

研究レビュー

(1) 何故励起電子状態では2重結合まわりの回転が起こるのか：光異性化反応の動的分極モデル

基底電子状態ではC=C2重結合まわりの回転は起こらず、その結果シス/トランス幾何異性が生ずる。しかし、2重結合を光によって電子的に励起すると、回転が起こり異性化反応が進行する（光異性化反応）。我々は時間分解ラマン分光によって、光異性化反応が進行する *trans*-スチルベンの S_1 状態において、中央の炭素-炭素結合が2重結合であることを示した。即ち、 S_1 *trans*-スチルベンでは、確かに2重結合まわりの回転が起きている。では、どのようにして2重結合回りの回転が起きるのだろうか？我々は、 S_1 *trans*-スチルベンのC=C伸縮振動数と異性化反応速度の溶媒依存性が、線形の相関を持つ事を見出し、その解析からC=C2重結合がC-C（またはC-C）単結合へ分極し、その結果回転が可能になるという新しいモデルを提出した（図1）。このモデルでは、C=C2重結合の分極は、溶媒場の揺らぎによって動的に誘起される（溶媒誘起動的な分極）。最近、このモデルをさらに支持する実験結果が得られた。図2は、 S_1 *trans*-スチルベンのC=C伸縮振動数と異性化反応速度 k_{iso} の相関を3種の溶媒（ヘキサン、オクタン、デカン）について異なる温度5点で調べたものである。各温度に対して線形の相関があり、かつ反応速度がゼロの極限で同一の振動数に収斂している。この関係は、動的な分極モデルの予測と完全に一致する。

A-4) J. Phys. Chem. **106**, 3614-3620 (2002).

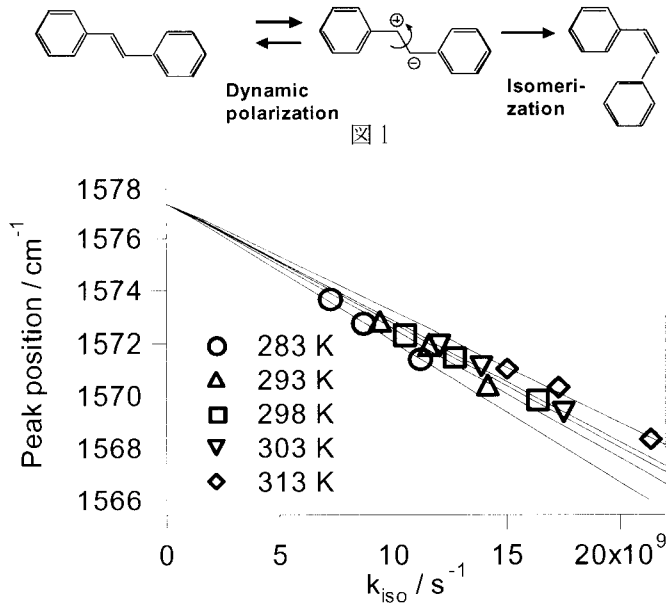


図2

(2) 2-アミノピリジン/酢酸系における超高速段階的2重プロトン移動反応機構の解明

プロトンが一連のサイトを次々に移動し運搬されるプロトンリレーは、生体膜の内部と外部の間にpH勾配を作り出し、ATP合成を駆動することによって、多くの生物過程で重要な役割を果たしている。光誘起2重プロトン移動反応は、プロトンリレーの素過程として、強い興味を持たれ、これまで多くの研究がなされてきた。この2重プロトン移動が、協奏的（2つのプロトンが同時に移動）に進行するのか、段階的（2つのプロトンが順番に移動）に進行するのかについては、この10年間大きな論争が続いている。我々は、ピコ秒時間分解蛍光分光を用いて、2-アミノピリジン/酢酸系の光誘起2重プロトン移動による互変異性化反応の機構を調べた。その結果、励起直後に酢酸のプロトンが2-アミノピリジンの環窒素に移動してプロトン化2-アミノピリジンカチオンラジカルが生成し、続いて2-アミノピリジンのアミノ基のプロトンが5ピコ秒の時定数で酢酸アニオンに移動して互変異性化が完了することがわかった（図1）。すなわち、2-アミノピリジン/酢酸系では、プロトン移動が段階的に起こることを、対イオン型中間体を分光学によって同定して疑いの余地なく証明した。また、2番目のプロトン移動反応速度が顕著な温度依存性を示すことを見出したが、アレニウスプロットから得られた活性化エネルギーにH/D同位体効果が見られなかった。この結果は、既存の理論では説明がつかない。現在、対イオン型中間体の溶媒誘起動的な分極の概念を導入した新しい理論を用いた解析を試みている。

A-3) J. Phys. Chem. **106**, 2305-2312 (2002).

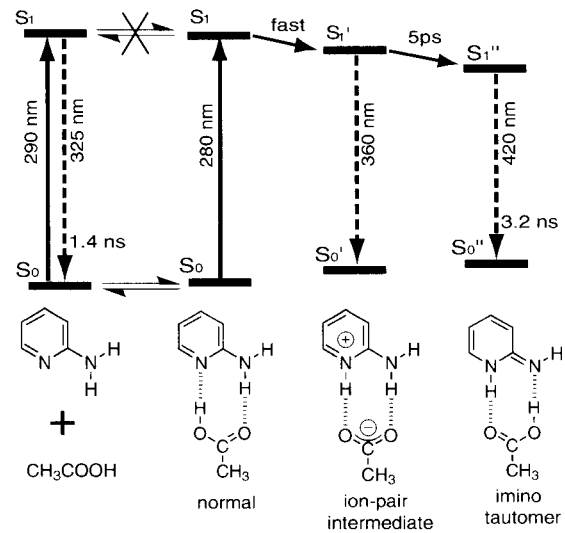


図3

STRUCTURAL CHEMISTRY

Annual Research Review

(1) "How Rotation around a Double Bond Takes Place in the Excited Electronic State; The Dynamic Polarization Model of Photoisomerization"

Rotation around a C=C double bond is prohibited in the ground electronic state at room temperature, giving rise to the *trans/cis* geometrical isomerism. If we photoexcite the double bond electronically, however, the rotation becomes feasible and conversion between the *trans* and *cis* isomers takes place (photoisomerization). We previously showed that the central carbon-carbon bond of *trans*-stilbene in the S_1 state, where the isomerization actually proceeds, is a double bond and not a single bond. The rotation certainly occurs around the double bond of S_1 *trans*-stilbene. Why and how? From the analysis of a newly found linear relationship between the solvent dependent C=C stretch frequency and the rate of isomerization, we proposed a model in which occasional polarization of the C=C double bond into a C^+-C^- (or $\dot{C}-\dot{C}$) single bond facilitates the rotation (Fig. 1). The polarization is induced dynamically by solvent fluctuation (**solvent induced dynamic polarization**). Recently, we obtained further experimental support for this model. Fig. 2 shows the plot of the C=C stretch frequency of S_1 *trans*-stilbene vs the rate of isomerization k_{iso} in three different solvents (hexane, octane and decane) at five different temperatures. The plot makes five straight lines converging to the same point at the zero isomerization rate. This result is fully consistent with our model of dynamic polarization.

A-4) J. Phys. Chem. **106**, 3614-3620 (2002).

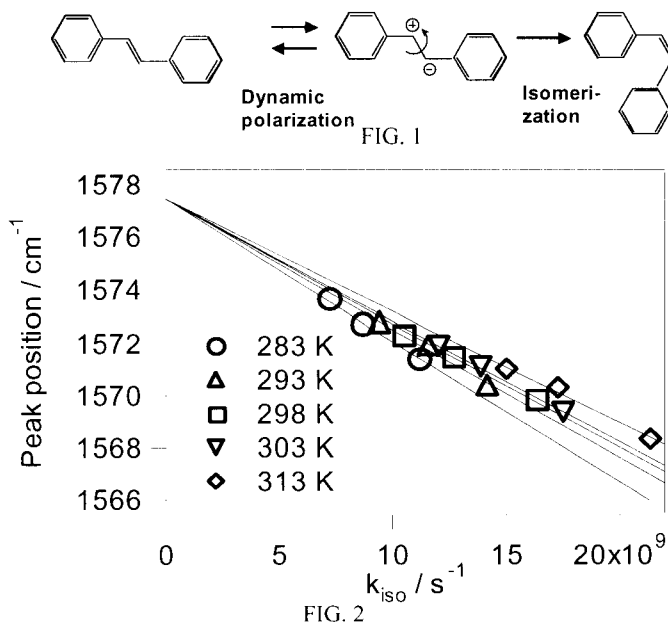


FIG. 2

(2) "Ultrafast Stepwise Double Proton Transfer Reaction in the Excited State of 2-Aminopyridine/Acetic Acid Complex"

Proton relay, in which a proton is transported by successive transfers between prearranged donor/accepter pairs, is involved in many biological processes. It plays an important role in producing a pH gradient across a membrane that facilitates the ATP synthesis. Photoinduced double proton transfer has been attracting much attention as a prototype model of the proton relay. There has been a controversy over the last decade as to whether the double proton transfer proceeds in a concerted way (two protons move simultaneously) or in a stepwise fashion (two protons move one after another). We studied the photoinduced double-proton-transfer tautomerization reaction in the excited state of the 2-aminopyridine/acetic acid complex by picosecond time-resolved fluorescence spectroscopy. It has been found that, immediately after the photoexcitation, the proton of the acetic acid moiety transfers to the ring nitrogen of 2-aminopyridine to form the protonated cation radical of 2-aminopyridine and then the proton of the amino group transfers, with a time constant of 5 ps, to the acetic acid moiety to complete tautomerization (Fig. 3). **This is the first example of a stepwise double proton transfer reaction** in which the zwitterionic intermediate is identified unambiguously by time-resolved spectroscopy. The rate of the second proton transfer shows a marked temperature effect but the behavior is somewhat extraordinary; there is no appreciable H/D isotope effect on the activation energy obtained from the Arrhenius plot. No existing theory can account for this puzzling result. We are now trying to solve the problem by a new theoretical approach that considers the solvent induced dynamic polarization of the zwitterionic intermediate.

A-3) J. Phys. Chem. **106**, 2305-2312 (2002).

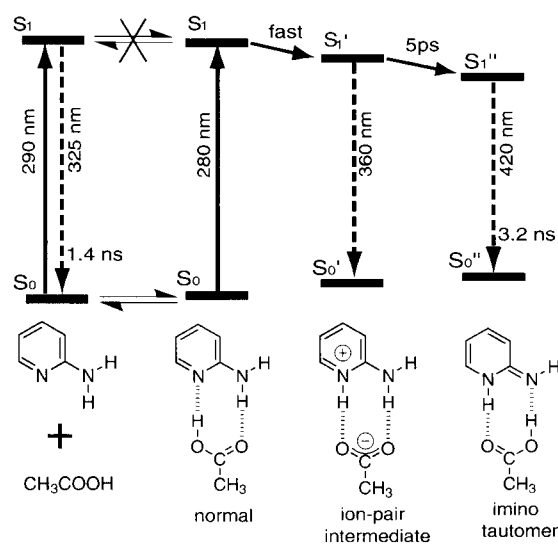


FIG. 3

A. Original Papers

- 1) Y.-K. Min, H. Hiramatsu, and H. Hamaguchi: "Infrared Electroabsorption Spectroscopic Study of Association Structures of 5CB in the Solution, Isotropic Liquid and Nematic Liquid Crystal States.", *Chem. Lett.*, 68-69 (2002).
- 2) (A. Samanta), S. Saha, H. Ishikawa and H. Hamaguchi: "Excited State Structure of N-(4-cyanophenyl)carbazole by Time-Resolved Infrared Absorption Spectroscopy.", *Chem. Lett.*, 340-341 (2002).
- 3) H. Ishikawa, K. Iwata and H. Hamaguchi: "Picosecond Dynamics of Stepwise Double Proton Transfer Reaction in the Excited State of the 2-aminopyridine/Acetic acid System.", *J. Phys. Chem.*, **106**, 10, 2305-2312 (2002).
- 4) K. Iwata, R. Ozawa and H. Hamaguchi: "Analysis of the Solvent- and Temperature-dependent Raman Spectral Changes of S1 trans-Stilbene and the Mechanism of the Trans to Cis Isomerization: Dynamic Polarization Model of Vibrational Dephasing and the C=C Double-bond Rotation.", *J. Phys. Chem.*, **106**, 14, 3614-3620 (2002).
- 5) H. Hamaguchi and K. Iwata: "Physical Chemistry of the Lowest Excited Singlet State of Trans-Stilbene in Solution as Studied by Time-resolved Raman Spectroscopy.", *Bull. Chem. Soc. Jpn.*, **75**, 883-897 (2002).
- 6) S. Kaminaka, (T. Ito), (H. Yamazaki), (E. Kohda) and H. Hamaguchi: "Near-infrared multichannel Raman spectroscopy toward real-time in vivo cancer diagnosis.", *J. Raman Spectrosc.*, **33**, 498-502 (2002).
- 7) H. Hiramatsu and H. Hamaguchi: "Association Structures of N-methylacetamide in Solution Studied by Infrared Electroabsorption Spectroscopy.", *Chem. Phys. Lett.*, **361**, 457-464 (2002).
- 8) K. Ishii and H. Hamaguchi: "Picosecond time-resolved multiplex CARS spectroscopy using optical Kerr gating.", *Chem. Phys. Lett.*, **367**, 672-677 (2002).
- 9) (T. Mizushima), (G. Monde), (S. Murata), K. Ishii and H. Hamaguchi: "Mechanistic studies of direct and sensitized photolysis of methyl (4-nitrophenyl) diazoacetate in the presence of an electron-donating amine: photochemical generation of the diazoalkane radical anion.", *J. Chem. Soc.*, **2**, 1274-1282 (2002).
- 10) (M. Mizuno), H. Hamaguchi, and (T. Tahara): "Observation of Resonance Hyper-Raman Scattering of all-trans-Retinal.", *J. Phys. Chem. A*, **106**, 3599-3604 (2002).

B. Reviews

- 1) M. Hashimoto, T. Yuzawa, C. Kato, K. Iwata and H. Hamaguchi, in "Handbook of Vibrational Spectroscopy", ed. J. M. Chalmers and P. R. Griffiths, John Wiley and Sons Ltd., Chichester, (2002).

C. Proceedings

- 1) H. Ishikawa, K. Iwata and H. Hamaguchi: "Picosecond Dynamics of Photoinduced Stepwise Double Proton Transfer Reaction in the 2-Aminopyridine/Acetic Acid System.", The Proceedings of the Third Asian Photochemistry Conference, 29 (2002).