Three Conformers of 2-Furoic Acid: Structure Changes Induced with Near-IR Laser Light

6 AUTHORS, INCLUDING:

Three Conformers of 2-Furoic Acid: Structure Changes Induced with Near-IR Laser Light

Anna Halasa,[†] Leszek Lapinski,[†] Igor Reva,[‡] Hanna Rostkowska,[†] Rui Fausto,[‡] and Maciej J. Nowak*,[†]

[†]Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland
[‡]CQC, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal

Ⓢ *Supporting Information*

ABSTRACT: Conformers of 2-furoic acid were studied using the matrix-isolation technique combined with narrow-band near-IR excitations with tunable laser light. Two conformers of the compound were trapped from the gas phase into low-temperature Ar or Ne matrixes with the population ratio of nearly 1:1. The two forms differ from each other by 180° rotation of the carboxylic group with respect to the furan ring. In both structures, the OH group adopts the cis orientation, with its H atom directed toward the C=O bond of the O=C−O−H group. Narrow-band near-IR excitations of the OH stretching overtone vibrations resulted in transformation of one of the initially observed conformers into a third conformational structure. This near-IR-induced isomerization concerned rotation of the OH group from the initial cis orientation to the trans conformation with the hydrogen atom directed toward the oxygen atom of the furan ring. In the photoproduced conformer, the hydrogen-bond-like O−H···O interaction (between O−H and the oxygen atom of the furan ring) is rather weak. Nevertheless, this interaction stabilized the structure so that it was present in the matrix for several hours after the near-IR-induced generation. The spontaneous conversion of the photogenerated, higher-energy form back into the more stable conformer with the carboxylic group in cis orientation was monitored for 2-furoic acid isolated in Ar and Ne matrixes. The speed of this process was found to be dependent on temperature and on the matrix material. The experimentally determined half-life times of this conformational conversion occurring in the dark are $t_{1/2} = 1390$ min (Ar, 5.5 K); $t_{1/2} = 630$ min (Ar, 15 K); $t_{1/2} = 240$ min (Ne, 5.5 K). The three conformers of 2-furoic acid observed in the present work were identified by comparison of their infrared spectra with the spectra theoretically calculated for the candidate structures.
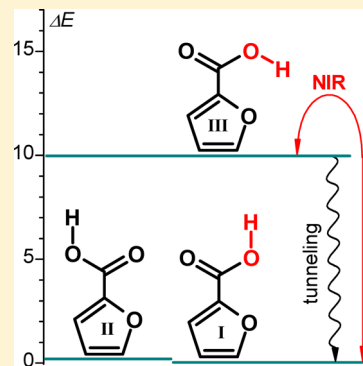
1. INTRODUCTION

2-Furoic acid (called also furan-2-carboxylic acid or pyromucic acid) is one of the smallest compounds with the carboxylic group attached to an unsaturated, planar ring. From the conformational point of view, an important feature of 2-furoic acid is the vicinal position of the carboxylic moiety and the oxygen heteroatom of the furan ring (Chart 1). This allows a

Chart 1. Structures of 2-Furoic Acid and 2-Picolinic Acid
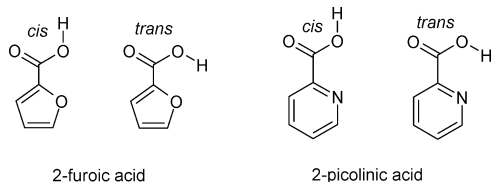
hydrogen-bond-like O−H···O interaction between the ring heteroatom and the OH group of the carboxylic fragment. For compounds where such interactions are absent (e.g., formic acid, acetic acid),[1,2] the carboxylic acid group adopts preferentially the cis conformation (O=C−O−H dihedral equal to 0°). In 2-furoic acid, the hydrogen-bond-like O−H···O interaction is possible only in the conformer where the

carboxylic group adopts the trans orientation (Chart 1) with the OH fragment heading toward the ring. One of the purposes of the present work is investigation of the influence of the interaction described above on the relative stabilities of different conformers of 2-furoic acid.

Studies of conformational equilibria in compounds having a carboxylic group attached to a heterocyclic ring in the α position (with respect to a heteroatom) are very scarce. In fact, we can only refer to the conformational structure observed for monomeric 2-picolinic acid. In this compound, the O−H···N interaction substantially lowers the energy of the conformer with the carboxylic group adopting the trans geometry (Chart 1). The conformer stabilized by this interaction was theoretically predicted as the lowest-energy form of 2-picolinic acid.[3,4] This conformer was found to strongly dominate in the gas phase[4] as well as in low-temperature Ar matrixes (see Figure S1 in the Supporting Information).

Following the example of 2-picolinic acid, one might expect that also in 2-furoic acid the O−H···O interaction between the hydrogen atom of the carboxylic group and the oxygen atom of

the furan ring should make the conformer with the trans orientation of the carboxylic group more stable than the conformers with cis geometry of this fragment. However, it does not need to be necessarily so. The five-membered furan ring enforces the H···O distance (215 pm) in 2-furoic acid to be longer by 15 pm than the H···N distance (200 pm)[5] in 2-picolinic acid with six-membered heterocyclic ring. Moreover, in the two compounds the ring heteroatoms are different, and the O−H···O hydrogen-bond-like interaction in 2-furoic acid can be weaker than the O−H···N hydrogen-bond-like interaction in 2-picolinic acid. Therefore, the conformer of 2-furoic acid with the trans orientation of the carboxylic group does not necessarily need to be the most stable form of the compound.

In the current work, we investigated 2-furoic acid monomers isolated in low-temperature argon and neon matrixes. The compound is a good example of a molecule with two conformationally relevant degrees of freedom (internal rotation of the OH group within the carboxylic moiety and the torsion of the whole carboxylic fragment with respect to the furan ring). Relative stability of the conformers of 2-furoic acid was studied both computationally and experimentally. Furthermore, the structures of the forms trapped in solid argon or neon environment were manipulated by selective excitation of their first OH stretching overtones with narrow-band tunable near-IR light. Finally, a spontaneous hydrogen-atom tunneling, leading to conversion of the higher-energy conformer of 2-furoic acid into the lower-energy form, was observed and analyzed.

2. EXPERIMENTAL SECTION

The sample of 2-furoic acid (purity 98%) used in the present study was a commercial product supplied by Sigma-Aldrich. The solid compound was placed in a glass tube connected through a needle valve to the vacuum chamber of a helium-cooled cryostat. At room temperature, the pressure of gaseous 2-furoic acid over the solid crystals in the evacuated tube was sufficient for preparation of low-temperature matrixes. Vapor of 2-furoic acid was codeposited with large excess of inert gas (argon or neon) onto a CsI window cooled to 15 K (argon matrixes) or 5.5 K (neon matrixes). Two types of closed-cycle refrigerators were used in the matrix-isolation experiments: APD Cryogenics DE-202A (able to cool down to 10 K) and Sumitomo SRDK-408D2 (able to cool down to 3.3 K). Infrared spectra of the matrixes were recorded using a Thermo Nicolet Nexus 6700 FTIR spectrometer equipped with a KBr beam splitter and a DTGS detector (for measurements in the mid-IR range) or with a CaF$_2$ beam splitter and an InGaAs detector (for measurements in the near-IR range). Monomers of 2-furoic acid trapped in low-temperature matrixes were irradiated with narrow-band near-IR laser light. Two sources of tunable near-IR light were used: (i) continuous-wave tunable diode laser Toptica DL100 pro design (fwhm <1 MHz, 40 mW) and (ii) the idler beam of the Quanta-Ray MOPO-SL pulsed (10 ns) optical parametric oscillator (fwhm 0.2 cm^{-1}, repetition rate 10 Hz, pulse energy 10 mJ) pumped with a pulsed Nd:YAG laser. The wavelengths of the near-IR light were measured with HighFinesse WS-5 wavelength meter. The conformational conversions induced by near-IR light emitted by each of the applied lasers were qualitatively the same. To protect matrixes from light with wavenumbers greater than 1700 cm^{-1}, in the experiments on spontaneous conformational transformations, infrared spectra were recorded with a long-pass filter (see the

transmission curve in Figure S2 in the Supporting Information) placed between the spectrometer source and the matrix sample. In some experiments, a high-pressure mercury lamp HBO 200 (fitted with cutoff filters and a water filter) was applied to irradiate the matrix with filtered UV light.

3. COMPUTATIONAL SECTION

The geometries of 2-furoic acid conformers were fully optimized at the DFT(B3LYP),[6−8] MP2,[9] and QCISD[10] levels of theory. The relative energies of the conformers were calculated using the QCISD and MP2 methods, at geometries optimized at the corresponding levels of theory. The harmonic vibrational frequencies and IR intensities were calculated using the DFT(B3LYP), QCISD, and MP2 methods. To approximately correct for the neglected anharmonicity, the harmonic frequencies were scaled by factors of 0.95 (for wavenumbers higher than 2000 cm^{-1}) and 0.98 (for wavenumbers lower than 2000 cm^{-1}).[13] The theoretical normal modes were analyzed by carrying out potential-energy distribution (PED) calculations, performed according to the procedure described in refs 11 and 12. The set of internal coordinates used in the PED analysis was defined following the recommendations of Pulay et al.[14] These coordinates are listed in Table S1 in the Supporting Information. Cartesian force constants were transformed into the force constants with respect to the molecule-fixed internal coordinates. Potential-energy-distribution matrices have been calculated, and the elements of these matrices greater than 10% are given in Tables S2, S3, and S4 (Supporting Information).

The potential-energy surface (PES) of 2-furoic acid was computationally probed by carrying out one-dimensional and two-dimensional scans. At each step along a one-dimensional scan, the value of a chosen coordinate (O=C−O−H dihedral angle or O−C−C=O dihedral angle) was fixed, and all the remaining coordinates, describing the geometry of the molecule, were optimized. At each point of the two-dimensional scan, values of both conformationally relevant dihedral angles (O=C−O−H and O−C−C=O) were fixed, and geometry of the molecule was partially optimized with this restriction.

All quantum-mechanical computations were carried out for monomeric molecules of 2-furoic acid in vacuo, using the Gaussian 09 program[15] with the standard 6-31++G(d,p) or 6-311++G(d,p) basis sets.

4. RESULTS AND DISCUSSION

4.1. Relative Energies of 2-Furoic Acid Conformers. In the molecule of 2-furoic acid there are two conformational degrees of freedom: (i) rotation of the OH group around the C−O bond within the carboxylic moiety and (ii) rotation of the whole carboxylic group with respect to the furan ring. Therefore, the O=C−O−H and O−C−C=O dihedral angles were chosen as the coordinates, along which the potential-energy surface (PES) of 2-furoic acid was scanned. A two-dimensional scan of the PES of the molecule, computed at the MP2/6-31++G(d,p) level, is presented in Figure 1. Energy at each of the points presented in this figure was obtained by fixing the O=C−O−H and O−C−C=O torsional coordinates at chosen values and optimizing all other geometry parameters. Four minima, corresponding to the conformational structures shown in Table 1, were found on the PES of 2-furoic acid (Figure 1). The relative energies of these four conformers, calculated at the DFT(B3LYP)/6-31++G(d,p), MP2/6-31+
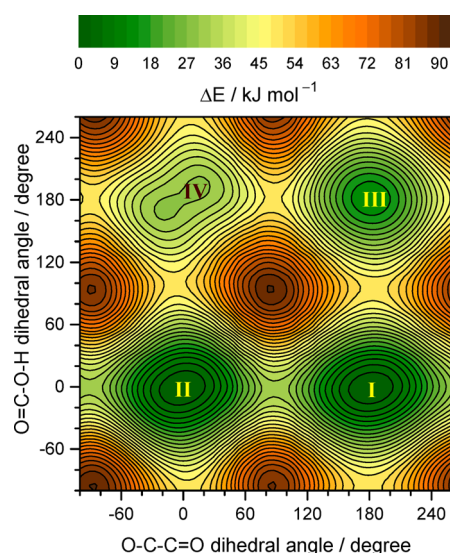
Figure 1. Two-dimensional potential-energy surface calculated, at the MP2/6-31++G(d,p) level of theory, for the molecule of 2-furoic acid. The two dihedral angles used as reaction coordinates are specified on the left and on the bottom of the frame. The color bar at the top designates the relative energy scale. The electronic energy of conformer **I** was chosen as the relative zero. The isoenergy lines are traced with an interval of 3 kJ mol^{-1}.

+G(d,p), and QCISD/6-31++G(d,p) levels, are collected in Table 1. All applied methods predict the lowest energies for structures **I** and **II**. According to the DFT, MP2, and QCISD calculations, these two forms are nearly isoenergetic. In both forms **I** and **II**, the OH bond of the carboxylic moiety adopts the cis orientation. These conformers differ from each other by 180° rotation of the whole carboxylic COOH group with respect to the furan ring.

The calculated relative energy of form **III**, with the hydrogen atom of the carboxylic group directed toward oxygen heteroatom of the ring, is significantly higher [by 11 kJ mol^{-1} (DFT), 10 kJ mol^{-1} (QCISD), or 12 kJ mol^{-1} (MP2)]. This suggests that in the gas phase populations of forms **I** and **II** should be similar, each of them constituting nearly 50% of the

total population of the compound. Alongside the dominating forms **I** and **II**, also conformer **III** should be populated, but in a very small amount (ca. 0.9% at room temperature). The computed relative energy of isomer **IV** is very high (higher than 28 kJ mol^{-1}, at the DFT, MP2, and QCISD levels); hence, a negligible population of this form in the gas phase should be expected.

4.2. The Conformers of 2-Furoic Acid Trapped in Low-Temperature Matrixes. Monomers of 2-furoic acid were trapped from the gas phase into low-temperature argon and neon matrixes. The mid-IR spectra of matrix-isolated 2-furoic acid are presented in Figure 2. These experimental spectra are well reproduced by the sum of the theoretical spectra calculated [at the DFT(B3LYP)/6-311++G(d,p) level] for conformers **I** and **II**. In the experimental spectra, several characteristic bands appear as doublets, for example, the bands due to the OH stretching vibrations (νOH, found at 3567 and 3574 cm^{-1}, Ar), the C=O stretching vibrations (νC=O, found at 1752 and 1767 cm^{-1}, Ar), and the OH torsional vibrations (τOH, found at 540 and 517 cm^{-1}, Ar). This is especially well visible for the compound trapped in solid argon, where the picture is not obscured by multiple matrix sites occupied by isolated molecules (Figure 2). Also in the 2νOH overtone range of near-IR spectrum recorded after deposition of the Ar matrix, a doublet of absorptions appears at 6980 and 6966 cm^{-1} (see Figure 3). Comparison with the calculated spectra strongly suggests that the observed doublets are spectral indications of conformers **I** and **II** trapped, in similar amounts, from the gas phase into low-temperature matrixes. This assumption is directly and unequivocally confirmed by the conformational transformations induced by near-IR irradiation of matrix-isolated 2-furoic acid (see section 4.3).

As far as conformer **III** is concerned, providing a direct experimental evidence of its existence in a low-temperature matrix is not a straightforward task. Because of the small population of **III**, expected on the basis of theoretical computations, it is not easy to distinguish low-intensity IR spectral indications of **III** from numerous absorptions due to **I** and **II**. In that respect, reliable conclusions were drawn from analysis of conformational transformations induced by near-IR irradiation (see section 4.3).

Table 1. Relative Electronic Energies (kJ mol^{-1}) Corrected for Zero-Point Vibrational Energy ($\Delta E = \Delta E_{el} + \Delta ZPE$) of 2-Furoic Acid Conformers^a

	I	II	III	IV
ΔE (DFT)	0.0	0.9	10.9	28.2
ΔE (QCISD)	0.0	0.2	10.0	29.0
ΔE (MP2)	0.3	0.0	11.7	29.0

^{a}Relative electronic energies (ΔE_{el}) were calculated using the DFT(B3LYP), QCISD, and MP2 methods at geometries optimized at the same level. These energies were corrected for ΔZPE energies calculated at the DFT(B3LYP), QCISD, and MP2 levels, respectively. The 6-31++G(d,p) basis set was used in these calculations.
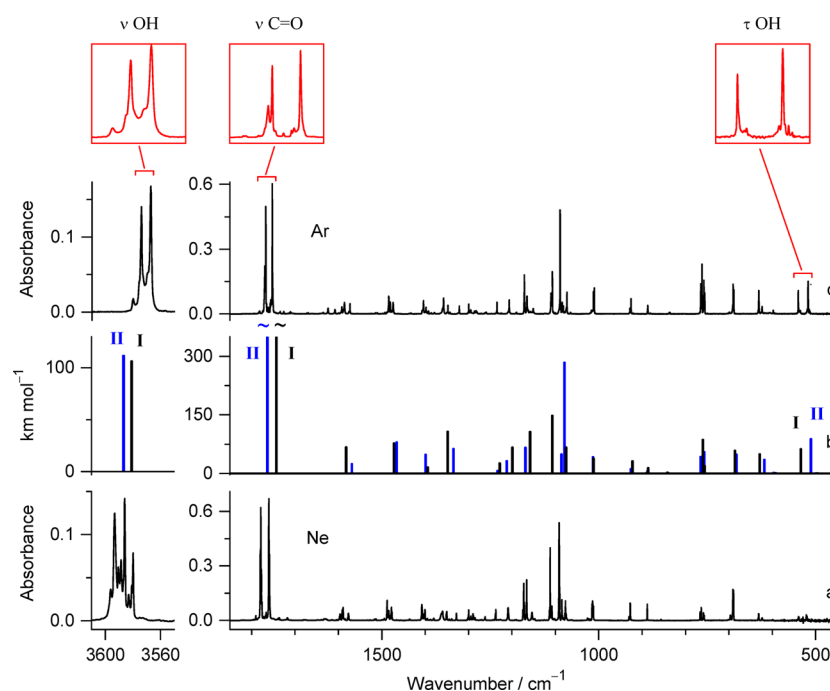
Figure 2. Mid-infrared spectra of 2-furoic acid monomers isolated in (a) neon; (c) argon matrixes compared with (b) the results of harmonic DFT(B3LYP)/6-311++G(d,p) calculations carried out for conformer **I** (black) and conformer **II** (blue). The theoretical wavenumbers were scaled by factors of 0.98 (for the 2000−400 cm^{-1} range) and 0.95 (for the 4000−2000 cm^{-1} range). The two strongest bands in the theoretical spectra were truncated. The boxes present doublet bands due to the νOH, νC=O, and τOH vibrations observed in the infrared spectrum of 2-furoic acid trapped in an Ar matrix.
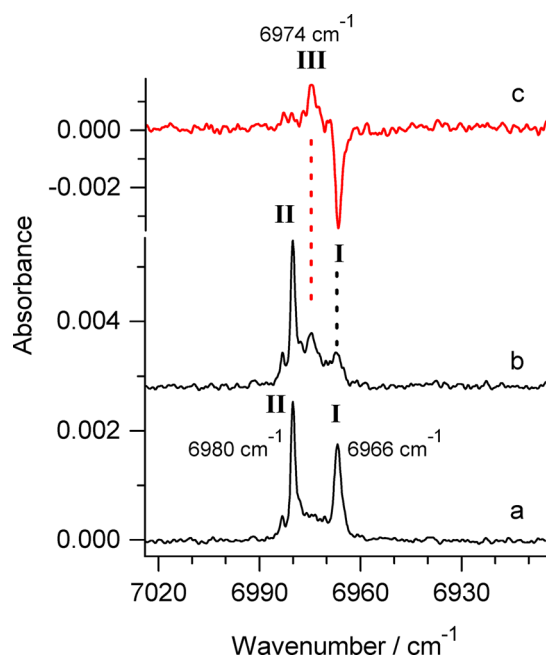

Figure 3. Fragment of the near-infrared spectrum of 2-furoic acid isolated in an Ar matrix: (a) recorded after deposition of the matrix and (b) after irradiation at 6966 cm^{-1}; (c) difference spectrum: trace (b) minus trace (a).

4.3. Light-Induced Transformations of 2-Furoic Acid Conformers.
4.3.1. Near-IR-Induced Conformational Changes in 2-Furoic Acid Isolated in Ar Matrixes.
Monomers of 2-furoic acid trapped in Ar matrixes were irradiated with monochromatic near-IR light, generated in a tunable diode laser or in a tunable optical parametric oscillator. The irradiations

were carried out at the wavelengths where the most intense 2νOH bands were found in the near-IR spectrum of the compound. For 2-furoic acid isolated in solid Ar, two 2νOH absorptions (at 6980 and 6966 cm^{-1}, see Figure 3) appear in the near-IR spectrum. Irradiation of the matrix at 6980 cm^{-1} did not lead to any changes in the populations of the isolated conformers. The near-IR and mid-IR spectra collected after the irradiation at 6980 cm^{-1} were the same as those recorded before any irradiation.

A conformational transformation was induced by excitation at 6966 cm^{-1}, corresponding to other 2νOH absorption observed in the near-IR spectrum (Figure 3). The structural changes occurring upon irradiation at this wavelength were revealed by intensity changes of absorption bands in the near-IR and mid-IR spectra, with respect to the intensities observed in the spectra recorded before any irradiation. One set of near-IR and mid-IR bands decreased in intensity, the bands belonging to another set remained unchanged, whereas intensities of a third set of bands, very weak in the initial spectra, substantially increased (Figures 3 and 4). Analysis of the spectral changes observed in the 2νOH, νOH, νC=O, and τOH regions, carried out by comparison with the theoretical spectra of **I** and **II** (Figure 4), clearly shows that conformer **I** reacts upon near-IR excitation, whereas structure **II** should be assigned to the nonreactive species. The juxtaposition of the experimental and theoretical spectra (shown in Figure 4) suggests also that the photogenerated form is conformer **III** of 2-furoic acid. In the theoretical spectrum of **III**, a characteristic, very strong band due to βOH vibration is predicted at 1309 cm^{-1}. In the experimental spectra of near-IR-irradiated matrixes, very strong bands grew at 1321 cm^{-1} (Ar); see Table S4 in the Supporting Information. Moreover, the band due to the νC=O vibration in **III** is predicted to appear at
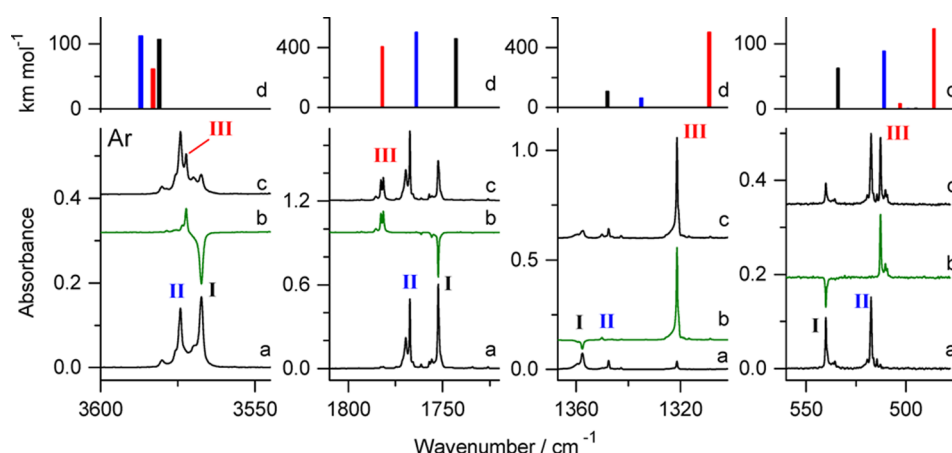
Figure 4. Fragments of the mid-infrared spectra of 2-furoic acid isolated in an Ar matrix: (a) recorded after deposition of the matrix; (c) after irradiation at 6966 cm^{-1}; (b) difference spectrum: trace (c) minus trace (a); (d) the spectra calculated at the DFT(B3LYP)/6-311++G(d, p) level for conformer **I** (black), conformer **II** (blue), and conformer **III** (red). The computed wavenumbers were scaled by factors of 0.98 (for the 2000−400 cm^{-1} range) and 0.95 (for the 4000−2000 cm^{-1} range).
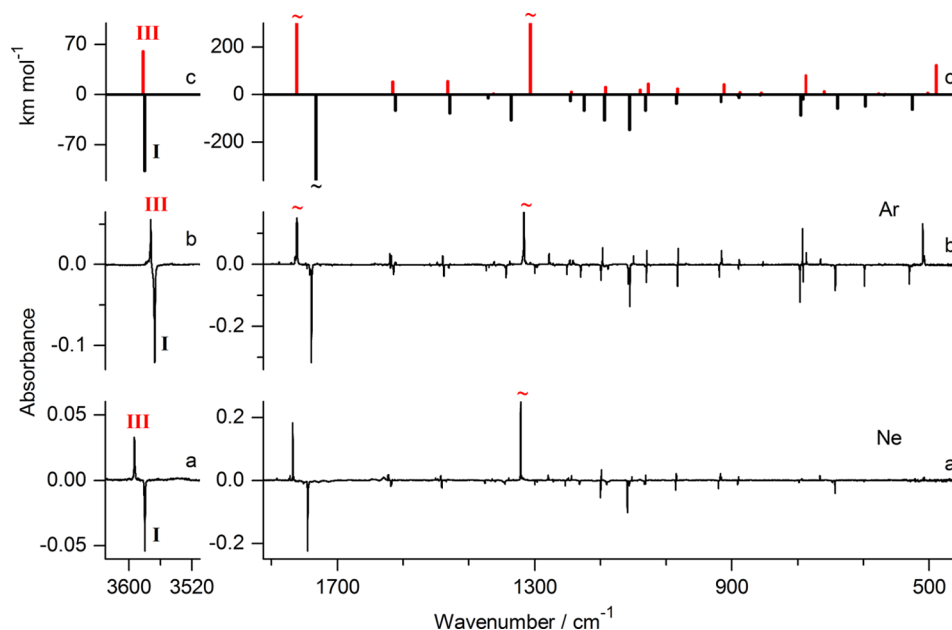

Figure 5. Comparison of the difference spectra (traces a and b) obtained by subtraction of the spectrum recorded before any irradiation from that recorded after near-IR irradiation at 6966 cm^{-1} (Ar) and at 6992 cm^{-1} (Ne); with (c) the results of harmonic DFT(B3LYP)/6-311++G(d,p) calculations for conformers **I** (represented as negative bars) and **III** (represented as positive bars). The theoretical wavenumbers were scaled by factors of 0.98 (for the 2000−400 cm^{-1} range) and 0.95 (for the 4000−2000 cm^{-1} range). The strongest bands in the experimental and theoretical spectra were truncated.

higher wavenumber than the analogous νC=O bands in the spectra of conformers **I** and **II**. And indeed, in the experimental spectra, the νC=O band increasing upon near-IR irradiation grows at a higher wavenumber with respect to the strong νC=O bands present in the spectra recorded before any irradiation (see Figure 4). Assignment of the conformer consumed by near-IR excitation to structure **I** and identification of the photoproduced form as structure **III** is confirmed by the analysis of the whole mid-IR spectrum (Figure 5). The experimental pattern of bands decreasing and increasing upon near-IR irradiation are well reproduced by the spectra calculated for **I** and **III**, respectively. Hence, the observed near-IR-induced conformational change is the **I** → **III** transformation (Scheme 1). This structural alteration concerns displacement of the hydrogen atom that changes the

orientation of the OH group in the carboxylic moiety from cis to trans.

All the IR bands due to photogenerated form **III** grew at the spectral positions, where very-low-intensity absorptions were present in the spectrum recorded before any irradiation (Figure 6). This demonstrates that a small population of conformer **III** was trapped from the gas phase and frozen into low-temperature matrixes. The experimental observation of a very small population of form **III**, together with much higher populations of **I** and **II**, is in full agreement with the theoretical prediction. Note that the population of **III**, observed after deposition of a matrix, is probably somewhat smaller than that present in the gas phase. The hydrogen-atom tunneling, occurring in low-temperature matrixes (see section 4.4), results in spontaneous transformation of the higher-energy form **III**

Scheme 1. Observed Conformers of 2-Furoic Acid and the Photoreaction Scheme[a]
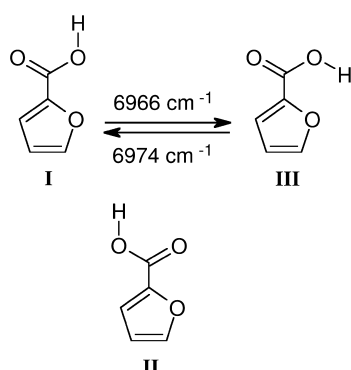
[a]Wavenumbers promoting the reaction refer to the compound isolated in an Ar matrix.
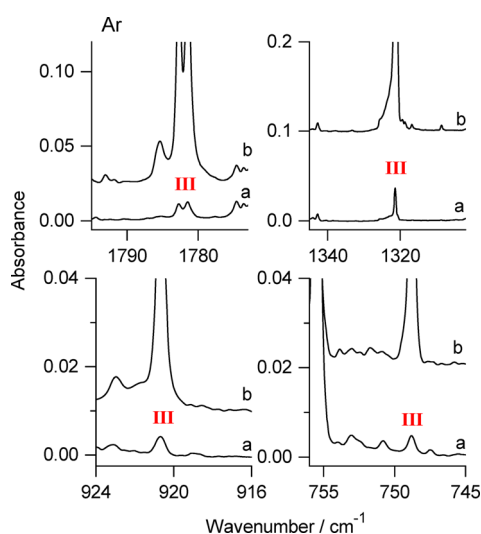

Figure 6. Spectral indications of the presence of conformer **III** in a freshly deposited Ar matrix. Fragments of the mid-infrared spectra of 2-furoic acid isolated in an Ar matrix: (a) recorded after deposition of the matrix; (b) recorded after irradiation at 6966 cm^{-1}.

into the lower-energy conformer **I**. This process reduces the population of matrix-isolated **III** during the period of matrix deposition (ca. 100 min). Obviously, spontaneous **III** → **I** tunneling continues throughout the whole experiment.

In the near-IR region of the spectrum recorded after irradiation at 6966 cm^{-1} (Ar), the 2νOH band of photo-produced form **III** grew at 6974 cm^{-1} (Figure 3). Subsequent excitation of **III** at this wavenumber (6974 cm^{-1}) resulted in depopulation of form **III** and repopulation of conformer **I** (Figure 7). Hence, the photoreversibility of the **I** ↔ **III** conformational transformation was demonstrated. Using consecutive irradiations at 6966 and 6974 cm^{-1}, we were able to shift the population from conformer **I** to **III** and in the opposite **III** → **I** direction. No detectable changes in the population of form **II** accompanied the near-IR-induced conversions of **I** into **III** and **III** into **I** (see the difference spectra in Figure 7).

4.3.2. Near-IR-Induced Conformational Changes in 2-Furoic Acid Isolated in Ne Matrixes. In the spectra of 2-furoic acid freshly trapped in Ne matrixes, the pattern of absorption bands due to the νOH vibrations (Figure 8a) is more complex
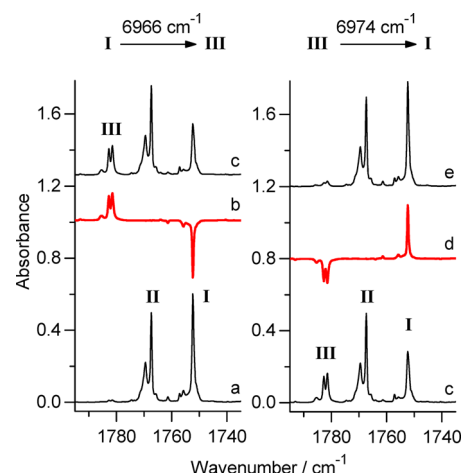

Figure 7. Near-IR-induced transformations of conformer **I** into conformer **III** (left panel) and of **III** into **I** (right panel): (a) the spectrum recorded after deposition of an Ar matrix; (c) the spectrum recorded after irradiation at 6966 cm^{-1}; (e) the spectrum recorded after subsequent irradiation at 6974 cm^{-1}; (b) difference spectrum: trace (c) minus trace (a); (d) difference spectrum: trace (e) minus trace (c). Observe no change of the population of conformer **II** upon irradiations at 6966 and at 6974 cm^{-1}.
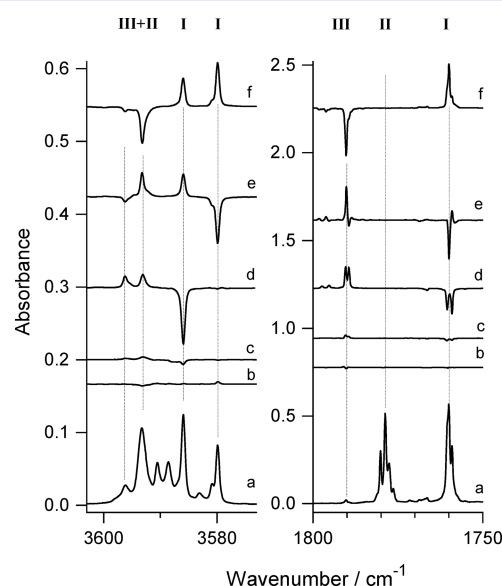

Figure 8. Near-IR irradiations of 2-furoic acid isolated in a Ne matrix. (a) Fragments of the spectrum recorded after deposition of the matrix; (b−f) effects of consecutive irradiations presented as the difference spectra (after irradiation minus before that irradiation): (b) after irradiation at 7020 cm^{-1}; (c) after irradiation at 7010 cm^{-1}; (d) after irradiation at 7005 cm^{-1}; (e) after irradiation at 6992 cm^{-1}; (f) after subsequent irradiation at 7020 cm^{-1}.

than the simple pattern, consisting of two νOH bands, observed in the spectra of the compound isolated in solid Ar (Figure 2). Equally complex is the set of 2νOH bands found in near-IR range of the spectrum of 2-furoic acid isolated in Ne matrixes (Figure 9). Interestingly, the pattern of the 2νOH bands looks very analogous to that of the νOH bands, only with wavenumbers approximately doubled. The most probable reason for multiple νOH and 2νOH bands, observed for 2-furoic acid in Ne matrixes, is trapping of isolated molecules in different cages (sites) of solid neon.
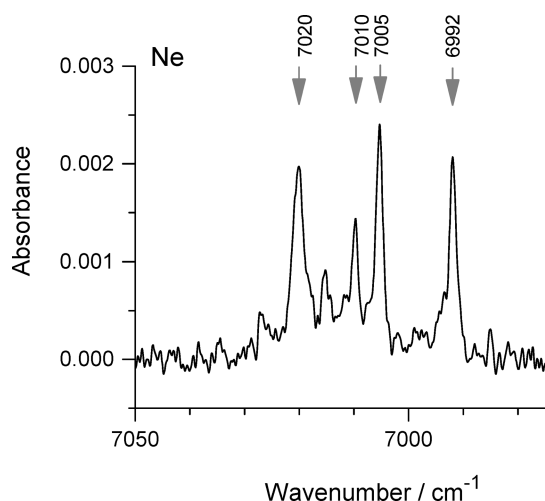
Figure 9. Fragment of the near-IR spectrum of 2-furoic acid isolated in a Ne matrix. Arrows indicate the wavenumbers applied during laser irradiations of the matrix.

Irradiation at 7020 cm^{-1} caused only very tiny changes in the infrared spectra of 2-furoic acid isolated in Ne matrixes (Figure 8b). The effect of irradiation of Ne matrixes at 7010 cm^{-1} was also very small (Figure 8c). By analogy with the experiments carried out for Ar matrixes, the 2νOH bands at 7020 and 7010 cm^{-1}, found in the spectra of Ne matrixes, can be interpreted as spectroscopic signatures of conformer **II** trapped in different sites. Small spectral changes induced by excitation at 7020 cm^{-1} can be treated as results of excitation of conformer **III** slightly populated in Ne matrixes prior to any irradiation. The reason why **III** was excited by irradiation at 7020 cm^{-1} (where 2νOH band due to **II** is present in the absorption spectrum) is the overlap of the 2νOH bands due to **II** and **III** conformers in the spectra of 2-furoic acid isolated in solid Ne (vide infra, see also Figure S3 in the Supporting Information).

Pronounced changes in the spectra of 2-furoic acid isolated in Ne matrixes were induced by irradiation at 7005 cm^{-1} (Figure 8d). Upon excitation at this wavenumber a set of infrared absorptions (involving the νOH band at 3586 cm^{-1} and the νC=O band at 1760 cm^{-1}) decreased in intensity, whereas intensities of a set of initially very small bands (such as the νOH bands at 3596 and 3593 cm^{-1} and the νC=O band at 1790 cm^{-1}) increased substantially. These spectral changes can be interpreted as indications of the **I** → **III** conformational transformation concerning the molecules in one of the trapping sites of Ne matrix (site "A"). Subsequent irradiation at 6992 cm^{-1} had similar effect (Figure 8e). In the 2000–400 cm^{-1} range of the spectrum, most of the decreasing bands were at the same (or very close) wavenumbers as those decreasing upon irradiation at 7005 cm^{-1}. Also the bands growing after irradiation at 6992 cm^{-1} appeared at nearly the same wavenumbers as those growing upon irradiation at 7005 cm^{-1}. This strongly suggests that excitation at 6992 cm^{-1} induced the **I** → **III** transformation, analogous to that occurring upon irradiation at 7005 cm^{-1}, but concerning the molecules trapped in another matrix site (site "B"). As can be seen in Figure 8e, irradiation of the Ne matrix at 6992 cm^{-1} caused not only the **I** → **III** conversion but also transformation of the local matrix environment, so that the population of conformer **I** trapped in the site A (characterized by the νOH absorption at 3586 cm^{-1}) grew at the cost of the population of **I** trapped in site B (characterized by the νOH absorption at 3580 cm^{-1}).

Among the bands growing upon irradiations at 7005 and 6992 cm^{-1}, the characteristic and very strong absorption appeared at 1328 cm^{-1} (Figure 5a and Figure S4 in the Supporting Information). This provides further evidence supporting the interpretation of the processes induced by excitations at 7005 and 6992 cm^{-1} in terms of **I** → **III** conformational change. Note that the νOH band due to conformer **III** (growing at 3593 cm^{-1}) overlaps with the νOH band of form **II** already present in the spectrum recorded before any irradiation. The same is the case for the 2νOH overtone bands in the spectra of conformers **II** and **III**, both appearing at 7020 cm^{-1}. This accidental overlap causes intensity changes at the spectral positions of νOH and 2νOH bands due to **II**, in spite of the fact that the population of **II** does not change upon near-IR irradiations of matrix-isolated 2-furoic acid. Lack of near-IR-induced changes in population of **II** is well illustrated by no change of the intensity of the νC=O band due to form **II** at 1779 cm^{-1} (see the difference traces b, c, d, e, and f in the right panel of Figure 8).

Photoreversibility of the **I** ↔ **III** near-IR-induced conformational conversion in a Ne matrix was experimentally proven by excitation of 2-furoic acid at 7020 cm^{-1}, where the 2νOH overtone absorption due to **III** grew upon previous irradiations at 7005 and 6992 cm^{-1}. Interpretation of the effects of irradiation at 7020 cm^{-1} is quite easy; all the intensity changes presented in Figure 8f indicate occurrence of the **III** → **I** transformation, leading to depopulation of form **III** and repopulation of form **I**, in both trapping sites of a Ne matrix. Indeed, after the final irradiation at 7020 cm^{-1}, the mid-IR and near-IR spectra of 2-furoic acid isolated in Ne matrix were nearly the same as those recorded before any irradiation.

4.3.3. Effects of UV Irradiation on 2-Furoic Acid Monomers. In a dedicated experiment, monomers of 2-furoic acid trapped in an Ar matrix were irradiated with broadband UV light. Irradiation at $\lambda > 270$ nm led to generation of conformer **III**, the same form that was produced upon near-IR excitation at 6966 cm^{-1} (see Figure S5 in the Supporting Information). In contrast with the effects of near-IR irradiation, where conformer **III** was populated only at cost of **I**, by UV($\lambda > 270$ nm) excitation, increase of population of **III** was accompanied by decrease of population of **I** and of **II**. This shows that UV excitation, providing significantly more energy to the molecule, allows rotation of the whole carboxylic group or a hydrogen-atom transfer within this group. By the UV($\lambda > 270$ nm) excitations, alongside the conformational conversions in 2-furoic acid, there occurred some photodecomposition of the compound. This was indicated by appearance of the spectral signatures of evolving CO_2.

Irradiation at shorter UV wavelengths ($\lambda > 230$ nm) resulted in further, more vigorous photodecomposition of 2-furoic acid. Among the emerging IR bands of the photoproducts, those due to CO_2 and furan[16,17] were identified. This indicates photodecarboxylation as one of the important channels of UV-induced decomposition of 2-furoic acid.

4.4. Spontaneous Conversion of the Higher-Energy Conformer III to the Most Stable Form I.
Low-temperature argon and neon matrixes, with form **III** populated by near-IR excitation at 6966 cm^{-1} (Ar) or at 6992 cm^{-1} (Ne), were kept for several hours at low temperature and in the dark. The progress of the spontaneous processes changing the conformational structure of matrix-isolated molecules was periodically monitored by recording the mid-IR spectra. The spectra were collected in the limited 1700–450 cm^{-1} range, with a filter

(transmitting only light with $\tilde{\nu} < 1700$ cm^{-1}, see Figure S2 in the Supporting Information) placed between the spectrometer sources and the matrix. This protected the studied molecules from excitations with energies higher than 20 kJ mol^{-1} (which is an energy equivalent of 1700 cm^{-1}). When spectra were not recorded, the spectrometer beams were totally blocked with a metal plate.

Three experiments of this kind were performed: (i) with an Ar matrix kept at 15 K, (ii) with an Ar matrix kept at 5.5 K, and (iii) with a Ne matrix kept at 5.5 K. In all three experiments, a spontaneous conversion of the photoproduced, higher-energy form **III** into the most stable conformer **I** was observed. During the whole monitored period, the mid-IR bands in the spectrum of **III** were systematically decreasing, whereas the intensities of the bands due to **I** were systematically increasing. Quantitatively, the progress of the **III** → **I** transformation was followed by periodical measurements of the intensity of the characteristic band in the spectrum of **III**, observed at 1321 cm^{-1} (Ar) and at 1328 cm^{-1} (Ne). The intensity decrease of this band is presented in Figure 10 as a function of time of keeping the matrixes in the dark.

Data shown in Figure 10 clearly demonstrate that the rate of the **III** → **I** spontaneous conversion depends on two factors: the matrix material and the temperature. For the matrixes kept at 5.5 K, the difference between the half-life time of **III** in an Ar matrix ($t_{1/2}$ = 1390 min) and the half-life time of **III** in a Ne matrix ($t_{1/2}$ = 240 min) is drastic. The progress of the **III** → **I** spontaneous conversion in solid neon is much faster than the analogous process occurring in solid argon. This observation is analogous to the trans → cis tunneling in formic acid,[18] where the process in solid neon was 2 orders of magnitude faster than in solid argon. However, it is not always the case that the hydrogen-atom tunneling, leading to a trans ↔ cis conformational change within a carboxylic group, systematically occurs much faster in neon than in argon matrixes. For example, spontaneous hydrogen-atom tunneling processes in such α-ketocarboxylic acids as pyruvic and cyclopropylglyoxylic acids[19] are several times faster for the compounds isolated in argon than in neon matrixes, whereas for oxamic acid[20] and phenylglyoxylic acid[19] the rates of hydrogen-atom tunneling are nearly the same in both matrixes.

The theoretically predicted barrier height for the **III** → **I** conversion is 37.7 kJ mol^{-1} (Figure 11b). Although this barrier is somewhat higher than the barrier for the **I** ↔ **II** conformational change (32.0 kJ mol^{-1}, see Figure 11a), this latter process does not occur, whereas the **III** → **I** conversion occurs spontaneously even at temperature as low as 5.5 K. This must be related to the fact that during the **III** → **I** transformation the only particle significantly changing its position is a light hydrogen atom, while the **I** ↔ **II** conversion would involve considerable movement of the whole carboxylic group including two heavy oxygen atoms. Hence, in the **III** → **I** process, hydrogen-atom tunneling can play an important role, but no quantum-tunneling effect is expected for the torsion of a carboxylic group consisting of much heavier atoms.

No dependence on temperature is often treated as a characteristic feature of a process governed by quantum tunneling. The results presented in Figure 10 clearly show that the **III** → **I** transformation in 2-furoic acid (isolated in solid Ar) is faster at 15 K ($t_{1/2}$ = 630 min) than at 5.5 K ($t_{1/2}$ = 1390 min). On the other hand, in a process involving considerable barrier (37.7 kJ mol^{-1}) and displacement of only one light particle (hydrogen atom), quantum tunneling
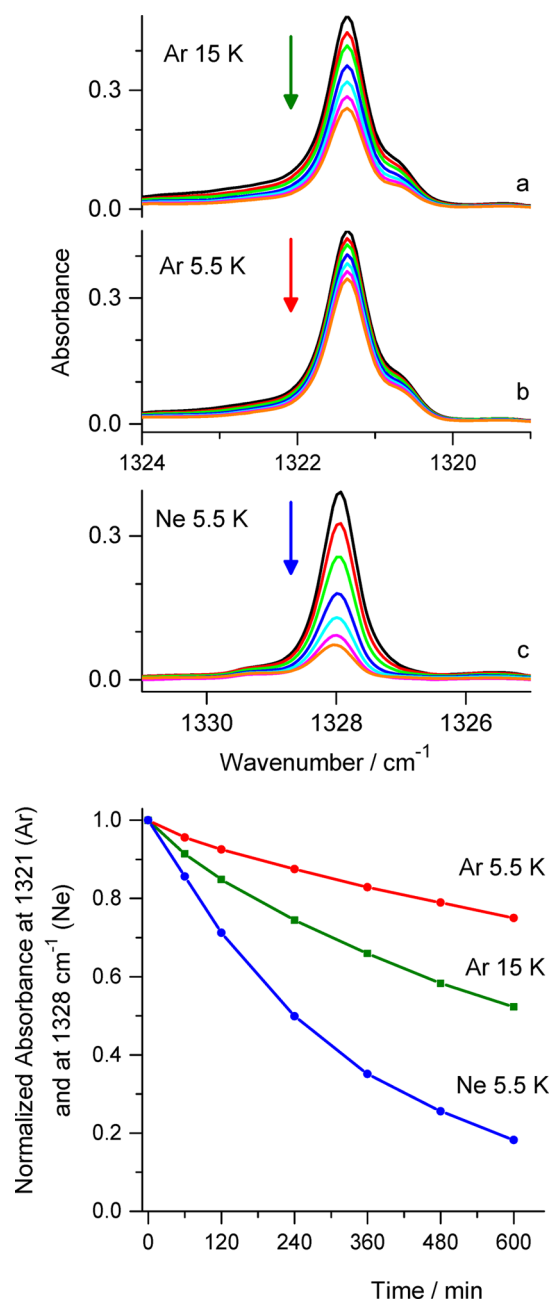

Figure 10. Comparison of the rate of the spontaneous **III** → **I** transformation occurring in the dark for 2-furoic acid isolated in solid Ar at 15 K (a), in solid Ar at 5.5 K (b), and in solid Ne at 5.5 K (c). The progress of the process was monitored as the intensity decrease of the bands due to conformer **III** observed at 1321 cm^{-1} (Ar) and at 1328 cm^{-1} (Ne). These bands appeared after irradiation at 6966 cm^{-1} (Ar) and at 6992 cm^{-1} (Ne). Arrows in panels (a), (b), and (c) designate the direction of changes. Bottom panel: decrease of the intensity of the band at 1321 cm^{-1} (Ar) as a function of time of keeping the Ar matrix in the dark and at 15 K (green) or at 5.5 K (red); decrease of the intensity of the band at 1328 cm^{-1} (Ne) as a function of time of keeping the Ne matrix in the dark and at 5.5 K (blue). Zero minutes indicates the time when irradiation at 6966 cm^{-1} (Ar) or at 6992 cm^{-1} (Ne) ceased.

obviously must play an important role. Therefore, it looks that quantum tunneling as well as temperature contribute (both as important, rate-determining factors) to crossing the barrier for the **III** → **I** conformational change. Temperature
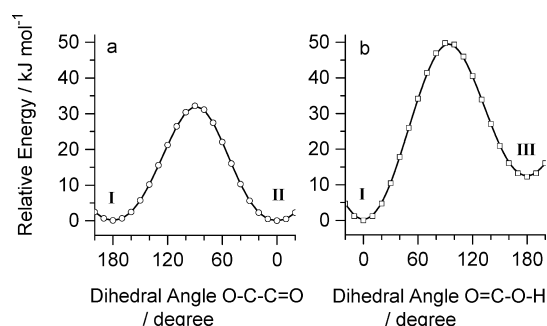
Figure 11. Barriers for interconversion: (a) between **I**–**II** and (b) between **I**–**III** conformers of 2-furoic acid, obtained by relaxed potential-energy scans carried out at the MP2/6-31++G(d,p) level. At each point a value of the O–C–C=O (panel a) or O=C–O–H (panel b) torsional angle was fixed, and all remaining geometry parameters were optimized.

dependence of tunneling rate was previously observed for formic,[1] acetic,[2] and glyoxylic[19] acids[21,22] isolated in low-temperature matrixes. This effect was interpreted in terms of participation of the solid-lattice phonon modes in the tunneling process.[1,22]

4.5. Remarks on the Infrared Spectra of 2-Furoic Acid Isolated in Low-Temperature Matrixes. The light-induced conformational changes, described in section 4.3, allowed separation of the infrared spectra of **I**, **II**, and **III** conformers of 2-furoic acid. The bands decreasing upon near-IR excitation at 6966 cm^{-1} (Ar) and at 7005 or 6992 cm^{-1} (Ne) were assigned to conformer **I**, the bands growing upon excitation at these wavenumbers were attributed to conformer **III**, whereas the bands unaffected by irradiation with near-IR light were interpreted as spectral indications of form **II**.

The mid-IR bands appearing in the experimental spectra of **I**, **II**, and **III** were assigned to the normal modes, theoretically calculated at the DFT(B3LYP)/6-311++G(d,p) level. The results of this assignment are given in Tables S2, S3, and S4 in the Supporting Information.

In the structure of forms **I** and **II**, the OH group within the carboxylic fragment adopts the cis orientation. The infrared bands due to the OH stretching vibrations (νOH) in conformers **I** and **II** appear at 3567 cm^{-1} (Ar) and 3574 cm^{-1} (Ar), respectively. These wavenumbers are typical of the bands due to the stretching vibrations of OH groups belonging to the carboxylic O=C–O–H moieties in a cis configuration. Analogous bands were found at 3551, 3555, 3567, 3556, 3561, and 3556 cm^{-1} in the spectra of, respectively, formic acid,[23] oxamic acid,[20] benzoic acid,[24] pyruvic acid,[19,25] glycolic acid,[26,27] and glyoxylic acid[19] isolated in Ar matrixes.

In the spectrum of form **III**, where the hydrogen atom of the OH group is directed to the oxygen atom of the ring, the νOH band appears at 3572 cm^{-1} (Ar). This is quite a high wavenumber, as for an OH group involved in a hydrogen-bond-like interaction with a heteroatom (oxygen of the furan ring). It shows that the O–H···O interaction in form **III** of 2-furoic acid is weak. Similar spectral positions of the νOH bands in forms **I**, **II**, and **III** indicate that the O–H···O hydrogen-bond-like interactions within the cis-oriented carboxylic groups (form **I** and **II**) are of the same strength as the O–H···O interaction with the oxygen atom of the ring (form **III**).

For comparison, in a compound such as 2-picolinic acid, where the interaction of the carboxylic OH group and the nitrogen heteroatom of the ring is strong, the νOH band is

shifted to a wavenumber as low as 3340 cm^{-1} (see Figure S1 in the Supporting Information). As a consequence of a weak interaction with the oxygen atom of 2-furoic acid ring, the conformers **I** and **II** (with the cis orientation of the carboxylic fragment) are more stable than form **III** with trans orientation of the O=C–O–H group. For 2-picolinic acid, where the interaction of the OH group with the heteroatom of the ring is much stronger, the conformer with the trans orientation of the O=C–O–H fragment is so much stabilized by the O–H···N interaction that this form is most populated in the gas phase and in low-temperature matrixes (see Figure S1 in the Supporting Information).

In the 650–450 cm^{-1} range of the mid-IR spectra of 2-furoic acid (Figure 2), a striking feature is the intensity difference between the bands due to the compound isolated in solid Ar and analogous bands recorded for Ne matrixes. For argon matrixes, the intensities of the bands in this region (relatively to the intensities of other bands in the mid-IR spectrum) correspond well to the theoretical prediction; the intensities of the low-frequency bands found in the spectrum of the compound isolated in neon matrixes are much lower. The bands in question (appearing in the 650–450 cm^{-1} range) are due to normal modes having significant contributions from the τOH vibrations (see Tables S2 and S3, in the Supporting Information). Similar influence of Ne matrix environment on the torsional vibrations of OH and NH$_2$ groups was observed in the recent study on oxamic acid.[20] Also for this latter compound, the intensities of the bands due to τOH and τNH$_2$ vibrations were several times lower in the spectra of Ne matrixes than in the spectra of Ar matrixes.

5. CONCLUSIONS

Conformers of 2-furoic acid were investigated for the compound isolated in Ar and Ne matrixes. Two forms of 2-furoic acid, both with the cis orientation of the OH group in the carboxylic fragment, were trapped from the gas phase to low-temperature, inert-gas environment. These two conformers differ by 180° rotation of the whole carboxylic group with respect to the furan ring. Near-IR excitation of the matrix-isolated compound led to conformational transformation of only one of these forms. As a result of excitation to 2νOH overtone, a third form of 2-furoic acid was generated (Scheme 1). In the structure of this form, the hydrogen atom of the OH group is oriented toward the oxygen atom of the furan ring. The observed near-IR-induced conformational change in 2-furoic acid concerned only the flip of the OH group within the carboxylic fragment from cis to trans configuration. In spite of the excitation energy (83.7 kJ mol^{-1}) significantly exceeding the barrier for rotation of the whole carboxylic group (32.0 kJ mol^{-1}), no near-IR-induced rotation of the carboxylic group, with respect to the furan ring, was detected.

Spontaneous transformation of the near-IR-generated conformer back into the form with cis orientation of the carboxylic group was observed for 2-furoic acid isolated in Ar and Ne matrixes. Dependence of the rate of this process on the matrix material and on temperature has been experimentally demonstrated.

Theoretical and experimental studies of relative stabilities of conformational structures of 2-furoic acid, as well as observations of νOH infrared band positions in the spectra of three forms of the compound, indicate that the hydrogen-bond-like interaction between the OH group and the oxygen atom of the furan ring is weak. That is why the structure where this

hydrogen-bond-like interaction exists is not more stable than the conformers, where this interaction is absent. Weakness of the O−H···O intramolecular interaction in 2-furoic acid can be related to the geometry of the five-membered ring, making the distance between the carboxylic hydrogen and the heteroatom in the ring longer than for analogous compounds (such as 2-picolinic acid) with the carboxylic group attached to a six-membered ring.

As far as we are aware, this is the first thorough study on conformers of 2-furoic acid and their light-induced and spontaneous transformations.

ASSOCIATED CONTENT

Supporting Information

Figure S1, presenting the mid-IR spectrum of 2-picolinic acid isolated in an Ar matrix; Figure S2, showing the transmission range of the long-pass filter used in the present work; Figures S3 and S4, illustrating the effect of near-IR irradiations of 2-furoic acid isolated in Ne matrixes; Figure S5, showing the result of UV irradiation of 2-furoic acid isolated in an Ar matrix; Table S1, collecting the internal coordinates used in the normal-mode analysis; Tables S2, S3, and S4 with the assignment of the mid-IR bands observed in the spectra of conformers **I**, **II**, and **III**, respectively, to the normal modes calculated for these structures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mjnowak@ifpan.edu.pl.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Pettersson, M.; Maçôas, E. M. S.; Khriachtchev, L.; Lundell, J.; Fausto, R.; Räsänen, M. Cis → Trans Conversion of Formic Acid by Dissipative Tunneling in Solid Rare Gases: Influence of Environment on the Tunneling Rate. *J. Chem. Phys.* **2002**, *117*, 9095−9098.

(2) Maçôas, E. M. S.; Khriachtchev, L.; Pettersson, M.; Fausto, R.; Räsänen, M. Rotational Isomerism of Acetic Acid Isolated in Rare-Gas Matrices: Effect of Medium and Isotopic Substitution on IR-Induced Isomerization Quantum Yield and Cis → Trans Tunneling Rate. *J. Chem. Phys.* **2004**, *121*, 1331−1338.

(3) Koczon, P.; Dobrowolski, J. C.; Lewandowski, W.; Mazurek, A. P. Experimental and Theoretical IR and Raman Spectra of Picolinic, Nicotinic, and Isonicotinic Acids. *J. Mol. Struct.* **2003**, *655*, 89−95.

(4) Peña, I.; Varela, M.; Franco, V. G.; López, J. C.; Cabezas, C.; Alonso, J. L. Picolinic and Isonicotinic Acids: A Fourier Transform Microwave Spectroscopy Study. *J. Phys. Chem. A* **2014**, *118*, 11373−11379.

(5) The distances were obtained by geometry optimizations at the DFT(B3LYP)/6-311++G(d,p) level.

(6) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(7) Lee, C. T.; Yang, W. T.; Parr, R. G. Development of the Colle−Salvetti Correlation-Energy Formula into a Functional of the Electron-Density. *Phys. Rev. B* **1988**, *37*, 785−789.

(8) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin Density Calculations: A Critical Analysis. *Can. J. Phys.* **1980**, *58*, 1200−1211.

(9) Møller, C.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46*, 618−622.

(10) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. Quadratic Configuration Interaction. A General Technique for Determining Electron Correlation Energies. *J. Chem. Phys.* **1987**, *87*, 5968−5975.

(11) Keresztury, G.; Jalsovszky, G. An Alternative Calculation of the Vibrational Potential Energy Distribution. *J. Mol. Struct.* **1971**, *10*, 304−305.

(12) Rostkowska, H.; Lapinski, L.; Nowak, M. J. Analysis of the Normal Modes of Molecules with D_{3h} Symmetry. Infrared Spectra of Monomeric *s*-Triazine and Cyanuric Acid. *Vibr. Spectrosc.* **2009**, *49*, 43−51.

(13) Lapinski, L.; Rostkowska, H.; Nowak, M. J.; Kwiatkowski, J. S.; Leszczynski, J. Infrared Spectra of Thiouracils: Experimental Matrix Isolation and Ab Initio Hartree-Fock, Post Hartree-Fock, and Density Functional Theory Studies. *Vibr. Spectrosc.* **1996**, *13*, 23−40.

(14) Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. Systematic Ab Initio Gradient Calculation of Molecular Geometries, Force Constants, and Dipole Moment Derivatives. *J. Am. Chem. Soc.* **1979**, *101*, 2550−2560.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

(16) Kuş, N.; Reva, I.; Fausto, R. Photoisomerization and Photochemistry of Matrix-Isolated 3-Furaldehyde. *J. Phys. Chem. A* **2010**, *114*, 12427−12436.

(17) Sánchez-García, E.; Mardyukov, A.; Studentkowski, M.; Montero, L. A.; Sander, W. Furan−Formic Acid Dimers: An Ab Initio and Matrix Isolation Study. *J. Phys. Chem. A* **2006**, *110*, 13775−13785.

(18) Marushkevich, K.; Khriachtchev, L.; Räsänen, M. High-Energy Conformer of Formic Acid in Solid Neon: Giant Difference Between the Proton Tunneling Rates of cis Monomer and trans−cis Dimer. *J. Chem. Phys.* **2007**, *126*, 241102.

(19) Gerbig, D.; Schreiner, P. R. Hydrogen-Tunneling in Biologically Relevant Small Molecules: The Rotamerizations of *α*-Ketocarboxylic Acids. *J. Phys. Chem. B* **2015**, *119*, 693−703.

(20) Halasa, A.; Lapinski, L.; Rostkowska, H.; Reva, I.; Nowak, M. J. Tunable Diode Lasers as a Tool for Conformational Control: The Case of Matrix-Isolated Oxamic Acid. *J. Phys. Chem. A* **2015**, DOI: 10.1021/jp501448m.

(21) Tsuge, M.; Khriachtchev, L. Tunneling Isomerization of Small Carboxylic Acids and Their Complexes in Solid Matrixes: A Computational Insight. *J. Phys. Chem. A* **2015**, DOI: 10.1021/jp509692b.

(22) Maçôas, E. M. S.; Khriachtchev, L.; Pettersson, M.; Lundell, J.; Fausto, R.; Räsänen, M. Infrared-Induced Conformational Interconversion in Carboxylic Acids Isolated in Low-Temperature Rare-Gas Matrices. *Vibr. Spectrosc.* **2004**, *34*, 73−82.

(23) Pettersson, M.; Lundell, J.; Khriachtchev, L.; Räsänen, M. IR Spectrum of the Other Rotamer of Formic Acid, cis-HCOOH. *J. Am. Chem. Soc.* **1997**, *119*, 11715−11716.

(24) Stepanian, S. G.; Reva, I. D.; Radchenko, E. D.; Sheina, G. G. Infrared Spectra of Benzoic Acid Monomers and Dimers in Argon Matrix. *Vibr. Spectrosc.* **1996**, *11*, 123−133.

(25) Reva, I. D.; Stepanian, S. G.; Adamowicz, L.; Fausto, R. Combined FTIR Matrix Isolation and Ab Initio Studies of Pyruvic Acid: Proof for Existence of the Second Conformer. *J. Phys. Chem. A* **2001**, *105*, 4773−4780.

(26) Reva, I. D.; Jarmelo, S.; Lapinski, L.; Fausto, R. First Experimental Evidence of the Third Conformer of Glycolic Acid: Combined Matrix Isolation, FTIR, and Theoretical Study. *Chem. Phys. Lett.* **2004**, *389*, 68−74.

(27) Halasa, A.; Lapinski, L.; Reva, I.; Rostkowska, H.; Fausto, R.; Nowak, M. J. Near-Infrared Laser-Induced Generation of Three Rare Conformers of Glycolic Acid. *J. Phys. Chem. A* **2014**, *118*, 5626−5635.

■ NOTE ADDED IN PROOF

Recently the following paper was published by Miyagawa et al.: Miyagawa, M.; Akai, N.; Nakata, M. UV-light induced conformational changes of 2-pyridinecaboxylic acid in low-temperature argon matrices. *J. Mol. Struct.* **2015**, DOI: 10.1016/j.molstruc.2015.01.014.