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Rotational isomers of small molecules in noble-gas solids: From monomers to hydrogen-bonded complexes

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Abstract

Molecular conformation, quantum tunneling, and hydrogen bonding play important roles in various photochemical processes. We have studied a number of small molecules possessing rotational isomerism (HONO, formic acid, acetic acid, *etc*.) isolated in noble-gas solid matrices. Selective vibrational excitation efficiently promotes the conformational change in the excited molecule, which allows preparation of higher-energy conformers. Stability of the higher-energy conformers is often limited by quantum tunneling of hydrogen as observed for some carboxylic acids (formic, acetic, *etc*.). The tunneling mechanism is supported by the strong H/D isotope effect and characteristic temperature dependence with a clear low-temperature limit. The reaction barrier height is an important factor in a tunneling process; however, other factors also play an essential role. The energy mismatch between the initial state of the higher-energy conformer and accepting state of the ground-state conformer is probably important. Hydrogen bonding can change tunneling decay rate of unstable conformers. The *trans–cis* formic acid dimer was prepared by vibrational excitation of the *trans–trans* form in neon and argon matrices. Tunneling decay of *cis* formic acid is substantially slower in the dimeric form compared to monomer, especially in solid neon. This stabilization effect is explained by a complexation-induced increase of reaction barrier, which is confirmed computationally. The complex between *cis* formic acid and water was prepared in an argon matrix and found to be stable at low-temperatures. These results show that intrinsically unstable conformational structures can be thermodynamically stabilized in asymmetrical hydrogen-bonded network. This effect occurs when the energy difference between conformers is smaller than the hydrogen bond interaction energy, which allows chemistry of unstable conformers to be studied.

Keywords: Molecular conformation; Quantum tunneling; Hydrogen bonding

1. Introduction

Molecular conformation is the characteristic three-dimensional shape of a molecule, and this determines many properties of matter, which is especially important in organic and biological chemistry [1]. Large molecules are often flexible and dynamic and can change their shape in response to changes in the environment or other factors; each possible shape is called a conformation, and a transition between them is called a conformational change. Rotational isomerism is a case of molecular conformation when the change is mainly applied to relative orientation (rotation) of a part of the molecule. The smallest molecule showing rotational isomerism is nitrous acid (HONO), and it has been extensively studied particularly because of the environmental value [2–4]. Another important example is formic acid (HCOOH, FA) that is the smallest organic molecule with rotational isomers [5–11]. These simple systems serve as benchmark models of conformational processes allowing fundamental understanding the mechanisms of conformational changes.

A molecular conformational change may be induced by many factors such as temperature, voltage, ion concentration, *etc*. Light-induced conformational change has been also attracted much attention in studies of practically important systems [12,13]. Many works have been done using broadband light sources in low-temperature matrices

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by Pimentel, Murto, Bondybey, Räsänen, Fausto, and other researches [2,14–24]. New opportunities were opened by narrowband tunable light sources [8,9,25–29]. In this situation, selective and efficient excitation of a chosen conformer is possible, which allows detailed studies of isomerization photoreactions. As an important example, the higher-energy conformer of formic acid was prepared in solid argon [8]. Matrix-site selectivity of light-induced rotational isomerization was demonstrated [28,29].

Quantum tunneling is an important concept in physics, chemistry, and biology [30]. The higher-energy *cis* conformers of some carboxylic acids (formic, acetic, *etc.*) convert to the lower-energy *trans* forms via dissipative tunneling of hydrogen through the torsional barrier, which limits their lifetime [31,32]. The quantum tunneling mechanism was confirmed by a strong H/D isotope effect and low-temperature reaction limit evident below 10 K.

Hydrogen bonding is another fundamental phenomenon determining many of the properties of matter [33–35]. Matrix-isolation provides a fruitful approach to study various non-covalently bonded compounds. For example, Mielke, Tokhadze, and co-workers have studied various complexes of HONO [36–38]. Heikilä et al. investigated complexes of HCN and HNC with water and could change the complex structure using narrowband IR light [39]. Lundel and co-workers performed extensive *ab initio* calculations of various complexes allowing matrix-isolation identification of their structures [40–42]. Coussan et al. used tunable IR light to interconvert complex structures [43,44].

Formic acid dimer is a simple organic system which can form a variety of hydrogen-bonded structures. This offers a valuable model to study properties and reactions involving the C–H$\cdots$O and O–H$\cdots$O non-covalently bonded systems. In the gas phase, FA molecules are mainly in *trans–trans* symmetric cyclic dimers, which is the lowest-energy dimeric form [45–47]. Other *trans–trans* dimers are higher in energy and such structures were found in helium droplets and argon matrices [48,49]. Three *trans–cis* dimers were computationally predicted [47]. The first *trans–cis*-FA dimer has been recently reported experimentally in an argon matrix [50] followed by the preparation of the first water complex with the higher-energy conformer *cis*-FA [51]. Tunneling decay of *cis*-FA in these complexes was significantly slowed down as compared to the monomer.

The examples mentioned so far show a close connection between fundamental phenomena of molecular conformation, quantum tunneling, and hydrogen bonding. The present contribution does not pretend to offer a detailed description on these important and broad topics. We critically review here a series of works on these phenomena performed recently in the University of Helsinki. The main research method is isolation of molecules (HONO, HCOOH, CH_3COOH, *etc.*) in various low-temperatures matrices. In order to promote structural changes, resonant vibrational excitation by an optical parametric oscillator with IR extension is employed ($\Delta\nu \sim 0.1\ cm^{-1}$, $\nu > 2500\ cm^{-1}$). The IR absorption spectra are measured at low-temperatures, and they provide (i) vibrational transitions of the initial isomer to be pumped and (ii) absorption bands of the produced rotational isomers to be assigned. The identification of rotational isomers is aided by *ab initio* computations. The main aim of these studies is the preparation of new high-energy rotational isomers, investigation of their structure and IR spectra. The obtained results shine light on intramolecular vibrational energy redistribution (IVR) processes. The IVR processes appear important both in light-induced rotational isomerization and quantum tunneling reactions. The ultimate goal would be laser control of chemical reactions. It is very challenging to obtain different products of a photochemical reaction from different rotational isomers.

2. Light-induced rotational isomerization

The idea of light-induced rotational isomerization is illustrated in Fig. 1 for formic acid (FA). *trans*-FA is the lower-energy form [5], and it is present in the matrix after deposition. The *trans*-FA molecule is transferred by narrowband IR light to an excited vibrational state. After excitation, the vibrational energy redistribution and randomization of the torsional coordinate occur; hence the excited molecule can relax with some probability to either *trans* or *cis* configurations. In order to promote rotational isomerization, the excitation energy should be high enough, at least not much smaller than the isomerization barrier. As a result, some of the excited molecules relax to the *cis* well, and the *trans* to *cis* conformational change occurs. The light-induced *trans* to *cis* isomerization is not obvious *a priori*; however, it was demonstrated experimentally [8]. Formic acid was excited at the OH stretching overtone and new bands appear as shown in Fig. 2 for the CO stretching mode. These light-induced bands were assigned to the higher-energy *cis* form of formic acid. The assignment was done using the theoretical spectrum reported by Goddard et al. [7]. It was the first experimental IR spec-

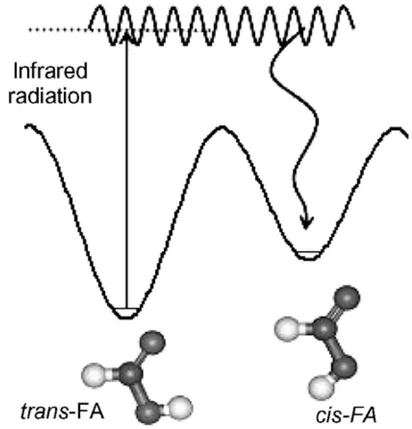

Fig. 1. Schematic representation of light-induced rotational isomerization.