

### 3C1) 원자-라디칼 반응 동력학의 교차 빔 연구

## A Crossed Beam Study of Atom-Radical Reaction Dynamics

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#### 1. 서 론

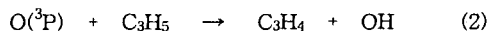
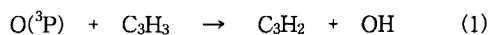
Reaction dynamics plays an essential role in understanding the microscopic mechanism of elementary chemical processes at the molecular level. Detailed studies of the reactions of atomic species such as hydrogen and second-row atoms with small closed-shell molecules have provided important insights into hydrocarbon synthesis, combustion, interstellar space and atmospheric chemistry. Despite its mechanistic significance, however, the investigations of atom-radical reaction dynamics are quite scarce in comparison to the extensive studies of atom-molecule reactions. In this presentation, we describe our recent experimental and theoretical studies of the reaction dynamics of  $O(^3P)$  with propargyl ( $C_3H_3$ ) and allyl ( $C_3H_5$ ), together with the description of the crossed beam apparatus.

#### 2. 연구 방법

The reactants  $O(^3P)$  and hydrocarbon radicals were generated by the photodissociation of  $NO_2$  and the supersonic flash pyrolysis of precursor allyl iodide and propargyl bromide, respectively. The reaction dynamics have been investigated by applying laser induced fluorescence (LIF) spectroscopy in a crossed beam configuration.<sup>1-4</sup> In addition, we have also performed *ab initio* calculations and *prior* and RRKM (Rice-Ramsperger-Kassel-Marcus) statistical estimations to facilitate the understanding of the potential energy surface, reaction mechanisms, major reaction channels and their dynamic character

#### 3. 결과 및 고찰

Several new exothermic channels (1)-(2) were observed, and the nascent internal state distributions of OH products in the channels (1) and (2) showed substantial bimodal internal excitations (Fig. 1).



On the basis of population analyses and comparison with *prior* calculations, the potential energy surface plays a critical role in understanding the reactive atom-radical scattering processes, and the dynamics of the each reaction is believed to proceed through two competing dynamical pathways. In the case of O-allyl system, the major low  $N$ -components with significant vibrational excitation may be described by the direct abstraction process, while the minor but extraordinarily hot rotational distribution of high  $N$ -components implies that some fraction of reactants is sampled to proceed through the indirect short-lived addition-complex forming process. In the case of O-propargyl system, the minor low  $N$ -component can be described by the statistical picture,

whereas the major hot rotational distribution undergoes the indirect short-lived complex mechanism.

We hope this work sheds some light on the gas-phase atom-radical dynamics at the molecular level, which has been very little explored so far.

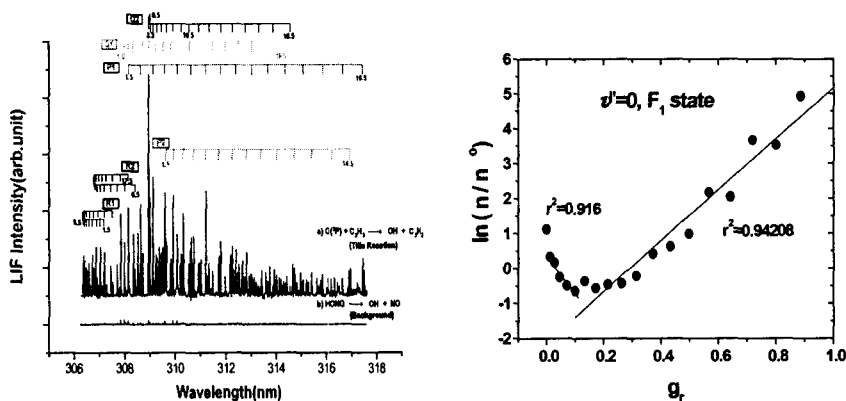


Figure 1. a) The LIF spectrum of the nascent OH ( $A^2\Sigma^+-X^2\Pi$ ) produced in the reaction of O( $^3P$ ) with C<sub>3</sub>H<sub>3</sub> and b) the statistical prior plot (-) of normalized rotational population.

#### 참고 문헌

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