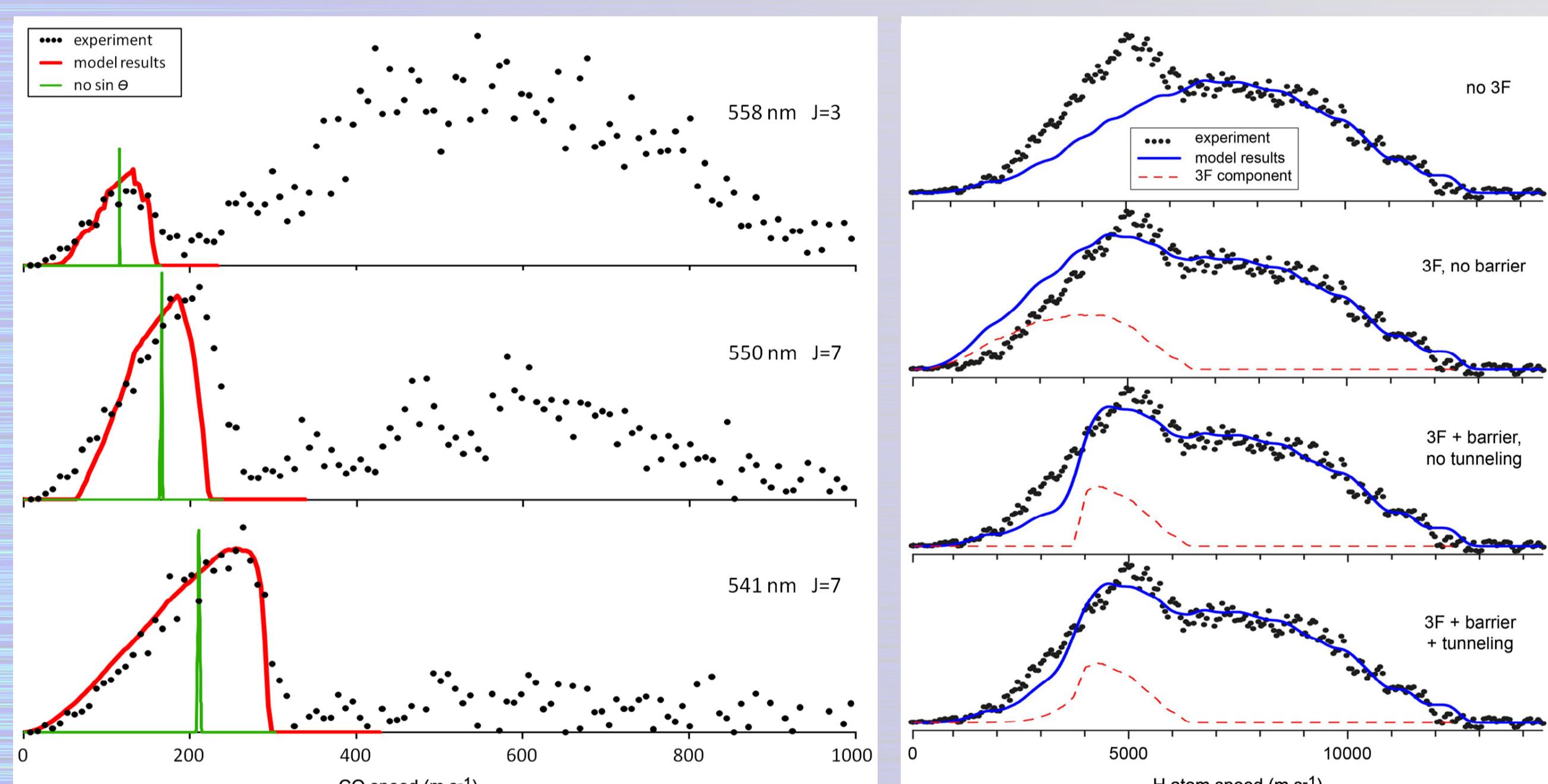
## Introduction

"Triple fragmentation" (3F) can be defined as the production of three photofragments after the absorption of a single photon. A 3F reaction may be classified as concerted, asynchronous, or stepwise. A stepwise 3F occurs in two distinct kinetic steps; one bond is broken first to liberate two fragments, one of which has sufficient energy to undergo further fragmentation. The dynamical signature of 3F is similar to that of the donor fragment in a roaming reaction; the energy disposal into the rotational and translational degrees of freedom of the 3F products is very low. [1] Therefore, an easy way to model 3F reactions would be useful for eliminating 3F as a candidate for unusual experimental product state distributions. We are developing a computer program for predicting 3F product state distributions, requiring only simple and easily attainable inputs, using Phase Space Theory (PST) and simple impulsive models.

## Results

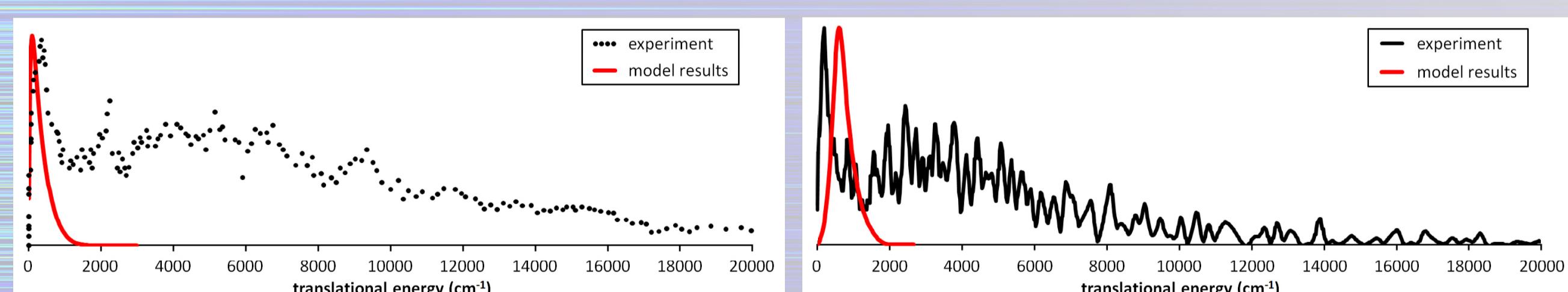
### $\text{H}_2\text{CO}$

Our calculated H and CO 3F product speed distributions agree with experimental measurements performed by our group, Figs 3 and 4. [2] The purpose of these measurements was to benchmark our model. A  $\sin \theta$  probability distribution for primary and secondary velocity directions is critical for the calculated CO speed distribution to match the experimental data.



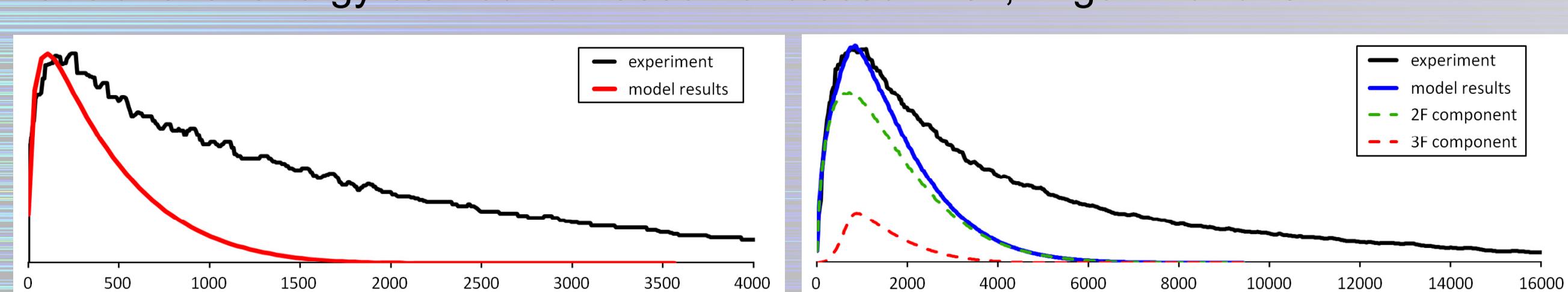
### $\text{CH}_3\text{OCHO}$

Lin and co-workers imaged H and CO ( $v=0$ ) arising from photolysis of  $\text{CH}_3\text{OCHO}$  at 243 and 234 nm. [3] They observed two distinct CO velocity and angular momentum distributions. The rotationally and translationally colder CO was attributed to roaming. Our 234 and 243 nm 3F calculations generate translational energy distributions that are very close to the experimental data, Figs 5 and 6.



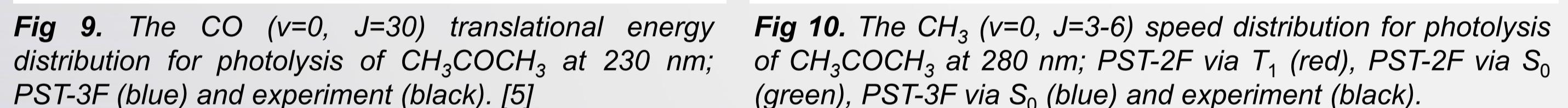
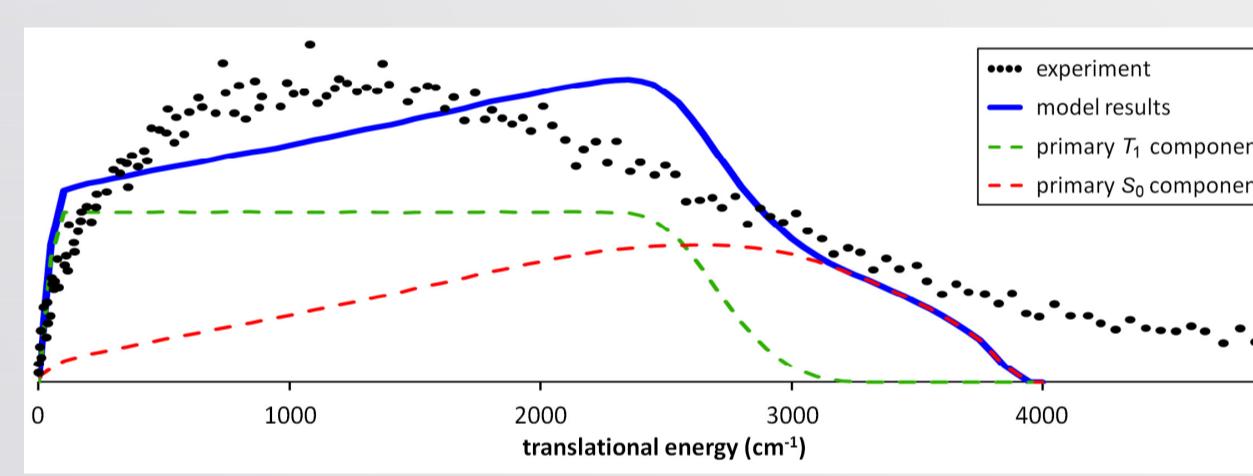
### $\text{CH}_3\text{CHO}$

Bañares and co-workers imaged H and CO ( $v=0$ ) from photolysis of  $\text{CH}_3\text{CHO}$  at 248 nm. [4] They observed two distinct CO velocity and angular momentum distributions. The translationally and rotationally cold CO component was attributed to roaming. Our 248 nm 3F calculation also fits the experimental data, including the H translational energy distribution used to discount 3F, Figs 7 and 8.

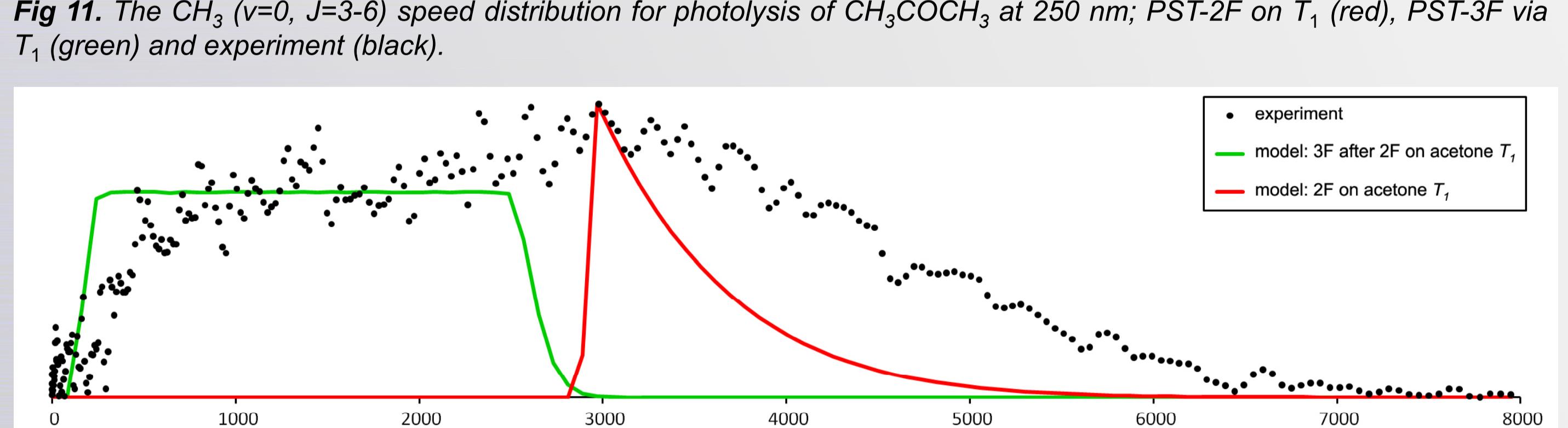
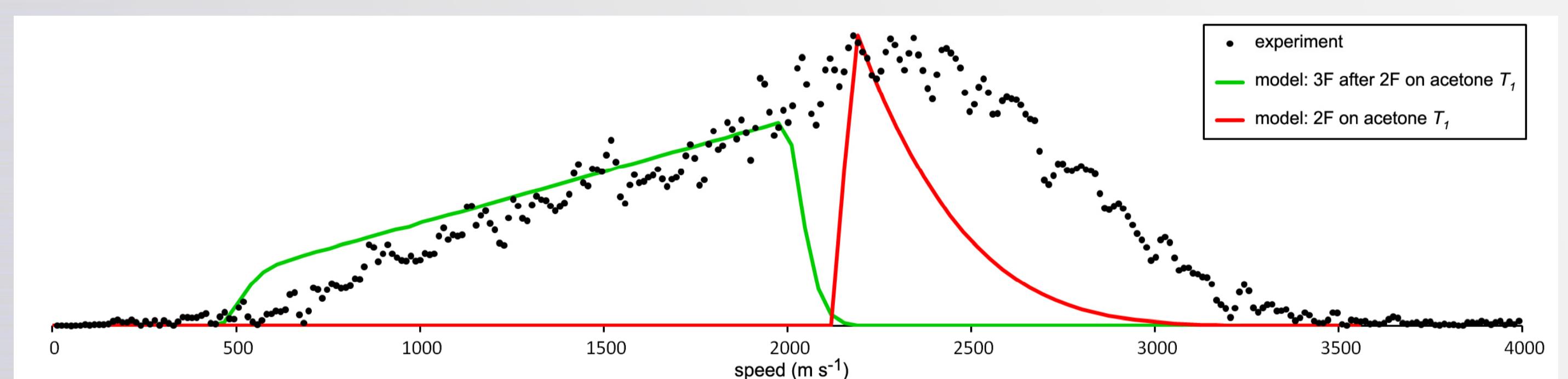


### $\text{CH}_3\text{COCH}_3$

Suits and co-workers imaged CO ( $v=0$ ) arising from photolysis of  $\text{CH}_3\text{COCH}_3$  at 230 nm. [5] They observed two distinct CO velocity and angular momentum distributions. The translationally hotter CO was attributed to 3F, with the primary dissociation occurring on the triplet surface ( $T_1$ ). Our early 3F calculations suggested that acetone primary dissociation (2F) might occur on  $S_0$  and  $T_1$ , Fig 9. However, the match with experiment and an unusual flat topped translational energy distribution raised more questions than answers.



Recent experiments performed by our group, probing  $\text{CH}_3$  fragments arising from photolysis of  $\text{CH}_3\text{COCH}_3$  at lower energies (314–245 nm), suggest 3F does occur exclusively via primary dissociation on the acetone  $T_1$  surface. At 280 nm,  $\text{CH}_3$  fragments are produced with speeds corresponding to the acetone  $T_1$  barrier height, Fig 10. Our model predicts no 3F via the acetone  $T_1$  surface at this energy. If acetone were dissociating on the  $S_0$  surface, our model would predict 3F  $\text{CH}_3$  at lower speed and 2F  $\text{CH}_3$  at even lower speed. As the photolysis energy increases, the 3F component grows in with a rather flat topped translational energy distribution. Our 3F model generates speed and translational energy distributions that are close to this experimental data, Figs 11 and 12.



## Conclusions

Our PST-3F theory was applied to stepwise 3F reactions in  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{OCHO}$  and  $\text{CH}_3\text{COCH}_3$ . The theory reproduced the experimental product distribution for both H and CO ( $v=0$ ) fragments from  $\text{H}_2\text{CO}$  3F. It also produced product state distributions for  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{OCHO}$  that could be used to explain cold components that have previously been assigned as roaming. For  $\text{CH}_3\text{COCH}_3$ , our PST-3F output matches the 3F component of  $\text{CH}_3$  speed distributions measured recently in our lab, when modelled with primary dissociation taking place on the acetone  $T_1$  surface. The PST-3F theory could become a useful tool for testing unusual product state distributions observed experimentally.

## References:

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(4) Rubio-Lago, Amaral, Arregui, Izquierdo, Wang, Zaouris, Kitsopoulos & Bañares, *Phys. Chem. Chem. Phys.*, **9**, 6123, (2007).

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