

氏名	下 條 竜 夫
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論文審査委員	主 査 齊 藤 修 二

論文内容の要旨

1. Introduction

Photodissociation of carbonyl compounds has been one of the research subjects to which extensive experimental and theoretical works are devoted. When they are excited at $n\pi^*$ type absorption band in the visible and ultraviolet regions, they undergo the rearrangement or fragmentation reaction.

Among them, the photodissociation dynamics of aldehydes has been less interested until recently. This is presumably due to the experimental difficulty in the measurement of energy distributions of radicals, such as HCO. Recently, Sappey and Crosley reported the LIF excitation spectra for the $B \leftarrow X$ transition of the HCO radical and have the rotational assignment. This allows us to study the photodissociation dynamics of carbonyl compounds which produce HCO in detail.

The purpose of this thesis is to investigate the photodissociation dynamics of carbonyl compounds by the measurement of the energy distributions of photofragments, especially the vibrational distribution of HCO.

2. Photodissociation dynamics of acetaldehyde

The absorption spectrum of acetaldehyde is located in the wavelength range between 250 and 350nm, which corresponds to the transition to the lowest singlet excited state of $n\pi^*$ type. Acetaldehyde dissociates into $CH_3 + HCO$ at excitation wavelengths shorter than 320.5nm (31211cm^{-1}).

Vibrationally excited HCO radicals have been observed in the photodissociation of acetaldehyde in a supersonic jet with the pump-probe technique. The threshold wavelength for the bending and CO-stretching excitations was determined to be at 308.7 and 302.6nm, respectively. The nascent vibrational distribution relative to the ground state has also been determined as a function of the excitation wavelength for the region 280–300nm.

The observed vibrational distribution in HCO is found to be consistent with a model in which the excess energy above the reaction barrier is statistically distributed among the fragments' degrees of freedom. The result indicates that the total available energy can be divided into two parts, one is the energy above the barrier and the other is that below the barrier. The former part of the available energy excites the vibrational modes in HCO statistically.

This energy distribution confirms that the photodissociation reaction occurs through the T_1 state. If it occurred through the S_0 surface as in the case of formaldehyde, it would have no (or very small) barrier on the exit channel. Therefore, almost all the exoergicity should be distributed among fragments' degrees of freedom. This is not in agreement with the present result that only the energy above the barrier is distributed to the vibrational mode of HCO.

3. Photodissociation dynamics of propionaldehyde

In order to compare with the case of acetaldehyde, photodissociation dynamics of propionaldehyde was investigated by the measurement of the LIF excitation and photofragment excitation spectra of propionaldehyde and the LIF excitation spectra of vibrationally excited HCO.

The LIF excitation spectrum and photofragment excitation spectrum of propionaldehyde in a

supersonic jet were obtained by scanning the excitation wavelength from 320nm to 340nm. The threshold for the production of the ground state HCO exists at 328.5nm.

Vibrationally excited HCO radicals upon propionaldehyde have been observed in a supersonic jet with the pump-probe technique. The threshold wavelength for the bending excitation has been determined to be 317.5nm. Similarly to the case of acetaldehyde, the observed vibrational distribution in HCO is consistent with a model in which the excess energy above the reaction barrier is statistically distributed among the fragments' degrees of freedom.

This result supports the generality of the idea that the total available energy can be divided into two parts, one is the energy above the barrier and the other is that below the barrier, the former accounting for the statistical excitation of the fragment vibrational mode.

4. Investigation of B state of vinyloxy radical

Although the absorption spectrum of the vinyloxy radical consists of a series of vibronic progressions appearing between 350nm and 280nm, only four main bands near the 0-0 band have been observed in the LIF excitation spectrum. This is presumably due to the predissociation of the radical in the excited state.

The vibronic structure of the vinyloxy radical in the B(2A^u) state was investigated by the hole burning technique in a supersonic free jet. Frequencies of the vibronic bands were determined accurately up to 4000cm⁻¹. It is shown that most of them can be assigned to the combinations of the v₄-v₉ vibrational modes, in agreement with the previous calculation.

No additional HCO was observed to that produced directly in the photodissociation of ethyl vinyl ether, which is the source of vinyloxy radical in this experiment. It is therefore most probable that the channel CH₂CHO → CH₃ + CO is dominant in the decay of the B(2A^u) state of the vinyloxy radical.

論文の審査結果の要旨

出願者は分子線源及び四重極質量分析計を装着した化学反応動力学解析用真空槽を製作し、これを用いて、アルデヒド化合物、特にアセトアルデヒド、プロピオンアルデヒドの光分解過程ならびにこれと対照的なビノキシラジカルの光分解過程の解明を行った。

アセトアルデヒドは250から350nmの光を吸収し、320.5nmより短波長の光により $\text{CH}_3 + \text{HCO}$ に分解することが知られている。出願者はアセトアルデヒドの光分解の分解光波長に対する依存性を調べた結果、308.7nmより短波長では変角振動が励起された HCO ラジカルが、302.6nmより短波長では CO 伸縮振動が励起された HCO ラジカルが生成することを初めて見出した。

出願者はこの結果を利用して、280-300nmにわたる励起波長で生成する HCO の振動状態の分布を詳細に調べた。反応生成物 HCO の振動分布を解析の結果、光分解エネルギーのうちフラグメント生成に用いられるエネルギーを除いた余剰エネルギーが、反応障壁以上と以下のエネルギーに分けられ、前者がフラグメントの運動の自由度にわたって統計的に分配されるというモデルで説明できることを示した。この結果は反応の余剰エネルギーがフラグメントの全てに配分される S_0 状態を経由するホルムアルデヒドの光分解と異なり、アセトアルデヒドは反応障壁をもつ T_1 状態を経由して分解することを示している。

出願者はこの反応機構を確かめる目的で、プロピオンアルデヒドの光分解反応も同様の手法により調べ、アセトアルデヒドの場合と同様な反応機構が支配していることを明らかにした。

更に出願者は、上記アルデヒド化合物とは異なる系統に属するビノキシラジカルの光分解を行い、ビノキシラジカルの振電バンドの詳細な解析をおこなうと共に、反応機構の検討もおこなった。

以上出願者の研究成果はアルデヒドの光分解反応の動力的解明としては学問的に高い水準にあり、また十分に価値のあるものである。よって審査委員会は出願論文が学位授与に値すると全員一致で判断した。

博士論文の審査修了後、関連する専門分野及びその基礎となる分野、すなわち、レーザー分光学およびその実験技術、分子線実験技術、反応動力学実験、解析法ならびに分子分光学の基礎、反応理論について口述による試験を行った。これに対して出願者は的確な対応を示した。また出願者は公開論文発表会において博士論文の主要点を意欲的に、また分かりやすく報告するとともに、発表後の質疑応答においても十分な対応を示した。なお、博士論文は十分なレベルの英語で作製され、出願者の英語能力は十分であると判断できる。以上の結果、出願者は学位取得に十分な学識を有すると判断する。