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Spontaneous tunneling and near-infrared-induced interconversion between the amino-hydroxy conformers of cytosine

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Spontaneous and near-infrared/infrared (NIR/IR)-induced interconversions between two amino-hydroxy conformers of monomeric cytosine have been investigated for the compound isolated in a low-temperature argon matrix. Combined use of a laser source (which provides narrowband NIR radiation) and a broadband NIR/IR source of excitation light allowed a detailed investigation of mutual conversions of the two conformers in question. The experiments carried out within the current work demonstrated that upon broadband NIR/IR irradiation (with the IR source of FTIR spectrometer) the population ratio of the two amino-hydroxy conformers changes towards a ratio corresponding to a photostationary state. Evolution of the conformer population ratio towards the photostationary ratio occurred independent of the initial ratio of conformers, which could be prepared by a population shift (in favor of one of the forms) induced by narrowband NIR excitation. Moreover, spontaneous tunneling conversion of the higher-energy conformer into a lower-energy form was observed for cytosine isolated in a low-temperature argon matrix kept in the dark. This process is slow and occurs on a time scale of days. The tunneling process, studied for matrix-isolated cytosine, clearly follows a dispersive type of kinetics rather than the classical monoexponential kinetics. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3683217]

INTRODUCTION

Conformers and conformational transformations, by rotation around a formally single bond, have been investigated since the onset of structural chemistry. Usually conformers are separated from each other by comparatively low-energy barriers, which can be easily crossed by thermal excitations at room temperature. Hence, in the majority of cases, conformational conversions are thermally induced and lead to an equilibrium determined by temperature and the Boltzmann distribution.

For the species trapped from the gas phase into a low-temperature matrix, the resulting conformational composition depends on the height of the energy barriers separating different conformers. If the barriers are high enough, then the conformers populated in the gas phase are frozen in a low-temperature matrix without changing their relative populations. For low barriers, the conformational ratio can change towards the low-temperature equilibrium by the process known as conformational cooling.[1]

Exposure to broadband near-infrared/infrared (NIR/IR) radiation can also induce alteration of the population ratio of conformers trapped in a low-temperature matrix. Excitation energy introduced to a molecule by absorption of NIR/IR light is often higher than the barriers separating the potential-energy minima corresponding to different conformers. Hence, molecules promoted to the first or second excited vibrational state are able to change their conformational structure. This occurrence was observed and explored for a number of molecules, such as glycolic acid[2,3] and ethylene glycol.[4] However, using this method, the possibility of manipulation of the conformational populations is limited.

Application of tunable narrowband NIR light sources brings the investigations on conformational conversions of matrix-isolated molecules onto a qualitatively higher level. Using narrowband NIR light sources it is possible to excite, in a selective way, only molecules adopting a particular conformational structure. If such irradiation leads to conversion into another conformer, then it is possible to totally depopulate a certain conformational form of a studied compound. The high selectivity of NIR vibrational excitation of matrix-isolated molecules makes this procedure a very powerful technique in the optical control of the relative populations in conformational mixtures. In addition, such an approach allows also a successful generation of higher-energy conformers, otherwise not observable experimentally, such as the C–O *cis* conformers of formic,[5] acetic,[6] and propionic acids,[7] as well as the *trans-trans* conformer of hydroxyacetone.[8] These higher-energy conformers were photoproduced upon narrowband NIR irradiation, stabilized in low-temperature inert environment and spectrally characterized. For formic acid[9] as well as for other carboxylic acids,[10] conformational transitions, induced by excitation with narrowband mid-IR light, were also reported.

Very interestingly, it was also found that for two conformational structures, differing only by a position of a light particle (hydrogen atom), a transformation of a higher-energy form into a lower-energy conformer can occur by tunneling. Such spontaneous transformations were observed for formic and acetic acids isolated in low-temperature matrices kept in the dark.[11–14] Another class of tunneling occurrences

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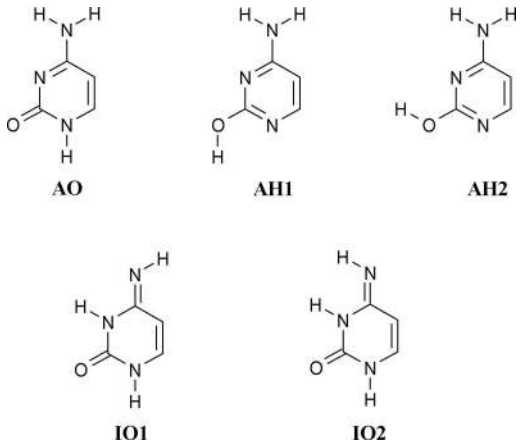

SCHEME 1. Most stable forms of cytosine monomers.

in noble-gas matrices concerns transformations of carbenes (such as hydroxymethylene or methylhydroxycarbene) to stable species (fomaldehyde and acetaldehyde) via spontaneous hydrogen-atom shift.[15,16]

Recently, we have carried out a study on irradiations of matrix-isolated cytosine with narrowband NIR and UV laser light.[17,18] As a result of these investigations, we were able to reliably identify all five low-energy isomers of monomeric cytosine (Scheme 1). Particularly interesting were the results of the narrowband NIR excitations[18] inducing selective and reversible interconversions between the two conformational structures of the dominating amino-hydroxy tautomer. Irradiation at 7013 cm^{-1} (first νOH overtone of **AH1** conformer) led to conversion of this form into **AH2**, whereas irradiation at 7034 cm^{-1} (first νOH overtone of **AH2** conformer) induced an opposite transformation.

In the current work, we report the investigations on conformational changes in isolated cytosine molecules induced by broadband and narrowband NIR/IR excitations. Combined use of narrowband and broadband exciting light sources enabled a clear insight into the observed NIR/IR-induced conformational conversions. Moreover, spontaneous tunneling conversion of the higher-energy **AH2** conformer into the lower-energy **AH1** form was observed and studied for cytosine monomers isolated in an argon matrix kept at 13 K and in the dark.

EXPERIMENTAL PROCEDURES

Cytosine used in the present study was a commercial product (99%) supplied by Sigma. In order to prepare Ar matrices solid cytosine was heated (to ~495 K) in a miniature glass oven placed in the vacuum chamber of a closed-cycle helium cryostat (APD Cryogenics) with a DE–202A expander. Vapors of cytosine were deposited together with large excess of argon (purity N60, supplied by Air Liquide) onto a CsI window cooled to 13 K. The IR spectra were recorded with 0.5 cm^{-1} resolution using a Thermo Nicolet 6700 FTIR spectrometer equipped with a KBr beam splitter and DTGS (deuterated triglycine sulfate) detector. Matrices were irradiated with the NIR light of 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. For UV irradiations the frequency-doubled signal beam of the same optical parametric oscillator was applied.

RESULTS AND DISCUSSION

Phototransformations of cytosine monomers induced by narrowband UV or NIR irradiation

Five most stable forms of cytosine monomers (see Scheme 1) are predicted by theoretical calculations using contemporary methods of quantum chemistry.[19–27] All of these five forms have been recently experimentally identified for cytosine isolated in low-temperature Ar matrices.[17] The amino-oxo **AO** form of cytosine was found to be consumed upon UV ($\lambda = 300$ nm) irradiation and transformed into the amino-hydroxy **AH** and imino-oxo **IO** tautomers (Fig. 1). Concomitantly, **IO1** form converts, in a syn-anti photochemical process, into **IO2** isomer.[17] Hence, after UV ($\lambda = 300$ nm) irradiation only **AH1**, **AH2** and **IO2** forms of cytosine are present in the matrix.

It has also been demonstrated[18] that upon narrowband NIR irradiation at 7013 cm^{-1} the most stable **AH1** amino-hydroxy form converts into **AH2** rotamer (Fig. 1), whereas narrowband NIR irradiation at 7034 cm^{-1} induces the conversion of **AH2** into **AH1**.[18] The large-scale changes of the IR spectrum of matrix-isolated cytosine, observed after narrowband NIR irradiations at 7013 cm^{-1} and at 7034 cm^{-1}, allowed an unquestionable identification of mid-IR bands belonging to the spectra of **AH1** and **AH2**.[18]

Phototransformations of cytosine monomers induced by broadband IR and NIR irradiation

Following the narrowband NIR irradiations at 7013 cm^{-1} or at 7034 cm^{-1}, matrices (with the ratio of amino-hydroxy rotamers significantly shifted in favor of **AH2** or **AH1**, respectively) were periodically monitored by taking the mid-IR spectra. This revealed that exposure to the broadband NIR/IR source (Ever-Glo ceramic bar) of the spectrometer induces changes in the relative population of **AH1** and **AH2** forms. Whichever the initial **AH1**:**AH2** ratio is [very low after the irradiation at 7013 cm^{-1} (Fig. 2(a)) or very high after the irradiation at 7034 cm^{-1} (Fig. 2(d))], the changes induced by broadband NIR/IR light of the spectrometer source lead to the same photostationary state (see Figs. 2–3). At this photostationary state, the total population of the amino-hydroxy tautomer is divided into **AH1** (53%) and **AH2** (47%) rotameric forms. That makes the photostationary **AH1**:**AH2** ratio equal to 1.1.

At any stage of the NIR/IR-induced conversion, the population ratio of **AH1** and **AH2** was determined on the basis of the intensity ratio of a chosen pair of bands (e.g., those at 1439 cm^{-1} due to **AH1** and at 1428 cm^{-1} due to **AH2**), scaled by the ratio of their absorption coefficients. In turn, the ratio of absorption coefficients was experimentally evaluated (see equations in the supplementary material)[34] as the intensity ratio of the bands in question, measured in the spectrum obtained by subtraction of the spectrum recorded after NIR irradiation at 7034 cm^{-1} from that recorded before any

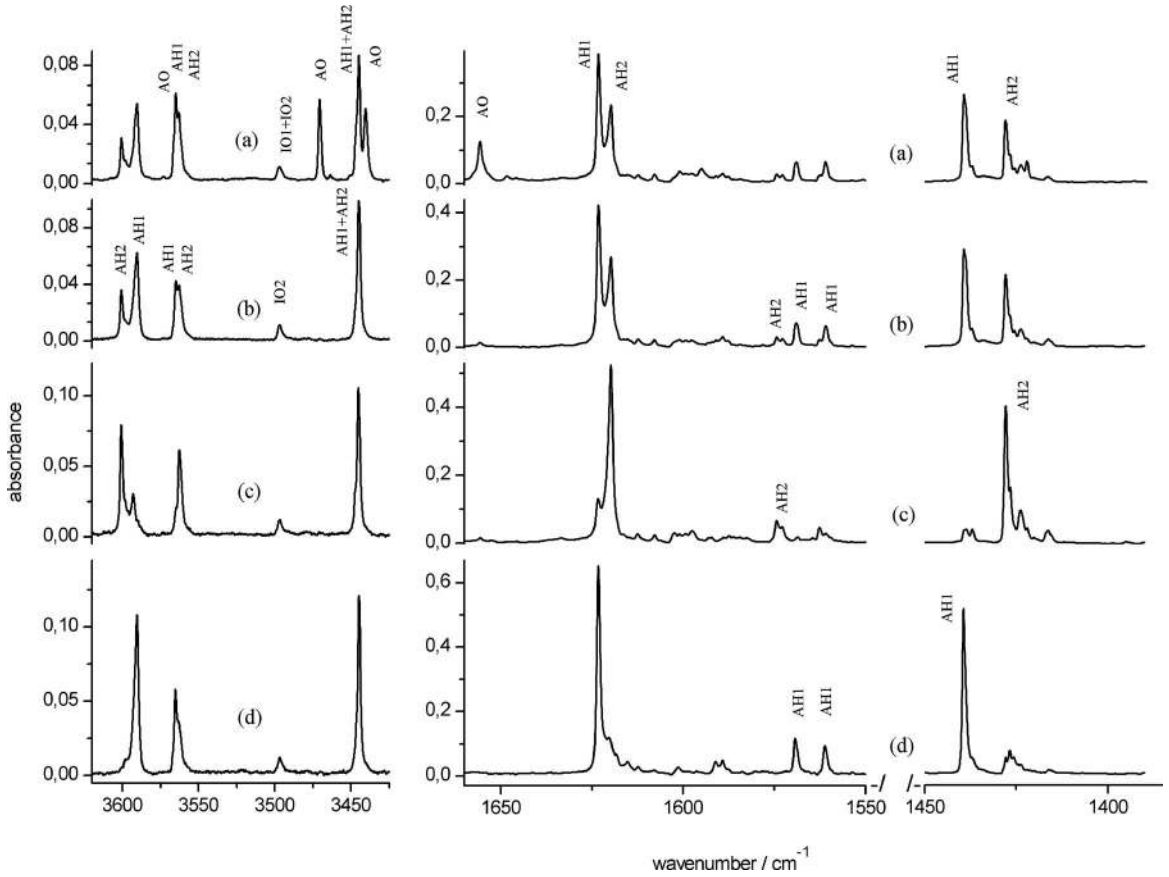

FIG. 1. Fragments of the infrared spectrum of cytosine isolated in an Ar matrix: (a) recorded after deposition of the matrix; (b) recorded after narrowband UV irradiation at 300 nm; (c) after subsequent narrowband laser NIR irradiation at 7013 cm^{-1}; and (d) after subsequent narrowband NIR irradiation at 7034 cm^{-1}.

irradiation. Advantage has been taken of the fact that at any stage of narrowband NIR irradiation the population increase of **AH1** should be equal to the population decrease of **AH2**. Analogously, the ratio of absorption coefficients can be determined from the difference of spectra recorded before and after NIR irradiation at 7013 cm^{-1}.

In order to investigate in more detail the **AH1** ↔ **AH2** phototransformation induced by broadband NIR/IR light, several bandpass IR filters were employed. Whatever the initial **AH1**:**AH2** ratio, no measurable change in relative populations of these forms was observed (on the time scale of 10–30 min) for matrix-isolated cytosine exposed to the light of the spectrometer source passed through a filter transmitting in the 1750−800 cm^{-1} range (see the filter characteristics in Fig. S1 in the supplementary material).[34] However, when this IR bandpass filter was substituted by another one transmitting light in the spectral range of 4250−1200 cm^{-1} (see the characteristics in Fig. S1), quite rapid changes in the **AH1**:**AH2** population ratio were observed. These observations demonstrate that not only near-IR excitation to overtones (at 7013 or 7034 cm^{-1}) but also excitation (in the 3610−3430 cm^{-1} range) to the first excited states of the OH or NH stretching vibrations induces mutual conversion of **AH1** and **AH2** conformers. Such occurrences can be rationalized by taking into account that the conformational change induced, e.g., by the excitation at 3601 cm^{-1} (to the first excited state of the OH stretching vibration in **AH2**) should be an over-the-barrier process. The energy of this excited vibrational state (43 kJ mol^{-1}) is indeed higher than the barrier for the **AH2** → **AH1** conversion, which was estimated,[21,22] at the MP2/6−311+G(2*d*,2*p*) and DFT(B3LYP)/6−311+G(2*df*,2*p*) levels of theory, to be 32 kJ mol^{-1} or 30 kJ mol^{-1}, respectively.

The population ratio of **AH1** and **AH2** rotamers was also investigated for freshly deposited matrices containing cytosine monomers. In a dedicated experiment, a low-temperature Ar matrix was deposited in the dark without being exposed to the spectrometer beam (Fig. 2(g)). The deposited matrix was monitored only with IR light passing through the 1750−800 cm^{-1} bandpass filter. In the matrix prepared under such conditions, the **AH1**:**AH2** ratio was assessed to be 2.1. This value should correspond to the population ratio of the two amino-hydroxy rotamers trapped from the gas phase (at 495 K) into a low-temperature matrix. On this basis, the energy difference between **AH1** and **AH2** can be assessed as equal to 3.1 kJ mol^{-1}, in favor of the first rotamer. This value is in excellent agreement with the results of the contemporary theoretical calculations, carried out at the CCSD(T), MP2, and DFT levels,[19–21,23,25–27] which predict this energy difference in the 2.8–3.1 kJ mol^{-1} range.

When the 1750−800 cm^{-1} bandpass filter was removed and the matrix was exposed to the radiation of the spectrometer source, changes in relative populations of **AH1** and **AH2** were observed (Figs. 2(g)–2(i)). After ∼100 min of such irradiation, a photostationary state was established, with the **AH1**:**AH2** ratio of 1.1. This ratio is the same as that obtained

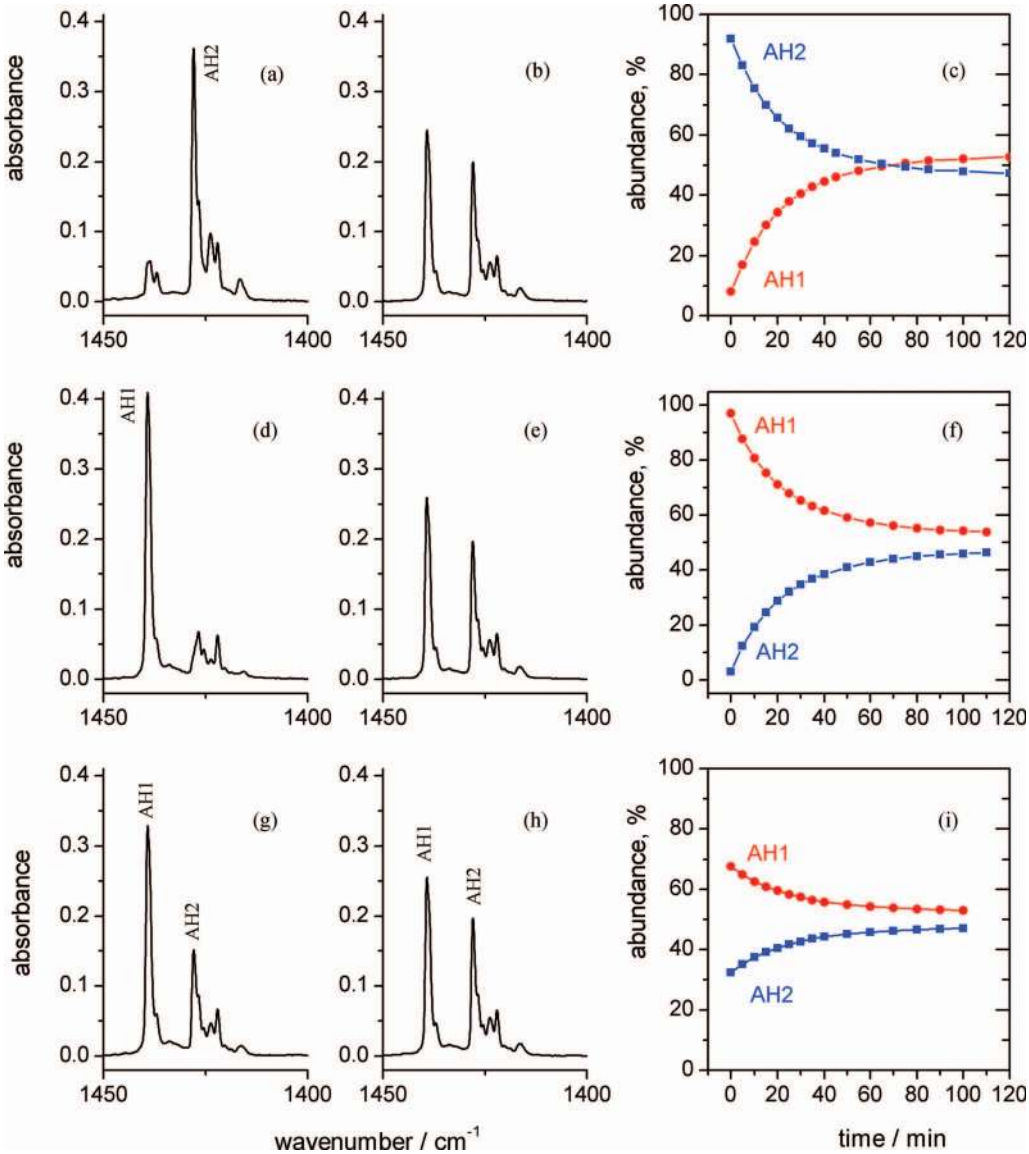

FIG. 2. Fragment of the infrared spectrum of cytosine isolated in an Ar matrix: (a) recorded after narrowband NIR irradiation at 7013 cm^{-1}; (b) after subsequent 120 min of exposure to the NIR/IR broadband radiation of the spectrometer source; (c) evolution of abundances of **AH1** and **AH2** rotamers with time of broadband NIR/IR irradiation [initial point corresponds to (a) and final point corresponds to (b)]; (d) recorded after narrowband NIR irradiation at 7034 cm^{-1}; (e) after subsequent 110 min of exposure to the NIR/IR broadband radiation of the spectrometer source; (f) evolution of abundances of **AH1** and **AH2** rotamers with time of broadband NIR/IR irradiation [initial point corresponds to (d) and final point corresponds to (e)]; (g) recorded after deposition of the matrix, monitored only through a filter transmitting in the spectral range 1750–800 cm^{-1}; (h) after subsequent 100 min of exposure to the NIR/IR broadband radiation of the spectrometer source; (i) evolution of abundances of **AH1** and **AH2** rotamers with time of broadband NIR/IR irradiation [initial point corresponds to (g) and final point corresponds to (h)].

for matrices with the **AH1**:**AH2** ratio strongly shifted in favor of one of the rotamers (by irradiation at 7013 or 7034 cm^{-1}) subsequently exposed to NIR/IR spectrometer beam (Fig. 3). In all previous studies[28,29] of cytosine isolated in solid argon, the low-temperature matrices were exposed (during deposition and recording of the spectra) to unfiltered light of the NIR/IR source of a spectrometer. That is why the **AH1**:**AH2** ratio observed in these works must have corresponded to the photostationary state rather than to the gas phase equilibrium of these two rotamers.

Tunneling in the dark: Conversion of AH2 into AH1

For matrix-isolated cytosine kept in the dark and monitored only with the spectrometer beam passing through the 1750−800 cm^{-1} filter, very slow changes of relative populations of **AH1** and **AH2** were observed. Whichever the initial **AH1**:**AH2** ratio, the direction of these changes was the same: the higher-energy **AH2** rotamer converted into **AH1**. In order to observe the changes of relative populations of **AH1** and **AH2** in a possibly largest scale, a dedicated experiment was carried out. In this experiment, a matrix with very high relative population of **AH2**, hence with the **AH1**:**AH2** ratio close to zero, was prepared by narrowband irradiation at 7013 cm^{-1} (Figs. 4(a) and 5). Then the matrix was kept in the dark for more than 52 h. Continuous transformation of **AH2** into **AH1** was observed throughout this whole period (Figs. 4 and 5) and the final **AH1**:**AH2** ratio recorded after the whole period of 52 h was 1.89 (see Fig. 6(b)).

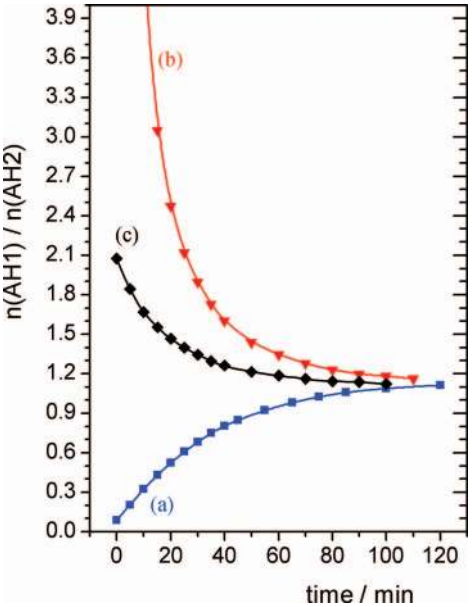

FIG. 3. Evolution of the population ratio of **AH1** and **AH2** rotamers with time of NIR/IR broadband irradiation with the light of the spectrometer source: (a) starting from the population ratio after narrowband irradiation at 7013 cm^{-1}; (b) starting from the population ratio [n(**AH1**)/n(**AH2**) > 100] after narrowband irradiation at 7034 cm^{-1}; and (c) starting from the population ratio after deposition of the matrix in the dark.

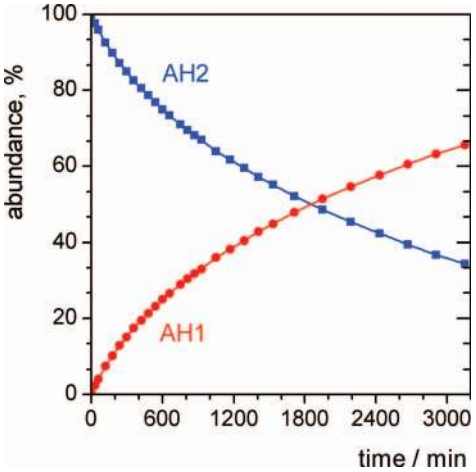

FIG. 5. Evolution of abundances of **AH1** and **AH2** rotamers with time of keeping the matrix in the dark at 13 K and monitoring only through a filter transmitting in the spectral range of 1750–800 cm^{-1}; the initial population distribution **AH1** (close to 0%) and **AH2** (close to 100%) was induced by narrowband laser NIR irradiation at 7013 cm^{-1}.

Evolution of the **AH1**:**AH2** ratio with time of keeping the matrix in the dark (presented in Figs. 6(b) and 6(d)) is very different from the evolutions shown in Fig. 3. This clearly shows that the process occurring in the dark is different from that induced by the broadband NIR/IR radiation. Whereas the latter process was always leading to a photostationary state (with the **AH1**:**AH2** ratio equal to 1.1), the process occurring in the dark converts always (independent of the **AH1**:**AH2** ratio) the higher-energy **AH2** form into the more stable **AH1** rotamer. The most plausible explanation of the process occurring in the dark is the spontaneous **AH2** → **AH1** tunneling. No conversion in the opposite direction was observed when a matrix with the **AH1**:**AH2** ratio higher than 100 (prepared

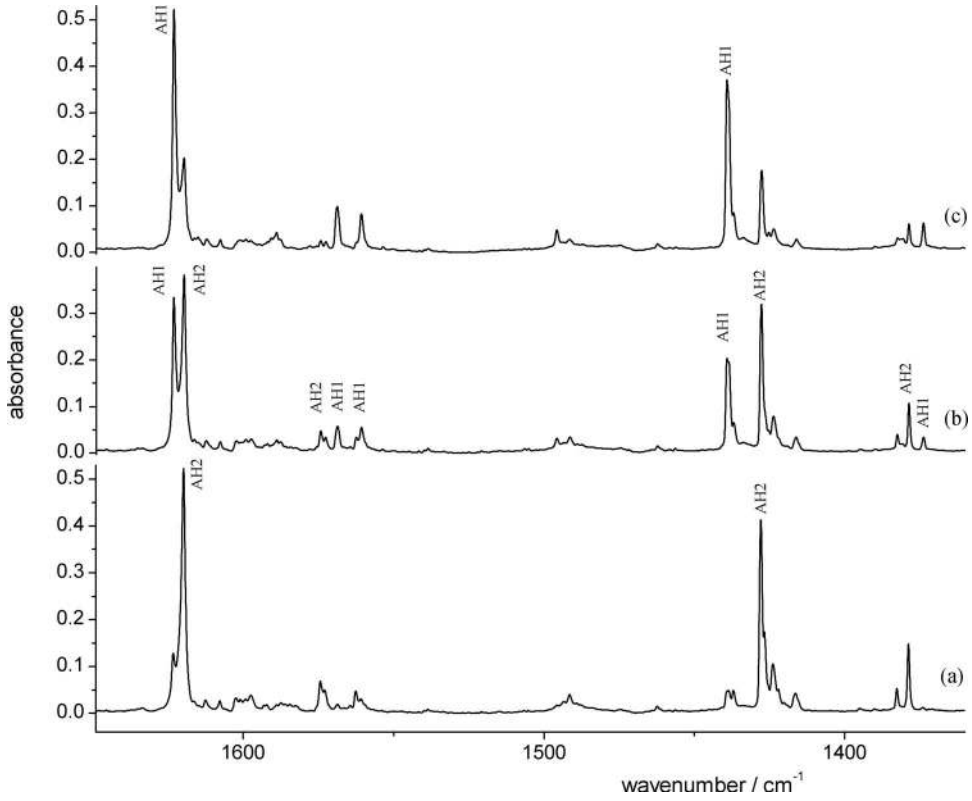

FIG. 4. Fragment of the infrared spectrum of cytosine isolated in an Ar matrix: (a) recorded after narrowband NIR irradiation at 7013 cm^{-1}; recorded after 815 min (b) or 3155 min (c) of keeping the matrix in the dark at 13 K and monitoring only through a filter transmitting in the spectral range of 1750–800 cm^{-1}.

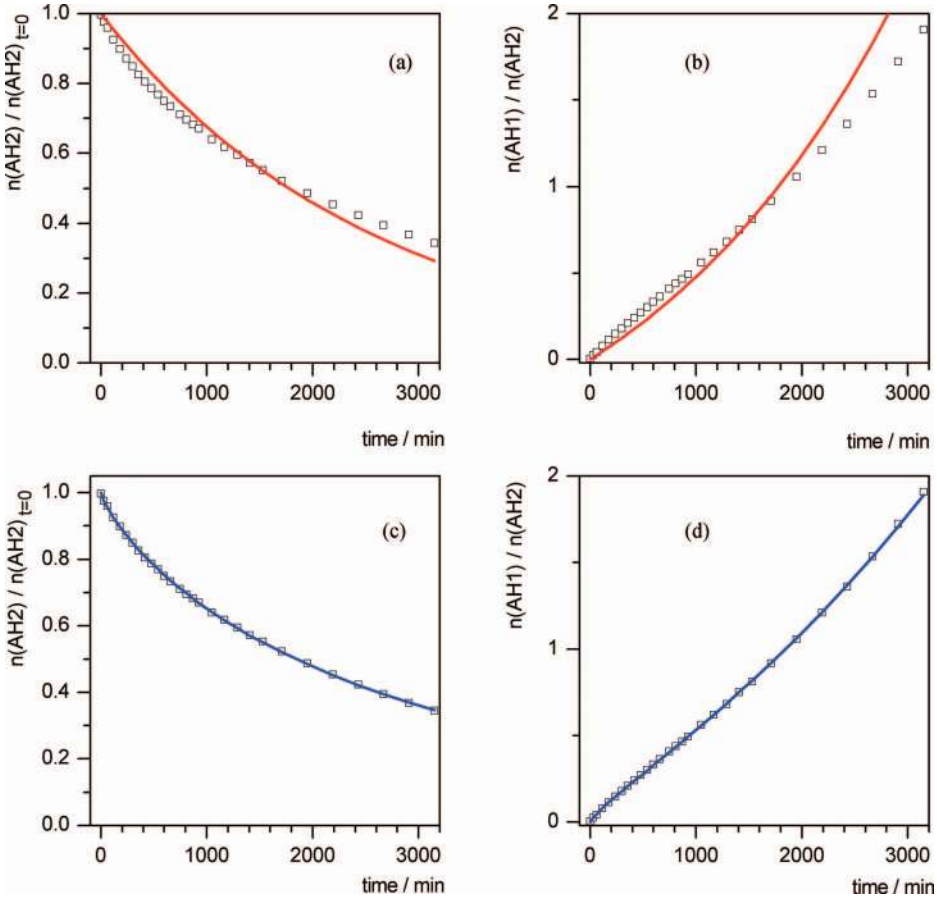

FIG. 6. Squares represent: ((a) and (c)) the evolution of the abundance of **AH2**; ((b) and (d)) the evolution of the population ratio of **AH1** and **AH2** rotamers with time of keeping the matrix in the dark at 13 K. Solid lines represent the best fits: ((a) and (b)) using the classical kinetics formulas $\frac{\mathrm{n(AH2)}}{\mathrm{n(AH2)}_{t=0}} = \mathrm{e}^{-t/\tau}$ and $\frac{\mathrm{n(AH1)}}{\mathrm{n(AH2)}} = \frac{(1-\mathrm{e}^{-t/\tau})}{\mathrm{e}^{-t/\tau}}$; ((c) and (d)) using the dispersive kinetics formulas $\frac{\mathrm{n(AH2)}}{\mathrm{n(AH2)}_{t=0}} = \mathrm{e}^{-Bt^{\alpha}}$ and $\frac{\mathrm{n(AH1)}}{\mathrm{n(AH2)}} = \frac{(1-\mathrm{e}^{-Bt^{\alpha}})}{\mathrm{e}^{-Bt^{\alpha}}}$. The optimized classical time constant is $\tau = 2564$ min; whereas for dispersive kinetics τ_{disp}, derived from the optimized values of B and $\alpha = 0.7955$ using the formula $B \equiv \frac{\alpha}{\tau_{disp}^{\alpha}}$, is $\tau_{disp} = 2192$ min.

by laser irradiation at 7034 cm^{-1}) was kept in the dark. Taking into account that at low temperature (13 K) thermal equilibrium of **AH1** and **AH2** forms (differing in energy by 3.1 kJ mol^{-1}) should correspond to the population ratio **AH1**:**AH2** $= 3 \times 10^{12}$, tunneling in the dark should lead to total conversion of **AH2** into **AH1**.

The speed of **AH2** tunneling into **AH1** was found to be different for cytosine molecules trapped in spectroscopically differentiable matrix sites. In comparison to the **AH2** molecules trapped in the main site, characterized by the IR absorption at 1428 cm^{-1}, the molecules trapped in the site characterized by the band at 1427 cm^{-1} converted faster, whereas the molecules trapped in the site characterized by the band at 1426 cm^{-1} converted slower. Similarly, dependence of the tunneling rate on the matrix site was previously observed for formic acid.[12]

Data presented in Figs. 5 and 6 were collected for a single, main spectroscopically differentiable site. Even for molecules within the same site, the tunneling conversion of **AH2** into **AH1** does not follow a single exponential kinetics with just one time constant τ :

$$\mathrm{n(AH2)} = \mathrm{n(AH2)}_{t=0}\mathrm{e}^{-t/\tau}. \quad (1)$$

The fit of function (1) to the experimentally observed decrease of **AH2** population is presented in Fig. 6(a). Initially, the process was faster than the average fit to classical kinetics equation (1). At later stages, the tunneling clearly slows down (see Figs. 6(a) and 6(b)). This suggests that the probability of tunneling is dependent on slight differences in the microenvironments, even within the same spectroscopically differentiable matrix site. The molecules trapped in the cage allowing faster tunneling convert at the initial stages of the experiment. At the later stages, the **AH2** → **AH1** conversion slows down, because it gets dominated by transformation of **AH2** molecules isolated in environments where the probability of tunneling is lower. Such behavior is typical of transformations of molecules embedded in somewhat inhomogeneous media.[30,31] Usually, the time evolution of such processes follows the equations of the so called dispersive kinetics, where

$$k(t) = Bt^{\alpha-1} \ (B, \alpha - \text{constants}). \quad (2)$$

This leads[30–32] to Eq. (3) for decrease of **AH2** population:

$$\mathrm{n(AH2)} = \mathrm{n(AH2)}_{t=0}\mathrm{e}^{-Bt^{\alpha}}. \quad (3)$$

The progress of the **AH2** → **AH1** tunneling during the experiment is very well reproduced by Eq. (3), see Figs. 6(c) and

6(d). On that basis, one can conclude that the matrix medium (even within a single, spectroscopically distinguishable site) is to some extent inhomogeneous. Parameter α can be treated as a measure of inhomogeneity of the medium. The value of $\alpha \approx 0.8$, obtained for the **AH2** → **AH1** tunneling at 13 K, suggests that, although the Ar matrix environment is not very disordered, the inhomogeneous character of this medium cannot be neglected.

The average time constant of the observed tunneling **AH2** → **AH1** conversion is $\tau \approx 36.5$ h (Fig. 6). This is several orders of magnitude a longer time than that found for the spontaneous rotation of the OH groups in compounds such as 1,4-dihydroxybenzene (hydroquinone).[33] The very substantial difference between the speed of the *cis* → *trans* tunneling transformation in 1,4-dihydroxybenzene and the time constant of the **AH2** → **AH1** tunneling in cytosine is obviously related with the depth of the minima of the forms in question and with the height of the barriers separating them. Although for both molecules the isomeric structures differ in rotation of an OH group by ∼180°, **AH1** and **AH2** forms of cytosine are stabilized by an attractive interaction of the hydrogen atom of the OH group with the lone electron pairs of the vicinal nitrogen atoms, whereas in *cis* and *trans* isomers of 1,4-dihydroxybenzene this stabilizing interaction is replaced by repulsion with the positively loaded hydrogen atoms of the CH groups. Consequently, the barrier for **AH2** → **AH1** tunneling in cytosine is ∼32 kJ mol^{-1} and the barrier for *cis* → *trans* tunneling in 1,4-dihydroxybenzene[33] is much lower, ∼10 kJ mol^{-1}. Although no strict correspondence between the barrier height (calculated with respect to one geometry parameter) and the speed of the tunneling process can be postulated, the factors described above explain the drastic difference in speed of tunneling processes in 1,4-dihydroxybenzene and in cytosine.

Throughout 52 h of keeping the matrix in the dark, the 1750–800 cm^{-1} region of the IR spectrum of isolated cytosine molecules was periodically monitored. These observations were performed for a matrix previously irradiated with UV (λ = 300 nm) light, hence for a matrix with nearly whole population of the imino-oxo tautomer converted into the higher-energy **IO2** form (see Fig. 1 and Ref. 17). During the period of 52 h, no changes of intensities were detected for the IR bands due to **IO1** and **IO2** observed in the 1750–800 cm^{-1} region. This indicates that no spontaneous transformation of the higher-energy **IO2** form into the lower-energy **IO1** form occurs in Ar matrices at 13 K. The reason for that is the very high barrier, ∼115 kJ mol^{-1} for the **IO2** → **IO1** conversion.[21]

CONCLUSIONS

NIR/IR-induced conversions between two amino-hydroxy conformers of monomeric cytosine were investigated by combined application of narrowband and broadband excitation light sources. This study demonstrated that upon excitation with broadband NIR/IR radiation, the population ratio of conformers changes towards a photostationary state. The final photostationary ratio of populations was found to be always the same, independent of the initial ratio of conformers, prepared by selective irradiation with narrowband NIR light. Conformational conversion occurred not only upon NIR excitation (at 7013 or 7034 cm^{-1}) to the second νOH excited vibrational state but also upon mid-IR excitation (in the 3610−3430 cm^{-1} range) to the first νOH excited vibrational state. This was demonstrated in a series of irradiations of matrix-isolated cytosine with broadband NIR/IR light passing through appropriate cut-off filters. The energy difference between the two amino-hydroxy conformers of cytosine was experimentally assessed to be equal to 3.1 kJ mol^{-1}.

A very interesting tunneling conversion of the higher-energy conformer into the lower-energy form was observed for matrix-isolated cytosine kept in the dark. The conformational transformation by hydrogen-atom tunneling was very slow, with the average time constant equal to ∼36.5 h. Because of the inhomogeneous character of the Ar matrix environment, this process did not follow the classical monoexponential kinetics, but followed nicely the equations of dispersive kinetics.

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[34]See supplementary material at http://dx.doi.org/10.1063/1.3683217 for the characteristics of the NIR/IR filters used in the study (Fig. S1) and description of the method of determination of the population ratio of **AH1** and **AH2** conformers on the basis of the intensity ratio of the IR bands.