

New Scheme for Interstellar Chemistry

This report features the work of Shih-Huang Lee and his co-workers published in *Astrophys. J.* **759**, 75 (2012).

Both chemical reactions and chemical dynamics in the gaseous phase attract a great interest of scientists working in the fields of combustion and atmospheric chemistry. In recent decades, this knowledge has been applied to interstellar chemistry to resolve the human dream of improving our understanding of our universe. C_4H_2 is classified as an interstellar molecule because it was observed in the direction of protoplanetary nebulae (PPNe) CRL 618 and CRL 2688, Titan's stratosphere, the cold dark Taurus Molecular Cloud 1, and elsewhere. Of its two isomers HCCCCH (butadiyne) and H_2CCCC (butatrienylidene) with linear carbon skeletons, butadiyne is more stable by 183 kJ mol^{-1} . Much attention has been devoted to butadiyne, less to butatrienylidene, and has been focused on the formation of butadiyne. A chemical kinetic scheme developed on measuring the rates of all reactions is commonly applied to models of atmospheric chemistry. As a result of a research program based on the abundant interstellar molecule C_2H_2 , a reaction $C_2H + C_2H_2 \rightarrow HCCCCH + H$ is proved to be an important channel of formation of butadiyne, which is generalized to $C_{2n}H + C_2H_2 \rightarrow HC_{2n+2}H + H$. In combustion and in interstellar space, the importance of carbon chemistry, such as in reactions of C, C_2 , C_2H with unsaturated hydrocarbons, cannot be neglected; the reaction between C_2 and C_2H_4 is also a candidate to form C_4H_2 .

Difficulties inevitably arise in delineating the primary reactions involved in sequences of rapid reactions, also regarding byproducts, secondary reactions following initial processes, and so on. An experiment conducted with a single collision between reactants coupled with a highly sensitive detec-

tion tool is necessary to reveal what happens during or directly after the collision. A crossed molecular-beam apparatus offers the chance for that exact reaction condition, and clear information about the products is attributed to the small molecular density in both beams, which makes the collision probability small. Moreover, the collision energy is readily controlled, and both the product intensity and the angular distribution are measurable. The concept of crossed molecular-beam machine is derived from the Nobel laureate, Prof. Yuan T. Lee, and his co-workers. Figure 1 is his hand drawn schematic diagram of crossed sodium beam and oxygen beam coupled with a rotatable mass spectrometer and a dye laser.

Evidence for the formation of butadiyne (C_4H_2) from $C + C_3H_3$ and $C_2H + C_2H_2$ is observed with this technique. For the reaction $C_2 + C_2H_4$, the flight-time profiles of products C_4H_3 , C_4H_2 , C_4H and C_4 are all the same, yielding the conclusion that a unique product, C_4H_3 , is formed, and the others are daughter ions of C_4H_3 ; C_4H_2 is hence not formed through this channel, despite being

indicated in a theoretical calculation. Dr. Lee and his co-workers thought that this inconsistency between experimental and theoretical results was unreasonable. They completed an extensive project on the reaction $C_2 + C_2H_4$ undertaken with the crossed molecular-beam machine located on **BL21A1** at NSRRC shown in the following part of this report.¹ Synchrotron radiation as a source of energy tunable in the vacuum ultraviolet (VUV) region is exploited for soft ionization, to replace hard ionization with electron impact, and to reveal the unique photoionization spectrum of each product. Besides the VUV source, they enhanced

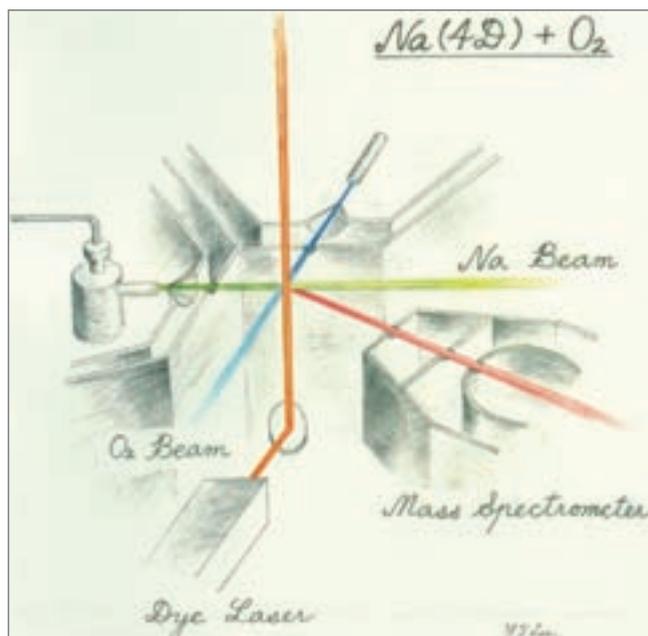


Fig. 1: Prof. Yuan T. Lee's hand drawn schematic diagram of crossed molecular-beam apparatus which involves two molecular beams, a laser beam path, and a rotatable mass spectrometer for detecting products flying to different angles. (courtesy of Prof. Yuan T. Lee)

the ratio of signal to noise and temporal resolution of the product flight enable recognition whether C_4H_2 is formed. Figure 2 is a typical Newton diagram represented by the product channel $C_4H_2 + H_2$ drawn by Dr. S.-H. Lee. The true contour form is obtained after measuring the time-of-flight (TOF) signal of each product at various angles (13° to 58°) shown as dashed lines in Fig. 2). Subject to conservation of momentum, the kinetic energies of products C_4H_3 and C_4H_2 differ, whereas the total kinetic energy is the same; thus the circles representing velocities of products vary in the Newton diagram. Furthermore, as each product channel has a disparate heat of formation, the distribution of translational energy is distinct for each. If C_4H_2 ions are wholly daughter ions of C_4H_3 products, the TOF profiles at all angles should be the same as they are determined just when C_4H_3 ions are formed. Black lines in Fig. 3 represent the TOF signal of C_4H_2 ions ($m/z = 50$).

All profiles in Fig. 3 have contributions from two parts: the blue ones are the profiles of C_4H_3 products obtained from experiments and the red ones are the results of subtraction, which gives clear evidence that part of

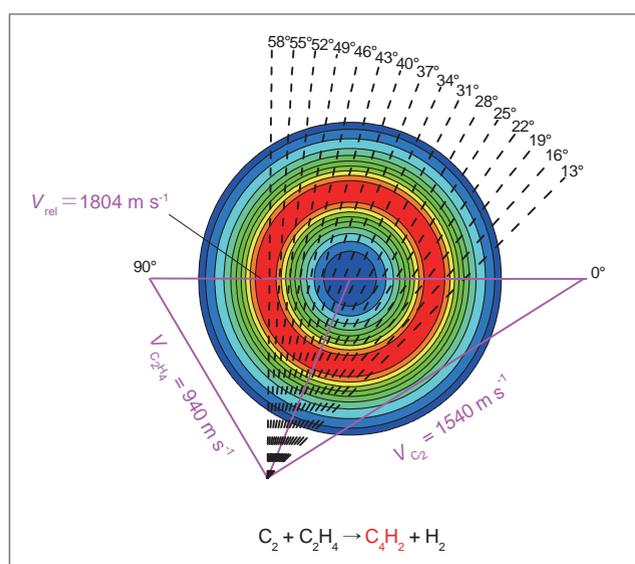


Fig. 2: Newton diagrams associated with two-dimensional product-velocity maps for reaction $C_2 + C_2H_4 \rightarrow C_4H_2 + H_2$. V_{C_2} and $V_{C_2H_4}$ are reactant velocities. V_{rel} is the relative velocity, 1804 m s^{-1} , between reactants C_2 and C_2H_4 . Dashed lines denote the detection axes at laboratory angles 13° – 58° . This figure has been redrawn by Dr. S.-H. Lee.

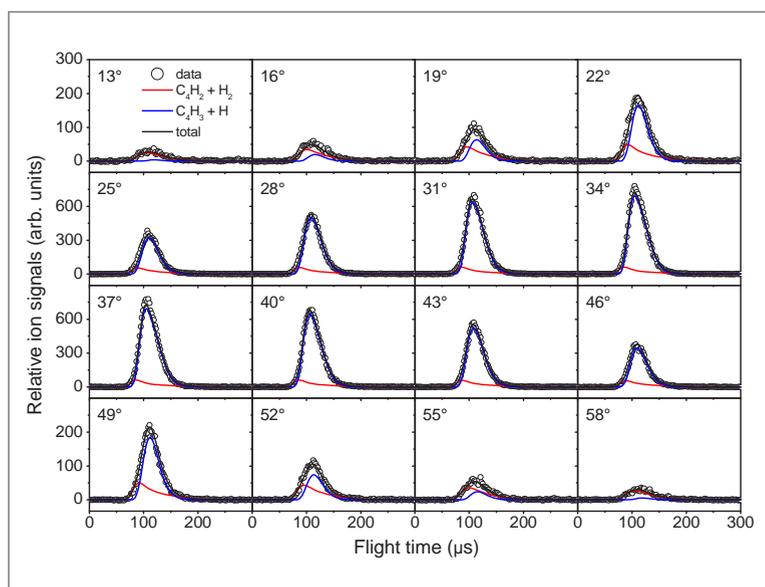


Fig. 3: Angle-specific TOF spectra of product C_4H_2 recorded at $m/z = 50$ with photoionization energy 11.1 eV . Open circles denote the experimental data, and solid curves the simulations. Each panel shows the corresponding laboratory angle Θ shown in Fig. 2. First and fourth rows have ordinate scales different from that of second and third rows. Blue curves represent the TOF distributions of daughter ion $C_4H_2^+$ of product C_4H_3 and red curves the TOF distributions of product C_4H_2 . Black curves are the sum of red and blue curves. This figure has been redrawn by Dr. S.-H. Lee.

C_4H_2 is formed from $C_2 + C_2H_4$ rather than only as a daughter ion of C_2H_3 .

Further investigation and analysis were undertaken utilizing a unique ionization energy, a unique photoionization spectrum for each product (even isomers of products), and the heat of formation coupled with available energy and translational energy. Varying photon energies, varied isomers of the same mass are emphasized and exhibited in the TOF distribution as isomers have distinct ionization energies and heats of formation. Although the C_4H_3 product has four possible isomers, TOF distributions are independent of photon energy; the measured ionization energy is 8.0 eV , consistent with preceding experimental and theoretical results for H_2CCCCH . H_2CCCC is dominant over $HCCCCH$ as the C_4H_2 product according to the matched available energy, ionization threshold and theoretical calculation. Adapting the information to interstellar conditions, such as temperature and UV photon flux, the achievement of this research undoubtedly helps to build models of interstellar chemistry.

Reference

1. S.-H. Lee, W.-J. Huang, Y.-C. Lin, and C.-H. Chin, *Astrophys. J.* **759**, 75 (2012).