Supplementary Material (ESI) for PCCP

Five isomers of monomeric cytosine and their interconversions induced by tunable UV laser light.

Electronic Supplementary Information

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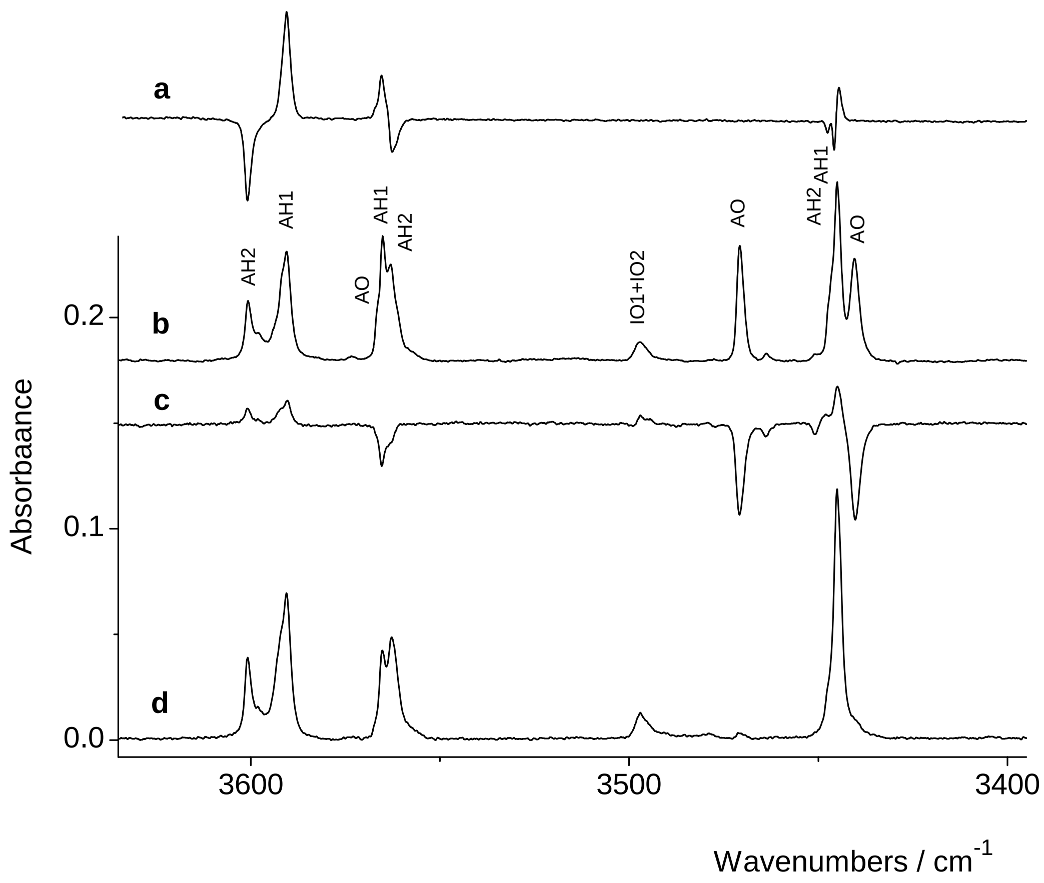


Figure S1. Fragment of the infrared spectrum of cytosine monomers isolated in an Ar matrix:
(**b**) recorded after deposition of the matrix;
(**d**) recorded after irradiation of the matrix with UV (λ = 300 nm) monochromatic laser light;
(**c**) subtraction result: spectrum **d** recorded after irradiation at 300 nm, minus spectrum **b** recorded after deposition of the matrix;
(**a**) subtraction result: the spectrum recorded after irradiation with monochromatic NIR 7034 cm^{-1} laser light, minus the spectrum recorded after irradiation with monochromatic NIR 7013 cm^{-1} laser light; The spectrum presented in trace **a** was obtained in a separate experiment. [Lapinski, L.; Nowak, M. J.; Reva, I.; Rostkowska, H.; Fausto, R. *Phys. Chem. Chem. Phys.* **2010**, *12*, 9615 - 9618.]

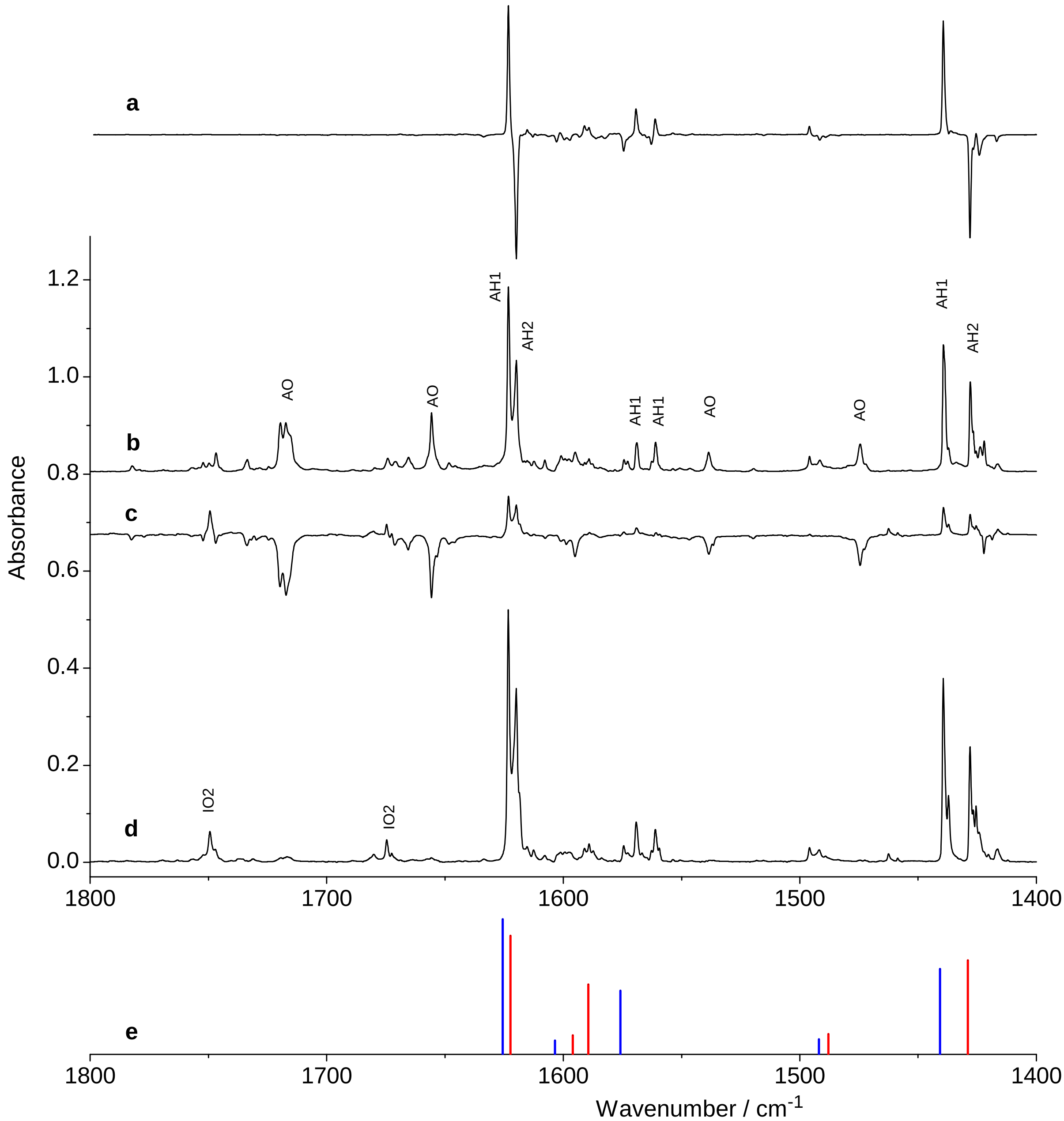


Figure S2. Fragment of the infrared spectrum of cytosine monomers isolated in an Ar matrix:
(**b**) recorded after deposition of the matrix;
(**d**) recorded after irradiation of the matrix with UV (λ = 300 nm) monochromatic laser light;
(**c**) subtraction result: spectrum **d** recorded after irradiation at 300 nm, minus spectrum **b** recorded after deposition of the matrix;
(**a**) subtraction result: the spectrum recorded after irradiation with monochromatic NIR 7034 cm^{-1} laser light, minus the spectrum recorded after irradiation with monochromatic NIR 7013 cm^{-1} laser light; The spectrum presented in trace **a** was obtained in a separate experiment. [Lapinski, L.; Nowak, M. J.; Reva, I.; Rostkowska, H.; Fausto, R. *Phys. Chem. Chem. Phys.* **2010**, *12*, 9615 - 9618.]
(**e**) theoretical spectra calculated at the DFT(B3LYP)/6-31++G(d,p) level for: (blue) **AH1** and (red) **AH2** forms of cytosine. Theoretical wavenumbers were scaled by 0.978.

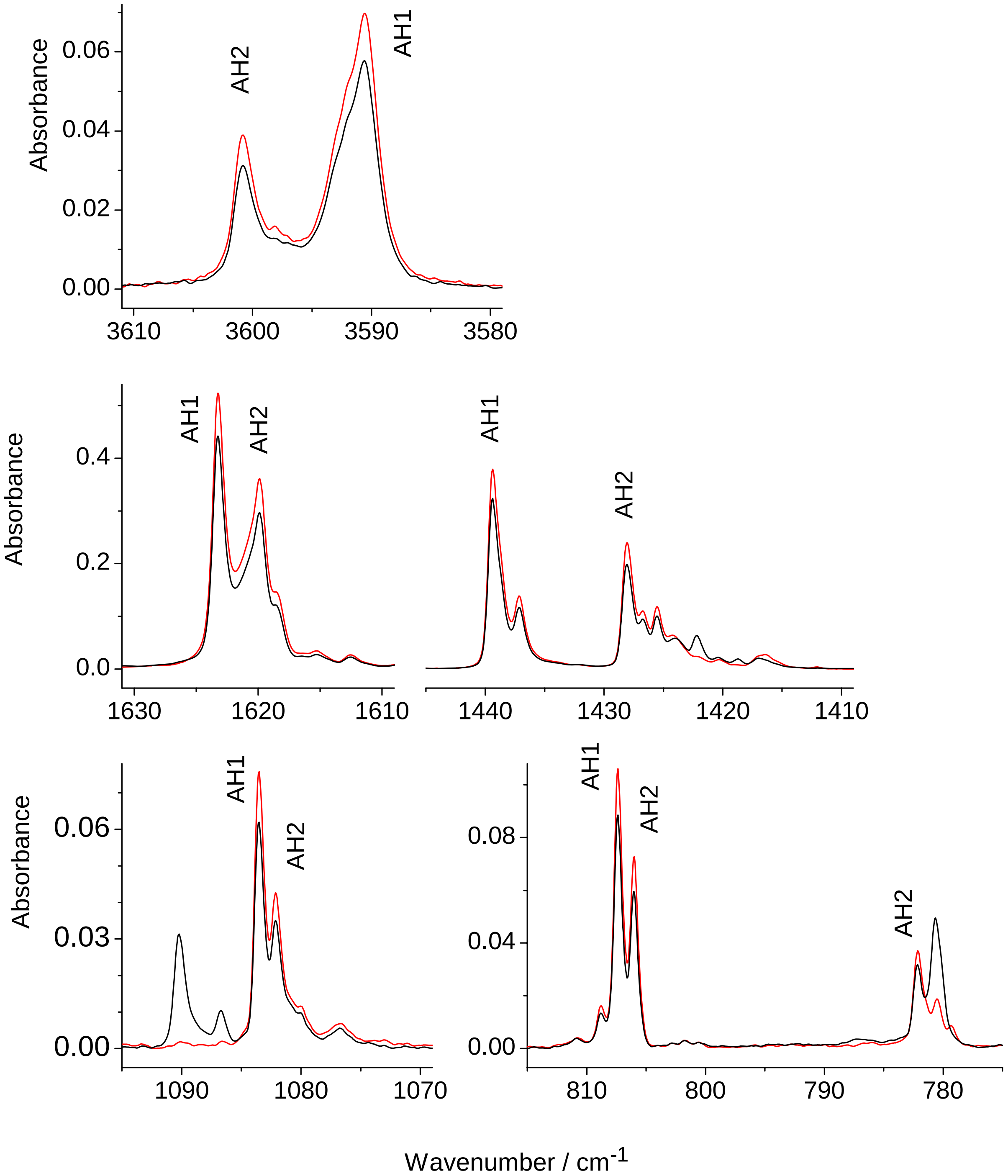
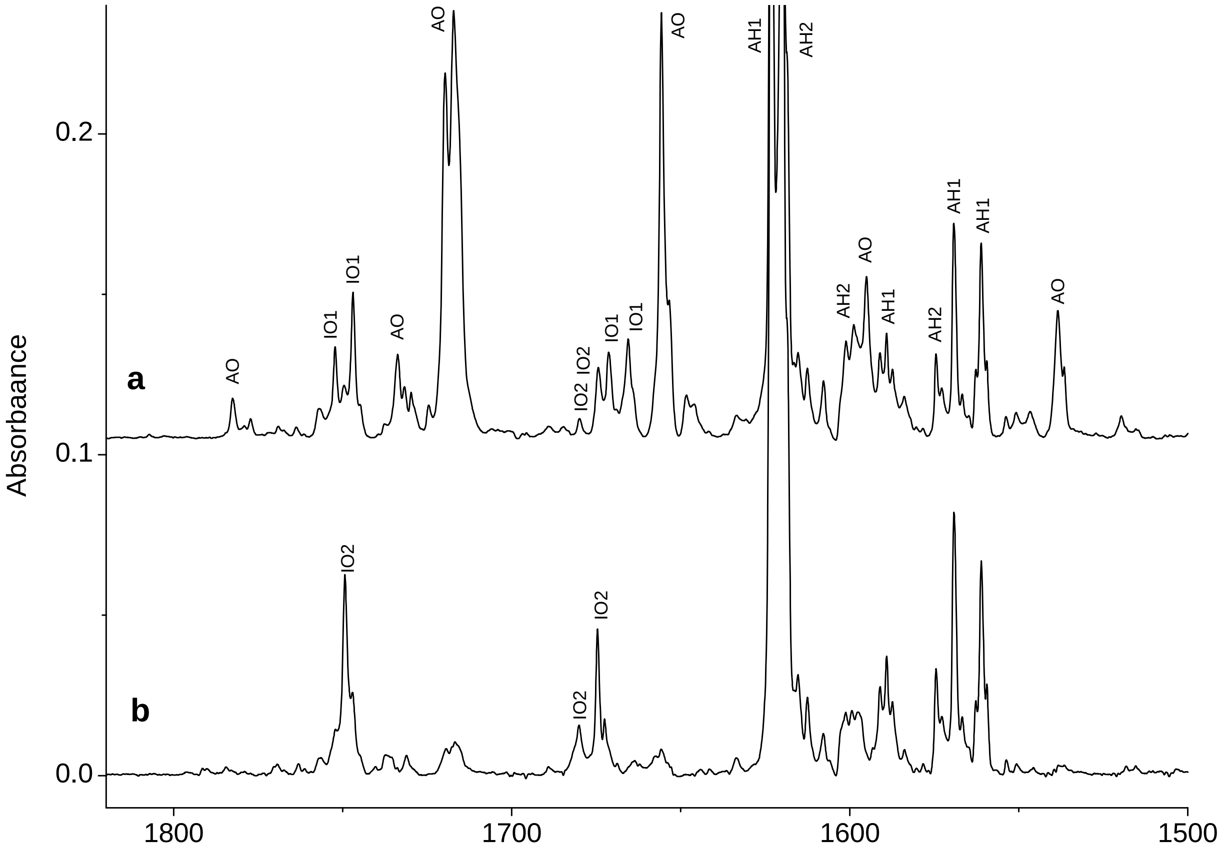


Figure S3. Spectral indications of the oxo→hydroxy phototautomeric reaction converting the **AO** tautomer into **AH1** and **AH2** forms. Fragments of the infrared spectrum of cytosine monomers isolated in an Ar matrix: (black) recorded after deposition of the matrix; (red) recorded after irradiation of the matrix with UV (λ = 300 nm) monochromatic laser light. The bands marked as **AH1** and **AH2** were attributed to these forms on the basis of their behavior upon NIR irradiations at 7034 cm^{-1} and at 7013 cm^{-1} (see Ref [Lapinski, L.; Nowak, M. J.; Reva, I.; Rostkowska, H.; Fausto, R. *Phys. Chem. Chem. Phys.* **2010**, *12*, 9615 - 9618.] and Figures S1, S2 in the **ESI** of the current paper).



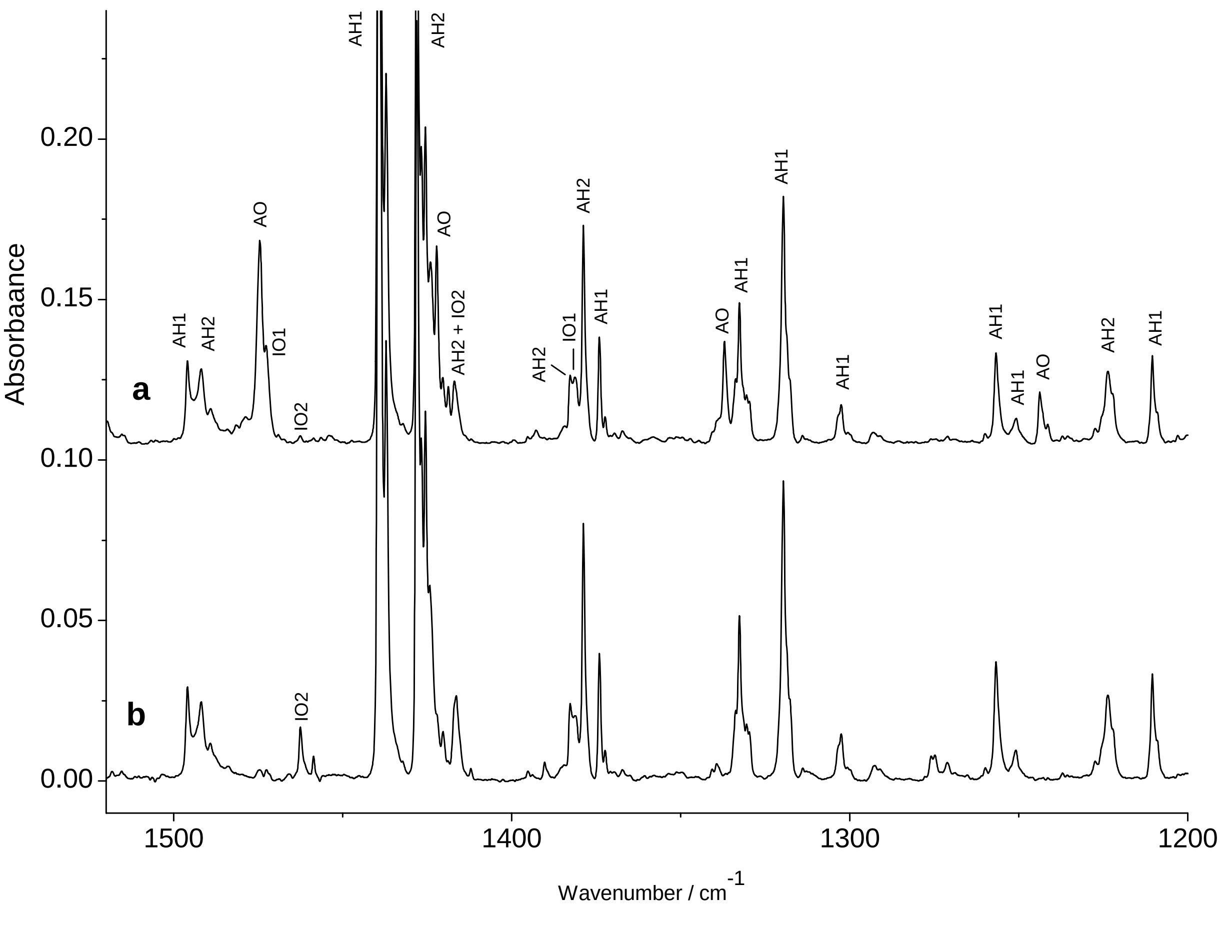


Figure S4 (part 1).

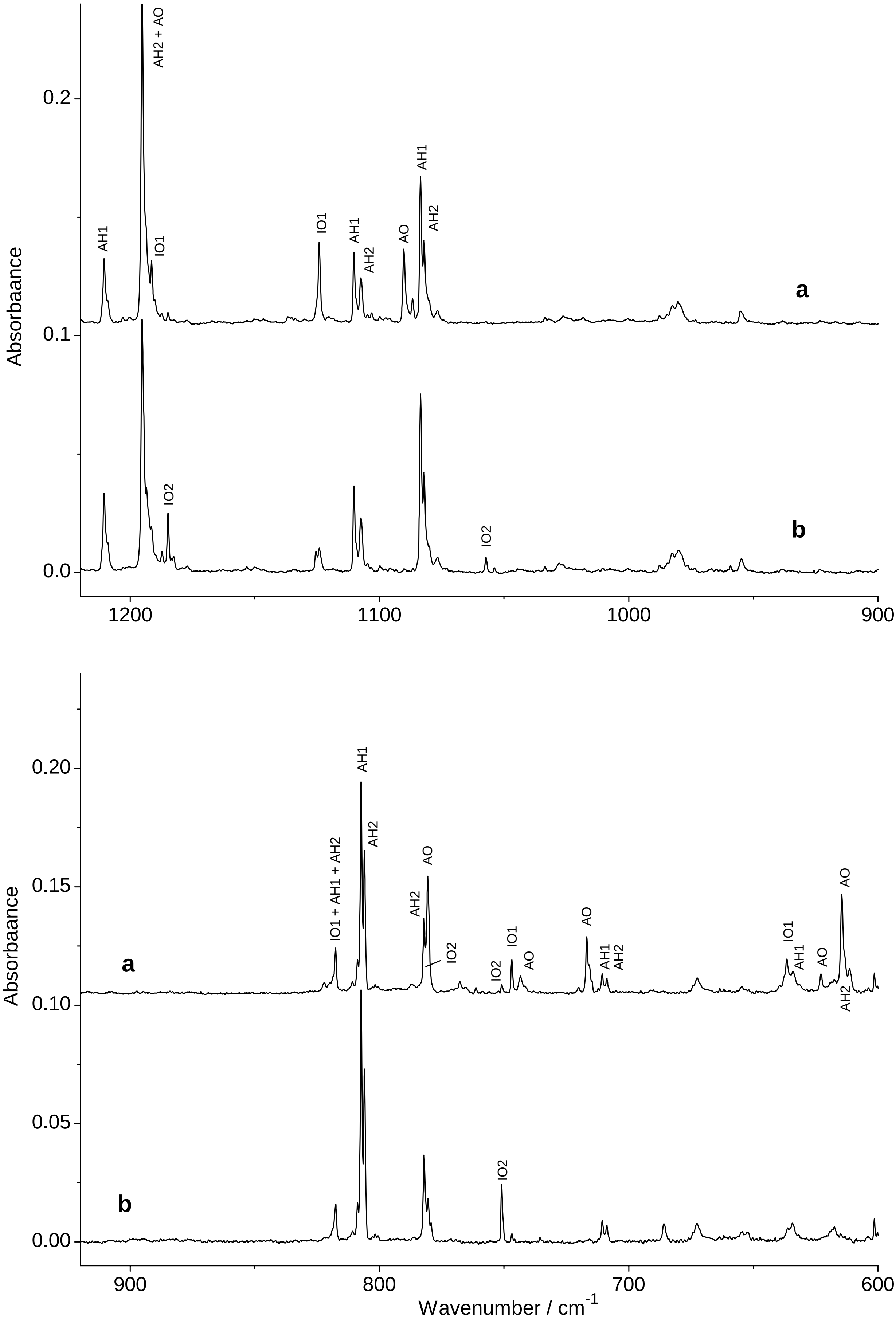


Figure S4 (part 2).

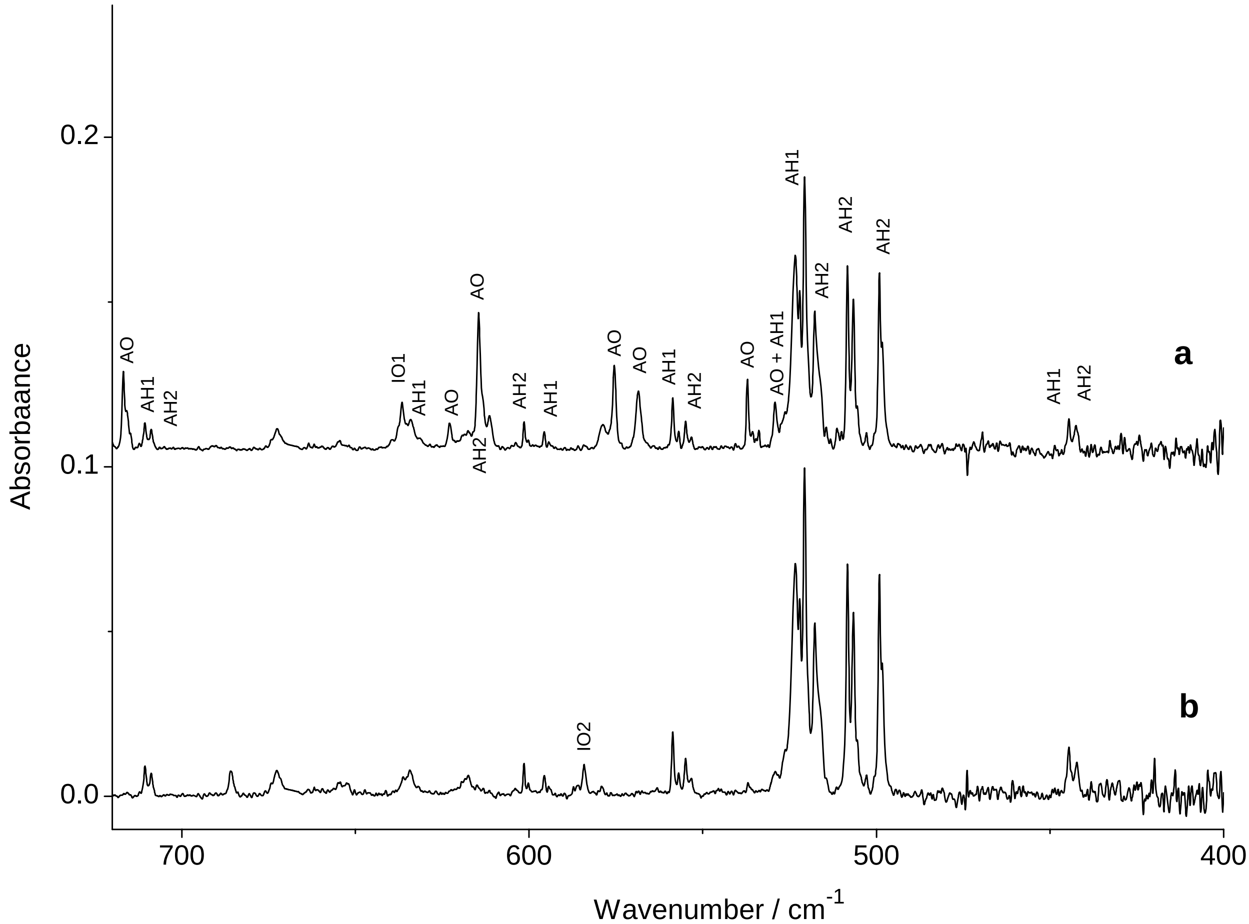


Figure S4 (part 3).

Infrared spectrum of cytosine monomers isolated in an Ar matrix: (a) recorded after deposition of the matrix; (b) recorded after irradiation of the matrix with UV (λ = 300 nm) monochromatic laser light; The bands were attributed to the particular **AH1**, **AH2**, **AO**, **IO1** or **IO2** forms on the basis of their intensity changes occurring upon UV and NIR irradiations (see detailed description in the text).

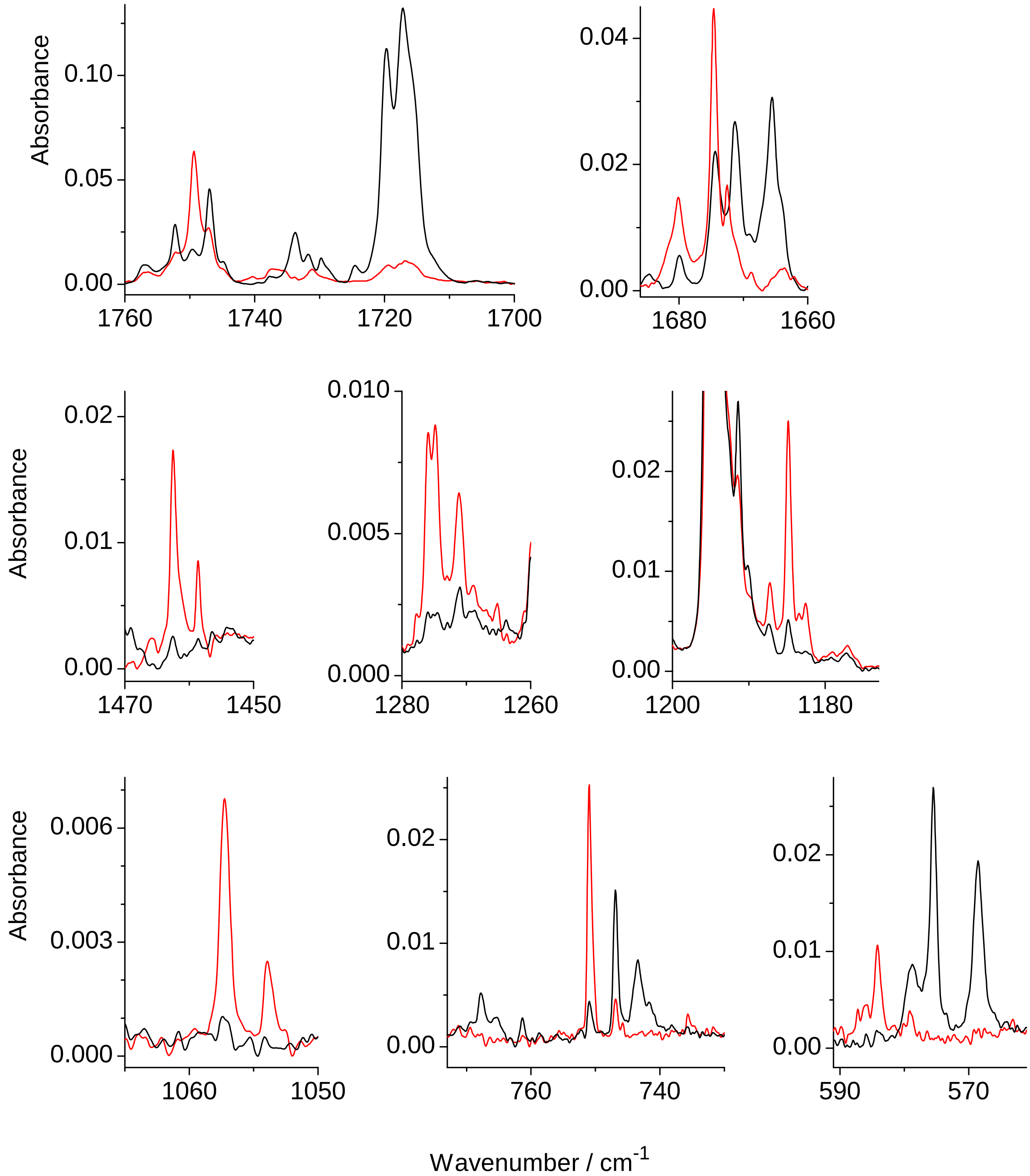


Figure S5. IR bands in the spectrum of **IO2** form increasing upon **IO1→IO2** conversion induced by UV (λ = 300 nm) monochromatic laser light. Fragments of the infrared spectrum of cytosine monomers isolated in an Ar matrix: (black) recorded after deposition of the matrix; (red) recorded after irradiation of the matrix with UV (λ = 300 nm) monochromatic laser light.

Table S1

IR bands observed in the spectrum of cytosine isolated in an Ar matrix and their assignment to **AH1**, **AH2**, **AO**, **IO1** or **IO2** forms of the compound.

wavenumber	integrated intensity	assignment to the isomeric form
cm^{-1}	arbitrary units	
3600.6	0.110	**AH2**
3590.3	0.266	**AH1**
3565.1	0.160	**AH1, AO**
3562.7	0.180	**AH2, AO**
3497.2	0.037	**IO1, IO2**
3470.8	0.140	**AO**
3463.8	0.009	**AO**
3450.8 3444.8	0.009 0.315	**AH1, AH2**
3440.3	0.180	**AO**
1782.6	0.023	**AO**
1756.8	0.020	**IO1**
1752.3	0.057	**IO1**
1749.2	0.030	**IO2**
1746.9	0.105	**IO1**
1733.8 1731.8 1729.6	0.114	**AO**
1719.7 1717.1	0.749	**AO**
1680.2	0,008	**IO2**
1674.4	0.041	**IO2**
1671.2	0.071	**IO1**
1665.7	0.100	**AO**
1655.7	0.345	**AO**
1648.1	0.055	**AO**
1623.3	0.943	**AH1**
1620.0	0.687	**AH2**
1607.7	0.035	
1601.0	0.056	**AH2**
1598.7	0.144	**AO, AH2**
1595.0	0.214	**AO**
1591.0 1589.2	0.140	**AH1**
1574.3	0.066	**AH2**
1569.2	0.138	**AH1**
1561.1	0.139	**AH1**
1553.8	0.012	**AH1**
1550.8 1546.5	0.048	**AO**
1538.4	0.126	**AO**
1519.7	0.020	**AO**
1495.8	0.050	**AH1**
1491.7	0.050	**AH2**
1474.5	0.135	**AO**
1472.6	0.024	**IO1**
1462.5	0.004	**IO2**
1439.6 1437.2	0.602	**AH1**
1428.0 1425.5	0.400	**AH2**
1422.2	0.072	**AO**
1416.9	0.019	**AH2, IO2**
1382.7	0.036	**AH2**
1381.0	0.010	**IO1**
1378.7	0.100	**AH2**
1374.0	0.044	**AH1**
1338.0	0.012	**AH2**
1337.0	0.055	**AO**
1332.0	0.095	**AH1**
1319.6	0.156	**AH1**
1302.8	0.025	**AH1**
1275.3	0.003	**IO2**
1259.8	0.005	**AH2**
1256.7	0.054	**AH1**
1250.8	0.013	**AH1**
1243.7	0.033	**AO**
1223.6	0.082	**AH2**
1210.5	0.048	**AH1**
1195.2	0.210	**AH2, AO**
1191.4	0.015	**IO1**
1184.8	0.005	**IO2**
1124.2	0.050	**IO1**
1110.2	0.038	**AH1**
1107.3	0.030	**AH2**
1090.1	0.049	**AO**
1083.5	0.069	**AH1**
1082.1	0.051	**AH2**
1076.9	0.013	**AH1**
1053.3	0.001	**IO2**
981.0	0.025	**AH1**
954.9	0.010	**AH1**
817.6	0.026	**IO1, AH1, AH2**
807.3	0.080	**AH1**
805.9	0.069	**AH2**
782.1	0.026	**AH2**
780.6	0.072	**AO, IO2**
767.6	0.005	**AO**
750.8	0.004	**IO2**
746.9	0.014	**IO1**
743.4	0.0163	**AO**
720.0	0.003	**AO**
716.8	0.038	**AO**
710.6	0.009	**AH1**
708.8	0.008	**AH2**
685.9	0.001	**IO2**
636.6	0.031	**IO1**

633.9	0.016	**AH1**
622.8	0.014	**AO**
617.9	0.006	**AH2**
614.5	0.070	**AO**
601.3	0.010	**AH2**
595.6	0.005	**AH1**
584.2	0.001	**IO2**
578.8 575.5	0.059	**AO**
568.5	0.038	**AO**
558.6	0.017	**AH1**
554.9	0.009	**AH2**

537.2	0.022	**AO**
529.2	0.017	**AO, AH1**
527.0 523.3 520.3	0.292	**AH1**
517.6	0.157	**AH2**
508.4 506.6	0.127	**AH2**
499.0	0.088	**AH2**
444.6	0.013	**AH1**
442.5	0.012	**AH2**

The wavenumber of the strongest component of multiplet band is underline.