QUANTUM CHEMISTRY

Annual Research Highlights

(1) "Ultrafast hydrogen scrambling in methyl-acetylene ions induced by intense laser fields"

Three-body Coulomb explosion processes of triply charged positive ions of methylacetylene and its isotopomer, methyl-d_3-acetylene, induced by an ultrashort intense laser field were investigated by the coincidence momentum imaging (CMI) method. The following two types of three-body decomposition pathways accompanying the proton ejection were identified in the CMI maps of methylacetylene:

I: $C_3H_4^{3+} \rightarrow H^+ + C_\gamma H_2^+ + C_\alpha C_\beta H^+$

II: $C_3H_4^{3+} \rightarrow H^+ + C_\beta C_\gamma H_2^+ + C_\alpha H^+$,

where three carbon atoms are labeled using α, β, and γ as $H{-}C_\alpha{\equiv}C_\beta{-}C_\gamma H_3$. Three types of the decomposition pathways with the $C_\beta C_\gamma$ bond breaking and three types of the decomposition pathways with the $C_\alpha C_\beta$ bond breaking were identified for methyl-d_3-acetylene. The obtained CMI maps revealed that a variety of different H/D migration processes coexist. As summarized in Fig. 1, the migration processes identified in the present study are (i) the migration of one H/D atom, (ii) the exchange between two H/D atoms, (iii) the migration of two H/D atoms, and (iv) the exchange of two H/D atoms and additional migration of one H atom, showing the high intramolecular mobility of H and D atoms within methylacetylene and methyl-d_3-acetylene in an intense laser field.

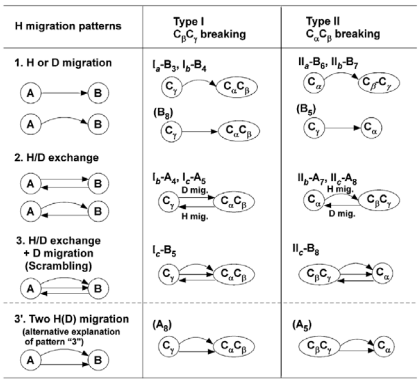

Fig. 1 The schematic diagram of proton/deuteron transfer. A straight arrow represents the complete migration of H and D. A curved arrow represents the migration of H and D that are eventually ejected as H^+ or D^+.

1.(1)-4) *Phys. Chem. Chem. Phys.*, **14**, 10640 (2012)

(2) "Hydrogen scrambling in ethane induced by intense laser fields: Statistical analysis of coincidence events"

In order to elucidate the extent of "migration and exchange" of the H and D atoms in the generation of triatomic hydrogen molecular ions from an ethane molecule induced by an intense laser field, CMI images were recorded for the fragment ions generated from CH_3CH_3, CD_3CD_3, and CH_3CD_3. From the analysis of the coincidence events, the yield ratio of H_3^+: H_2D^+: HD_2^+: D_3^+ generated from CH_3CD_3 was derived to be (8.01 ± 1.20) : (43.0 ± 5.4) : (43.1 ± 0.3) : (5.89 ± 0.10). This yield ratio, which is close to the statistical ratio of 1:9:9:1, and the observed isotropic angular distributions of the ejection directions of H_3^+ and its deuterated analogues show that an extensive H-D exchange process called hydrogen scrambling proceeds within the long-lived doubly charged parent molecule, $CH_3CD_3^{2+}$, prior to the decomposition.

1.(1)-5) *J. Chem. Phys.*, **136**, 204309 (2012)

(3) "Protonic structure of CH_3OH described by electroprotonic wave functions"

The electroprotonic ground-state wave function of CH_3OH was calculated by adopting multiconfiguration wavefunction theory developed for a system composed of electrons and protons. A CH_3OH molecule was treated as a quasidiatomic molecule, in which orbitals for both electrons and protons are described in the laboratory fixed cylindrical coordinate system with C and O atoms being fixed on the z axis. The calculated probability densities of the four protons show that the C atom is surrounded by three protons and the O atom by one proton, and that the dihedral angle of the O-H bond axis with respect to one of the C-H bond axes becomes 180°, exhibiting appropriately the conformational correlation between the two functional groups (Fig. 2). The optimized spatial configuration of the protons was found to be in good agreement with that obtained by the standard Born-Oppenheimer (BO)-based electronic structure calculations. The non-BO electroprotonic wave functions introduced here afford the basis for describing ultrafast hydrogen migration in hydrocarbon molecules in an intense laser field.

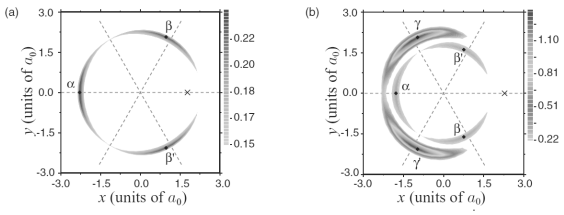

Fig. 2 Contour plots of the 2D conditional probability density for the proton distribution obtained using the electroprotonic ground-state wave function, which give the probabilities of finding a proton at (x,y) on the condition that another proton is located at (ρ_0, z_0, θ_0): (a) (ρ_0, z_0, θ_0) is taken at the peak position of the proton distribution in the hydroxyl group, and (b) (ρ_0, z_0, θ_0) is taken at the peak position of the proton distribution in the methyl group. The fixed proton position is represented by the cross in each plot.

1.(1)-8) *Phys. Rev.*, **A85**, 034504 (2012)

量子化学研究室

研究ハイライト

(1) 強光子場によるメチルアセチレンイオンの超高速水素スクランブリング

コインシデンス運動量画像（CMI）法によって、高強度超短パルスレーザー場によって誘起されるメチルアセチレン（$HCCCH_3$）とメチル-d_3-アセチレン（$HCCCD_3$）の三価イオンの三体クーロン爆発過程の研究を行った。メチルアセチレンの CMI マップから、以下に挙げる二種類のプロトン放出を伴う三体解離過程が同定された。

I: $C_3H_4^{3+} \rightarrow H^+ + C_\gamma H_2^+ + C_\alpha C_\beta H^+$

II: $C_3H_4^{3+} \rightarrow H^+ + C_\beta C_\gamma H_2^+ + C_\alpha H^+$,

ここで、$H{-}C_\alpha{\equiv}C_\beta{-}C_\gamma H_3$ のように三種類の炭素原子を表示した。メチル-d_3-アセチレンでは、$C_\beta C_\gamma$結合解離と $C_\alpha C_\beta$結合解離に対してそれぞれ三種類の分解過程が存在することが判明し、様々な H/D 移動過程が共存していることが分かった。図１に示すように、本研究では、(i) 一個の H/D 原子の移動、(ii) 二つの H/D 原子の交換、(iii) 二つの H/D 原子の移動、(iv) H/D 原子の交換と更なる H 原子移動、という４種類の水素移動過程が観測され、強光子場中のメチルアセチレン内において、H 原子や D 原子が高い分子内移動性を持つことが明らかにされた。

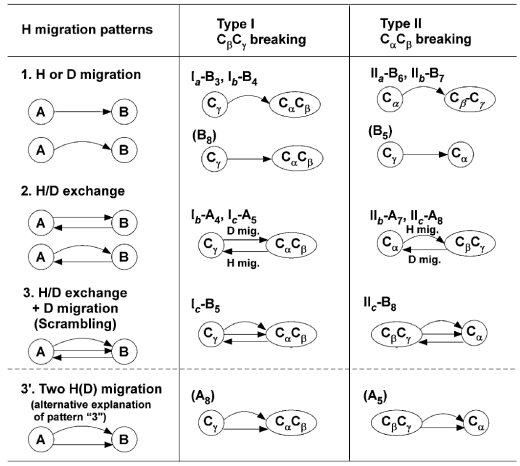

図２　H/D 移動過程の概略図。直線矢印は H/D 原子の完全な移動を示す。曲線矢印は H/D 原子移動の後に H^+/D^+として脱離する過程を示す。

1.(1)-4) *Phys. Chem. Chem. Phys.*, **14**, 10640 (2012)

(2) 強光子場によるエタンの水素スクランブリング：コインシデンス事象の統計的解析

強光子場によってエタン分子から三原子水素分子イオンが放出される過程において、H 原子や D 原子の移動や交換がどの程度引き起こされるのかを解明するために、CH_3CH_3、CD_3CD_3、および、CH_3CD_3 分子からの解離生成物イオンの CMI 画像観測を行った。観測されたコインシデンス事象を解析することによって、CH_3CD_3 からの $H_3^+ : H_2D^+ : HD_2^+ : D_3^+$収量比が、$(8.01 \pm 1.20) : (43.0 \pm 5.4) : (43.1 \pm 0.3) : (5.89 \pm 0.10)$と見積もられた。この収量比は、三原子水素分子イオン放出に至る二体クーロン爆発過程において著しい H-D 交換が起きていることを明示している。この収量比と三原子水素分子イオンの放出角度分布の等方性から、水素スクランブリングと呼ばれる統計的な H-D 交換が長寿命の前駆体二価イオンにおいて十分に進行した後に、三原子水素分子イオン放出されることが明らかとなった。

1.(1)-5) *J. Chem. Phys.*, **136**, 204309 (2012)

(3) 電子−プロトン波動関数で記述された CH_3OH 分子のプロトン構造

多配置波動関数理論を使って CH_3OH 分子の電子 - プロトン基底状態の波動関数を求めた。CH_3OH 分子は二原子様分子として取り扱った。即ち、電子とプロトンは軌道関数を用いて実験室固定の円筒座標系で記述し、z 軸上に C 原子核と O 原子核を配置した。計算された電子 - プロトン波動関数から、C 原子は 3 つのプロトンに、O 原子は 1 つのプロトンと結合していることが確認された。また、プロトンに対する条件付き確率分布密度の解析から、O-H 結合軸に対して、一つの C-H 結合軸が 180°の位置にあることが示され、本研究で得られた non-Born-Oppenheimer 波動関数から、通常の量子化学計算で得られる分子の幾何学的な構造を抽出できることを確認した（図２）。本研究で得られた non-Born-Oppenheimer 波動関数の構築は、強光子場中での超高速水素マイグレーションを解析するための第一歩と位置付けられる。

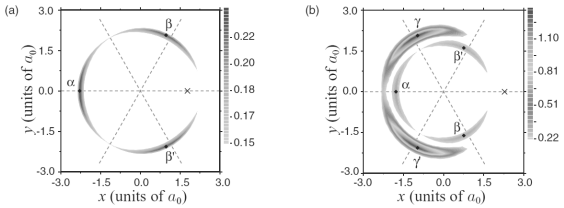

図２　プロトンに対する条件付き確率密度関数（z 軸方向には積分してある）。(a)は 1 つのプロトンを水酸基側のプロトン位置に固定した場合、(b)はメチル基側のプロトン位置に固定した場合の三つ子関数を表す。固定したプロトンの位置は×印で表されている。

1.(1)-8) *Phys. Rev.*, **A85**, 034504 (2012)

1. 原著論文

(1) Refereed Journals

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(2) その他

該当なし

2. 総説・解説

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2) E. J. Takahashi, T. Togashi, M. Aoyama, K. Yamakawa, T. Sato, A. Iwasaki, S. Owada, K. Yamanouchi, T. Hara, S. Matsubara, T. Ohshima, Y. Otake, H. Tanaka, T. Tanaka, H. Tomizawa, T. Watanabe, M. Yabashi, K. Midorikawa, and T. Ishikawa, "Enormous amplification of full-coherent radiation in the extreme ultraviolet region with a free-electron laser", *Multiphoton Processes and Attosecond Physics: Proceedings of the 12th International Conference on Multiphoton Processes (ICOMP12) and the 3rd International Conference on Attosecond Physics (ATTO3)*, 155-161, Springer-Verlag (2012).

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9) E. Lötstedt, T. Kato, and K. Yamanouchi, "Efficient ionization of acetylene in intense laser fields", *Multiphoton Processes and Attosecond Physics: Proceedings of the 12th International Conference on Multiphoton Processes (ICOMP12) and the 3rd International Conference on Attosecond Physics (ATTO3)*, 347-350, Springer-Verlag (2012).
10) R. Kanya, Y. Morimoto, and K. Yamanouchi, "Laser-assisted electron scattering and its application to laser-assisted electron diffraction of molecules in femtosecond intense laser fields", *Multiphoton Processes and Attosecond Physics: Proceedings of the 12th International Conference on Multiphoton Processes (ICOMP12) and the 3rd International Conference on Attosecond Physics (ATTO3)*, 351-356, Springer-Verlag (2012).
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3. 著書

1) K. Yamanouchi, "Quantum Meachanics of Molecular Structures", Springer-Veralg (Germany), 2012.
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4. その他

該当なし