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UV-Induced Trithione → Trithiol Triple Proton Transfer in Trithiocyanuric Acid Isolated in Low-Temperature Matrixes

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Trithiocyanuric acid ($C_3H_3N_3S_3$) monomers were studied using FTIR spectroscopy combined with the matrix isolation technique. The matrix-isolated compound adopted only the trithione tautomeric form, as revealed by its IR spectra. Upon UV irradiation ($\lambda > 270$ nm), the trithiol tautomeric form of trithiocyanuric acid (trimercaptotriazine) was generated. This is the first observation of an intramolecular triple trithione → trithiol photoinduced proton transfer. The substrate and the product of the photoreaction were identified by comparison of their IR spectra with the spectra theoretically calculated (at the DFT(B3LYP)/6-31++G(d,p) level) for the trithione D_{3h} and trithiol C_{3h} structures, respectively. The IR absorption bands observed in the experimental spectra were assigned to the calculated normal modes. The theoretical normal modes were analyzed in terms of symmetry-adapted internal coordinates. Consistent sets of symmetry coordinates applicable for the description of in- and out-of-plane movements of six-membered rings with D_{3h} and C_{3h} symmetry were defined for the first time.

Introduction

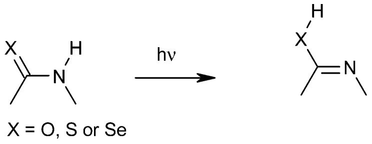
Proton transfer is one of the basic reactions in chemistry and biology.[1] Despite that, most proton-transfer reactions are not fully understood because of the complex interrelation between intra- and intermolecular effects. These processes are often interpreted within simplified schemes concerning isolated molecules or small molecular fragments. Basically, a proton can be transferred between the groups of the same molecule (intramolecular proton transfer) or from one molecule to another (intermolecular proton transfer).

Among intramolecular proton-transfer reactions, two types of light-stimulated processes may be distinguished. In the first type of photoprocess,[2,3] known as excited-state intramolecular proton transfer (ESIPT), the proton transfer occurs in the act of transition from the excited state of the substrate to the excited state of the product (phototautomer). In a molecule undergoing the ESIPT process, the proton donor and the proton acceptor are situated in a six- or five-membered quasi-ring closed by a hydrogen bond. Intramolecular hydrogen bonding is a prerequisite of the ESIPT reaction.

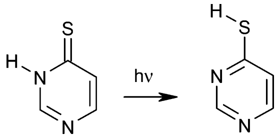
The second type of intramolecular proton-transfer photoreaction (Scheme 1) has been observed for matrix-isolated, monomeric carbonyl,[4] thiocarbonyl,[5−8] and selenocarbonyl[9] molecules without intramolecular hydrogen bonds. Intramolecular interactions between the proton donor and proton acceptor groups in these systems are much weaker than typical hydrogen bonds.[10] Generally, in the systems in question, the proton donor (N−H) and proton acceptor (C=O, C=S, or C=Se) groups form a four-membered quasi-ring.

Examples of this type of photoinduced proton transfer reaction were recently observed for monomers of simple thioamides (thioacetamide[11] and thiourea[12]) isolated in low-temperature inert gas matrixes. In these processes, the thione forms of the compounds were transformed, upon UV irradiation, into the corresponding thiol tautomers. Similar thione → thiol phototautomerization was found for thione heterocyclic compounds, such as 4-pyrimidinethione[13] (Scheme 2).

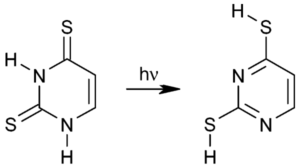
SCHEME 1 Photoinduced Proton-Transfer Reaction of the Second Type



SCHEME 2 Photoinduced Tautomerization Reaction in 4-Pyrimidinethione



SCHEME 3 Photoinduced Double Proton Transfer in 2,4-Dithiouracil



The dithione → dithiol photoreaction in matrix-isolated 2,4-dithiouracil was the first example of photoinduced intramolecular double proton transfer (Scheme 3) of the second type.[14] The photoproduct of this reaction was identified on the basis of good agreement between the IR spectrum recorded after UV irradiation and the theoretical spectrum calculated for the dithiol tautomer. So far, no triple intramolecular proton-transfer photoreactions have been observed.

These results prompted us to undertake a study of the photochemical behavior of trithiocyanuric acid (denoted further as TCA). In the trithione tautomeric form of TCA, there are three proton donor (N−H) groups and three proton acceptor

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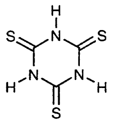
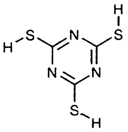
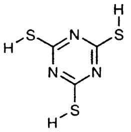
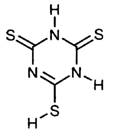
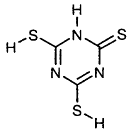
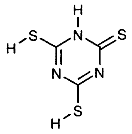
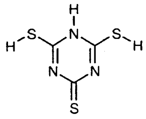
TABLE 1: Relative Energies (in kJ mol^{-1}) of Isomeric Forms of Trithiocyanuric Acid

							
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**
ΔE_{el}(MP2)	0	84.91	85.98	72.53	108.05	112.47	156.19
ΔZPE(DFT(B3LYP))	0	-28.16	-27.75	-10.83	-19.91	-20.41	-23.39
ΔE_{tot}	0	56.75	58.23	61.70	88.14	92.06	132.80

[a] ΔE_{el}(MP2): relative electronic energy calculated at the MP2/6-31++G(d,p) level. [b] ΔZPE(DFT(B3LYP)): relative zero-point vibrational energy calculated at the DFT(B3LYP)/6-31++G(d,p) level. [c] $\Delta E_{tot} = \Delta E_{el} + \Delta$ZPE.

TABLE 2: Symmetry Coordinates Used in the Normal-Mode Analysis for D_{3h} Trithione Tautomer I of Trithiocyanuric Acid (atom numbering as in Chart 1)

A'_1	
$S_1 = (6^{-1/2})\,(r_{1,2} + r_{2,3} + r_{3,4} + r_{4,5} + r_{5,6} + r_{6,1})^{a}$	νR1
$S_2 = (3^{-1/2})\,(r_{2,7} + r_{4,9} + r_{6,11})$	νCS1
$S_3 = (3^{-1/2})\,(r_{1,8} + r_{3,10} + r_{5,12})$	νNH1
$S_4 = (6^{-1/2})\,(\beta_{6,2,1} - \beta_{1,3,2} + \beta_{2,4,3} - \beta_{3,5,4} + \beta_{4,6,5} - \beta_{5,1,6})$	βR1
A'_2	
$S_5 = (6^{-1/2})\,(r_{1,2} - r_{2,3} + r_{3,4} - r_{4,5} + r_{5,6} - r_{6,1})$	νR2
$S_6 = (6^{-1/2})\,(\beta_{8,2,1} - \beta_{8,6,1} + \beta_{10,4,3} - \beta_{10,2,3} + \beta_{12,6,5} - \beta_{12,4,5})$	βNH1
$S_7 = (6^{-1/2})\,(\beta_{9,5,4} - \beta_{9,3,4} + \beta_{11,1,6} - \beta_{11,5,6} + \beta_{7,3,2} - \beta_{7,1,2})$	βCS1
E'	
$S_8 = (12^{-1/2})\,(-r_{1,2} + 2r_{2,3} - r_{3,4} - r_{4,5} + 2r_{5,6} - r_{6,1})$	νR3
$S_9 = {}^{1}/_{2}\,(r_{1,2} - r_{3,4} - r_{4,5} + r_{6,1})$	νR4
$S_{10} = (12^{-1/2})\,(r_{1,2} + 2r_{2,3} + r_{3,4} - r_{4,5} - 2r_{5,6} - r_{6,1})$	νR5
$S_{11} = {}^{1}/_{2}\,(-r_{1,2} + r_{3,4} - r_{4,5} + r_{6,1})$	νR6
$S_{12} = (6^{-1/2})\,(-r_{2,7} + 2r_{4,9} - r_{6,11})$	νCS2
$S_{13} = (2^{-1/2})\,(r_{2,7} - r_{6,11})$	νCS3
$S_{14} = (6^{-1/2})\,(2r_{1,8} - r_{3,10} - r_{5,12})$	νNH2
$S_{15} = (2^{-1/2})\,(r_{5,12} - r_{3,10})$	νNH3
$S_{16} = {}^{1}/_{2}\,(-\beta_{7,3,2} + \beta_{7,1,2} + \beta_{11,1,6} - \beta_{11,5,6})$	βCS2
$S_{17} = (12^{-1/2})\,(2\beta_{9,5,4} - 2\beta_{9,3,4} - \beta_{11,1,6} + \beta_{11,5,6} - \beta_{7,3,2} + \beta_{7,1,2})$	βCS3
$S_{18} = (12^{-1/2})\,(2\beta_{6,2,1} - \beta_{1,3,2} - \beta_{2,4,3} + 2\beta_{3,5,4} - \beta_{4,6,5} - \beta_{5,1,6})$	βR2
$S_{19} = {}^{1}/_{2}\,(\beta_{1,3,2} - \beta_{2,4,3} + \beta_{4,6,5} - \beta_{5,1,6})$	βR3
$S_{20} = {}^{1}/_{2}\,(-\beta_{12,6,5} + \beta_{12,4,5} + \beta_{10,4,3} - \beta_{10,2,3})$	βNH2
$S_{21} = (12^{-1/2})\,(2\beta_{8,2,1} - 2\beta_{8,6,1} - \beta_{10,4,3} + \beta_{10,2,3} - \beta_{12,6,5} + \beta_{12,4,5})$	βNH3
A''_2	
$S_{22} = (6^{-1/2})\,(\tau_{1,2,3,4} - \tau_{2,3,4,5} + \tau_{3,4,5,6} - \tau_{4,5,6,1} + \tau_{5,6,1,2} - \tau_{6,1,2,3})$	τR1
$S_{23} = (3^{-1/2})\,(\gamma_{8,6,1,2} + \gamma_{10,2,3,4} + \gamma_{12,4,5,6})$	γNH1
$S_{24} = (3^{-1/2})\,(\gamma_{9,3,4,5} + \gamma_{11,5,6,1} + \gamma_{7,1,2,3})$	γCS1
E''	
$S_{25} = (12^{-1/2})\,(2\tau_{1,2,3,4} - \tau_{2,3,4,5} - \tau_{3,4,5,6} + 2\tau_{4,5,6,1} - \tau_{5,6,1,2} - \tau_{6,1,2,3})$	τR2
$S_{26} = {}^{1}/_{2}\,(\tau_{2,3,4,5} - \tau_{3,4,5,6} + \tau_{5,6,1,2} - \tau_{6,1,2,3})$	τR3
$S_{27} = (2^{-1/2})\,(\gamma_{12,4,5,6} - \gamma_{10,2,3,4})$	γNH2
$S_{28} = (6^{-1/2})\,(2\gamma_{8,6,1,2} - \gamma_{10,2,3,4} - \gamma_{12,4,5,6})$	γNH3
$S_{29} = (2^{-1/2})\,(\gamma_{7,1,2,3} - \gamma_{11,5,6,1})$	γCS2
$S_{30} = (6^{-1/2})\,(2\gamma_{9,3,4,5} - \gamma_{11,5,6,1} - \gamma_{7,1,2,3})$	γCS3

[a] $r_{i,j}$ is the distance between atoms A_i and A_j; $\beta_{i,j,k}$ is the angle between vectors A_kA_i and A_kA_j; $\tau_{i,j,k,l}$ is the dihedral angle between the plane defined by A_i, A_j, A_k, and the plane defined by A_j, A_k, and A_l atoms; $\gamma_{i,j,k,l}$ is the angle between vector A_kA_i and the plane defined by atoms A_j, A_k, and A_l.

(C=S) groups. No intramolecular hydrogen bonds connect these moieties. Because the mechanism of the thione → thiol phototautomerism (of the type observed, for example, for 4-pyrimidinethione) is not known, it was not possible to predict a priori whether any UV-induced proton-transfer processes should occur for TCA or not. This question can be answered only on the basis of an experimental study.

Little is known about the tautomerism of TCA, although previous investigations demonstrated the predominance of the trithione form in hydrogen-bonded crystal networks.[15,16] To the best of our knowledge, there are no data on the thione → thiol tautomerism of TCA monomers either in the gas phase or in low-temperature inert gas matrixes, nor on the behavior of this compound on exposure to UV light. The current paper presents the observation of the UV-induced trithione → trithiol proton-transfer reaction occurring for monomeric TCA at 10 K. It is the first report of such a triple phototautomerization phenomenon.

TABLE 3: Wavenumbers ($\tilde{\nu}$/cm^{-1}), PED (%) of the Normal Modes of Trithione D_{3h} Isomer I of Trithiocyanuric Acid, and Absolute Intensities (A^{th}/km mol^{-1}) of the IR Bands Theoretically Calculated at the DFT(B3LYP)/6-31++G(d,p) Level

mode	$\tilde{\nu}$[a]	A^{th}	symmetry	PED[b]
Q1	3549	0.0	A'_1	νNH1(100)
Q2	3544	141	E'	νNH2(100)
Q2*[c]	3544	141	E'	νNH3(100)
Q3	1532	1116	E'	βNH2(59), νR3(19)
Q3*	1532	1116	E'	βNH3(59), νR6(19)
Q4	1356	0.0	A'_2	βNH1(97)
Q5	1352	263	E'	νR3(56), νR4(15), βNH2(12), βCS2(11)
Q5*	1352	263	E'	νR6(56), νR5(15), βNH3(12), βCS3(11)
Q6	1286	0.0	A'_1	νCS1(48), βR1(35), νR1(18)
Q7	1253	0.0	A'_2	νR2(102)
Q8	1109	322	E'	νR4(41), βNH2(28), νCS2(27)
Q8*	1109	322	E'	νR5(41), βNH3(28), νCS3(27)
Q9	967	0.0	A'_1	βR1(48), νR1(48)
Q10	903	14	E'	νCS2(47), νR4(17), βR2(17), νR3(14)
Q10*	903	14	E'	νCS3(47), νR5(17), βR3(17), νR6(14)
Q11	678	162	A''_2	γNH1(80), τR1(21)
Q12	628	0.0	E''	γNH2(111)
Q12*	628	0.0	E''	γNH3(111)
Q13	608	28	A''_2	γCS1(87), γNH1(22)
Q14	568	0.0	E''	γCS2(98)
Q14*	568	0.0	E''	γCS3(98)
Q15	453	0.0	A'_2	βCS1(100)
Q16	450	23	E'	βR2(68), νCS2(21)
Q16*	450	23	E'	βR3(68), νCS3(21)
Q17	436	0.0	A'_1	νCS1(50), νR1(34), βR1(17)
Q18	206	5	E'	βCS2(82), νR4(14)
Q18*	206	5	E'	βCS3(82), νR5(14)
Q19	130	0.0	E''	τR2(111)
Q19*	130	0.0	E''	τR3(111)
Q20	95	2	A''_2	τR1(88), γCS1(14)

[a] Theoretical frequencies were scaled by 0.98. [b] PEDs lower than 10% not included. [c] Q(i) and Q*(i) denote pairs of degenerate modes.

Experimental Section

Trithiocyanuric acid was a commercial product of 95% purity purchased from Aldrich. A solid sample of the compound was heated (to 430 K) in a glass microoven placed in the vacuum chamber of a continuous-flow helium cryostat. The vapors of the studied compound were deposited, together with a large excess of matrix gas, on a CsI window cooled to 10 K. Matrix gases of spectral purity of 6.0, argon and nitrogen, were supplied by Linde AG and Technische Gase, Leipzig. The IR spectra were recorded with 0.5 cm^{-1} resolution using a Thermo Nicolet Nexus 670 FTIR spectrometer equipped with a KBr beam splitter and a DTGS detector. Integral intensities of the IR absorption bands were measured by numerical integration. Matrixes were irradiated with the light from a high-pressure HBO 200 mercury lamp fitted with a water filter and a cutoff filter transmitting the light with $\lambda > 270$ nm. The typical irradiation time was 3 h.

Computational Methods

The equilibrium geometries of the trithiocyanuric acid tautomers/isomers were fully optimized at the MP2 level of theory.[17] The MP2 electronic energies for the optimized isomer geometries are collected in Table 1.

The harmonic frequencies of the normal modes were calculated at the DFT(B3LYP) level[18,19] at geometries optimized with the same theoretical method. The DFT(B3LYP) calculations are usually considered better-suited for prediction of vibrational spectra than those carried out with the MP2 method.[20] To correct for vibrational anharmonicity, basis set truncation, and the neglected part of electron correlation, the calculated DFT wavenumbers were scaled down by a single factor of 0.98. The *Gaussian 98* program[21] and the standard 6-31++G(d,p) basis set were used in all calculations.

Transformations of the force constants with respect to the Cartesian coordinates to the force constants with respect to the molecule-fixed symmetry coordinates allowed the normal-coordinate analysis to be performed as described by Schachtschneider.[22] The symmetry coordinates used in the potential energy distribution (PED) analysis of the trithione D_{3h} form and the trithiol C_{3h} form were specially generated for the purpose of the present work by applying the symmetry projection operators to the primitive stretching, in-plane bending, torsional, and wagging internal coordinates.[23] Tables 2 and 5 list these symmetry coordinates. The consistent sets of symmetry coordinates applicable for description of the in- and out-of-plane movements of six-membered rings with D_{3h} and C_{3h} symmetry are given for the first time. PED matrices[24] have been calculated, and the elements of these matrices greater than 10% are collected in Tables 3 and 6.

Results and Discussion

Trithiocyanuric Acid in Low-Temperature Matrixes. TCA may adopt one of twelve different structures: one isomer of the trithione tautomer, two isomers of the trithiol tautomer, and nine isomers of the mixed thione−thiol tautomers. The relative energy calculations, carried out in the present work at the MP2/6-31++G(d,p) level of theory, predict planar trithione tautomer **I** (Chart 1) to be the most stable form of the compound. It is apparent from the results collected in Table 1 that the other isomers of TCA are much higher in energy. The differences between the energy of form **I** and the energies of trithiol isomers **II** and **III** are larger than 55 kJ mol^{-1}. The energies of the mixed thione−thiol forms are even higher. The results of the theoretical assessment of the relative stabilities of the isomeric forms of TCA strongly suggest that only structure **I** should be adopted by molecules of the compound in the gas phase and trapped in a low-temperature matrix. These theoretical predictions are in accordance with previous calculations of Armstrong et al.[15] carried out at a somewhat lower (MP2/6-31G*) level. For the structurally related 2,4-dithiouracil molecule, the dithione tautomeric form was also theoretically predicted to be the most stable. This was the only form that was observed in matrix isolation experiments.[14,25]

The IR spectra of TCA isolated in Ar and N_2 matrixes are presented in Figure 1 and Figure 2A,C. These spectra are well-reproduced by the spectrum of trithione form **I** theoretically calculated at the DFT(B3LYP)/6-31++G(d,p) level. Detailed descriptions of the normal modes of trithione D_{3h} isomer **I** of the compound are given in Table 3, and the assignments of the experimentally observed bands are presented in Table 4.

The IR spectrum of TCA is very simple for a molecule consisting of twelve atoms. The reason for this simplicity is the high D_{3h} symmetry of the system. The normal modes belonging to A'_1, A'_2, and E'' representations are inactive in the infrared, and the degeneracy of the modes belonging to the E' representation reduces the number of bands that should appear in the IR spectrum at different frequencies.

Apart from their simplicity, an additional distinguishing feature of the IR spectra of TCA isolated in low-temperature matrixes is the shape of the bands assigned to the normal modes belonging to the degenerate representation E'. These bands appear in the experimental spectra as complex structures split into several components (see Figure 3). Most probably, the

TABLE 4: Wavenumbers ($\tilde{\nu}$/cm^{-1}) and Relative Intensities (I_{rel}) of the IR Bands in the Spectra of Trithiocyanuric Acid Isolated in Ar and N_2 Matrixes Assigned to the Normal Modes Predicted Theoretically for the D_{3h} Isomer (form I)[a]

Ar matrix		N_2 matrix		calculated			
$\tilde{\nu}$	I_{rel}	$\tilde{\nu}$	I_{rel}	modes[b]	$\tilde{\nu}^c$	A^{th}	approximate description
3427[d], 3424	402	3399, 3398, *3393*	640	Q2, Q2*	3544	282	νNH
1572, 1568, *1559*, 1553, 1523, *1519*, 1515	2182	1580, 1577, *1572*, 1567, *1531*, 1529	1955	Q3, Q3*	1532	2232	βNH, νR
1388, *1375*, 1369, 1336, *1309*	447	1361, *1357*, 1349	518	Q5, Q5*	1352	526	νR
1128, 1113, *1108*, 1105	686	*1121*, 1118	679	Q8, Q8*	1109	644	νR, βNH, νCS
690, *687*, 683	128	*729*, 720	85	Q11	678	162	γNH, τR
458, *455*, 453	55	*459*, 457	46	Q16, Q16*	450	46	βR, νCS
211	12	214	12	Q18, Q18*	206	10	βCS

[a] The theoretically calculated wavenumbers ($\tilde{\nu}$/cm^{-1}) and absolute intensities (A^{th}/km mol^{-1}) of the corresponding bands are also listed. [b] Detailed PED descriptions of the normal modes are given in Table 3. [c] Theoretical frequencies were scaled by 0.98. [d] The most intense components of the split bands are in italics.

TABLE 5: Symmetry Coordinates Used in the Normal-Mode Analysis for C_{3h} Trithiol Isomer II of Trithiocyanuric Acid (atom numbering as in Chart 1)

A′	
$S_1 = (3^{-1/2})\,(r_{7,10} + r_{9,12} + r_{11,8})^a$	νSH1
$S_2 = (3^{-1/2})\,(r_{2,7} + r_{4,9} + r_{6,11})$	νCS1
$S_3 = (6^{-1/2})\,(r_{1,2} + r_{2,3} + r_{3,4} + r_{4,5} + r_{5,6} + r_{6,1})$	νR1
$S_4 = (6^{-1/2})\,(r_{1,2} - r_{2,3} + r_{3,4} - r_{4,5} + r_{5,6} - r_{6,1})$	νR2
$S_5 = (3^{-1/2})\,(\beta_{10,2,7} + \beta_{8,6,11} + \beta_{12,4,9})$	βSH1
$S_6 = (6^{-1/2})\,(\beta_{9,5,4} - \beta_{9,3,4} + \beta_{11,1,6} - \beta_{11,5,6} + \beta_{7,3,2} - \beta_{7,1,2})$	βCS1
$S_7 = (6^{-1/2})\,(\beta_{6,2,1} - \beta_{1,3,2} + \beta_{2,4,3} - \beta_{3,5,4} + \beta_{4,6,5} - \beta_{5,1,6})$	βR1
E′	
$S_8 = (2^{-1/2})\,(r_{7,10} - r_{11,8})$	νSH2
$S_9 = (6^{-1/2})\,(2r_{9,12} - r_{7,10} - r_{11,8})$	νSH3
$S_{10} = (2^{-1/2})\,(r_{2,7} - r_{6,11})$	νCS2
$S_{11} = (6^{-1/2})\,(2r_{4,9} - r_{2,7} - r_{6,11})$	νCS3
$S_{12} = (2^{-1/2})\,(\beta_{10,2,7} - \beta_{8,6,11})$	βSH2
$S_{13} = (6^{-1/2})\,(2\beta_{12,4,9} - \beta_{8,6,11} - \beta_{10,2,7})$	βSH3
$S_{14} = (12^{-1/2})\,(2\beta_{9,5,4} - 2\beta_{9,3,4} - \beta_{7,3,2} + \beta_{7,1,2} + \beta_{11,5,6} - \beta_{11,1,6})$	βCS2
$S_{15} = {}^1/_2\,(\beta_{7,3,2} - \beta_{7,1,2} + \beta_{11,5,6} - \beta_{11,1,6})$	βCS3
$S_{16} = {}^1/_2\,(r_{1,2} - r_{3,4} + r_{4,5} - r_{6,1})$	νR3
$S_{17} = (6^{-1/2})\,(2r_{2,3} - r_{1,2} - r_{3,4} + 2r_{5,6} - r_{4,5} - r_{6,1})$	νR4
$S_{18} = (2^{-1/2})\,(r_{2,3} - r_{5,6})$	νR5
$S_{19} = {}^1/_2\,(r_{1,2} - r_{3,4} - r_{4,5} + r_{6,1})$	νR6
$S_{20} = {}^1/_2\,(\beta_{1,3,2} - \beta_{2,4,3} + \beta_{4,6,5} - \beta_{5,1,6})$	βR2
$S_{21} = (12^{-1/2})\,(2\beta_{6,2,1} - \beta_{1,3,2} - \beta_{2,4,3} + 2\beta_{3,5,4} - \beta_{4,6,5} - \beta_{5,1,6})$	βR3
A″	
$S_{22} = (6^{-1/2})\,(\tau_{10,7,2,1} + \tau_{10,7,2,3} + \tau_{12,9,4,5} + \tau_{12,9,4,3} + \tau_{8,11,6,5} + \tau_{8,11,6,1})$	τSH1
$S_{23} = (3^{-1/2})\,(\gamma_{9,5,4,3} + \gamma_{11,1,6,5} + \gamma_{7,3,2,1})$	γCS1
$S_{24} = (6^{-1/2})\,(\tau_{1,2,3,4} - \tau_{2,3,4,5} + \tau_{3,4,5,6} - \tau_{4,5,6,1} + \tau_{5,6,1,2} - \tau_{6,1,2,3})$	τR1
E″	
$S_{25} = (12^{-1/2})\,(2\tau_{12,9,4,5} + 2\tau_{12,9,4,3} - \tau_{10,7,2,3} - \tau_{10,7,2,1} - \tau_{8,11,6,1} - \tau_{8,11,6,5})$	τSH2
$S_{26} = {}^1/_2\,(\tau_{10,7,2,3} + \tau_{10,7,2,1} - \tau_{8,11,6,1} - \tau_{8,11,6,5})$	τSH3
$S_{27} = (6^{-1/2})\,(2\gamma_{9,3,4,5} - \gamma_{11,5,6,1} - \gamma_{7,1,2,3})$	γCS2
$S_{28} = (2^{-1/2})\,(\gamma_{7,1,2,3} - \gamma_{11,5,6,1})$	γCS3
$S_{29} = {}^1/_2\,(\tau_{2,3,4,5} - \tau_{3,4,5,6} + \tau_{5,6,1,2} - \tau_{6,1,2,3})$	τR2
$S_{30} = (12^{-1/2})\,(2\tau_{1,2,3,4} - \tau_{2,3,4,5} - \tau_{3,4,5,6} + 2\tau_{4,5,6,1} - \tau_{5,6,1,2} - \tau_{6,1,2,3})$	τR3

[a] $r_{i,j}$ is the distance between atoms A_i and A_j; $\beta_{i,j,k}$ is the angle between vectors A_kA_i and A_kA_j; $\tau_{i,j,k,l}$ is the dihedral angle between the plane defined by A_i, A_j, A_k, and the plane defined by A_j, A_k, and A_l atoms; $\gamma_{i,j,k,l}$ is the angle between vector A_kA_i and the plane defined by atoms A_j, A_k, and A_l.

shapes of these bands are due to matrix splitting. The matrix environment certainly does not adopt the same symmetry as the isolated molecule. Hence, the guest−host interactions could lead to the lifting of degeneracy, and the extent of this effect can be different in different matrix sites. This interpretation is supported by the observation of quite different shapes for the corresponding multiplets in the spectra of the compound isolated in argon and nitrogen matrixes (Figure 3).

Despite the small spectral shifts and the differences in shapes of the bands, the IR spectra of TCA isolated in Ar and N_2 matrixes are similar to each other. In the spectral region above 3000 cm^{-1}, only one structured band is observed near 3400 cm^{-1}, with maxima at 3427 and 3424 cm^{-1} (Ar) and 3399, 3398, and 3393 cm^{-1} (N_2). In principle, one can expect three bands corresponding to the stretching vibrations of the three NH groups, but the high D_{3h} symmetry of the molecule reduces this number to only two IR-active νNH modes that are degenerate. The frequency of these modes obtained by the DFT calculations corresponds to the wavenumber of 3544 cm^{-1}.

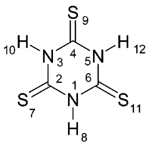
According to the theoretical calculations, the strongest band of the trithione tautomer should be positioned at 1532 cm^{-1}. In the experimental spectrum, the most pronounced, split band is that with a maximum at 1519 cm^{-1} (Ar). This strong band should be attributed to the bending vibration of the NH fragments. The presence in the spectrum of the weaker, structured absorption band with a maximum at 1559 cm^{-1} may be due to the matrix-induced lifting of the degeneracy of the βNH vibrations.

TABLE 6: Wavenumbers ($\tilde{\nu}$/cm^{-1}), PED (%) of the Normal Modes of Trithiol C_{3h} Isomer II of Trithiocyanuric Acid, and Absolute Intensities (A^{th}/km mol^{-1}) of the IR Bands Theoretically Calculated at the DFT(B3LYP)/6-31++G(d,p) Level

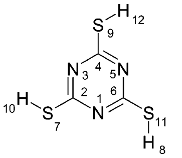
mode	$\tilde{\nu}^{a}$	A^{th}	symmetry	PED^{b}
Q1	2639	0.0	A′	νSH1(100)
Q2	2639	0.2	E′	νSH2(100)
Q2*^{c}	2639	0.2	E′	νSH3(100)
Q3	1507	773	E′	νR3(89)
Q3*	1507	773	E′	νR4(89)
Q4	1282	374	E′	νR5(78)
Q4*	1282	374	E′	νR6(78)
Q5	1272	0.0	A′	βR1(49), νCS1(26), νR1(25)
Q6	1208	0.0	A′	νR2(97)
Q7	971	0.0	A′	νR1(58), βR1(33)
Q8	943	0.0	A′	βSH1(82)
Q9	917	2	E′	βSH2(84)
Q9*	917	2	E′	βSH3(84)
Q10	837	127	E′	βR2(35), νCS2(32)
Q10*	837	127	E′	βR3(35), νCS3(32)
Q11	787	9	A″	τR1(67), γCS1(33)
Q12	620	0.0	E″	γCS2(89), τR2(10)
Q12*	620	0.0	E″	γCS3(89), τR3(10)
Q13	440	0.6	E′	νCS2(41), βR2(41)
Q13*	440	0.6	E′	νCS3(41), βR3(41)
Q14	420	0.0	A′	βCS1(90)
Q15	383	0.0	A′	νCS1(70), βR1(14), νR1(11)
Q16	337	0.0	E″	τSH2(100)
Q16*	337	0.0	E″	τSH3(100)
Q17	331	57	A″	τSH1(100)
Q18	182	2	E′	βCS2(85)
Q18*	182	2	E′	βCS3(85)
Q19	150	0.0	E″	τR2(90), γCS2(11)
Q19*	150	0.0	E″	τR3(90), γCS3(11)
Q20	131	0.7	A″	γCS1(67), τR1(33)

[a] Theoretical frequencies were scaled by 0.98. [b] PEDs lower than 10% not included. [c] Q(*i*) and Q*(*i*) denote pairs of degenerate modes.

CHART 1 Atom Numbering for Tautomers of Trithiocyanuric Acid



I



II

Two weaker, structured absorptions observed in the Ar matrix spectrum at 1388−1361 cm^{-1} and 1339−1293 cm^{-1} were assigned to the degenerate modes at 1352 cm^{-1} with a dominant contribution of the ring-stretching vibrations. It is worth noting that in this range the spectrum of TCA in N_2 matrix is much simpler and consists of only one structured band with a maximum at 1357 cm^{-1}, which is very close to the theoretically predicted wavenumber of 1352 cm^{-1}.

The split band at 1113 and 1108 cm^{-1}, found in the spectrum of the compound isolated in an Ar matrix and attributed to the ring-stretching vibrations coupled with bending vibrations of the NH and C═S groups, is observed in the spectrum of TCA in N_2 matrix as a multiplet of quite different shape (see Figure 3).

A typical feature of the IR spectra of the thione compounds is a strong band at ca. 1230 cm^{-1}, commonly ascribed to the stretching vibration of the C═S fragment.[26] Because of the high symmetry of the TCA molecule, such a band was not observed in the experimental spectrum of the compound. The corresponding normal mode Q6 (Table 3) with a theoretical wavenumber of 1286 cm^{-1} belongs to a fully symmetric representation and is not active in the IR absorption spectra.

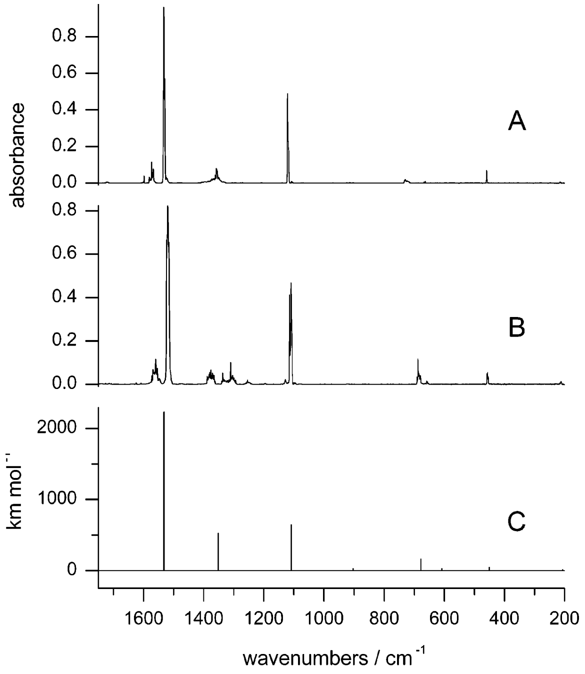


Figure 1. IR spectra of trithiocyanuric acid isolated in (A) nitrogen matrix and (B) argon matrix. (C) Spectrum of trithione tautomer **I** of the compound theoretically calculated at the DFT(B3LYP)/6-31++G-(d,p) level. Theoretical wavenumbers were scaled by a single factor of 0.98. The baselines of the experimental spectra were corrected.

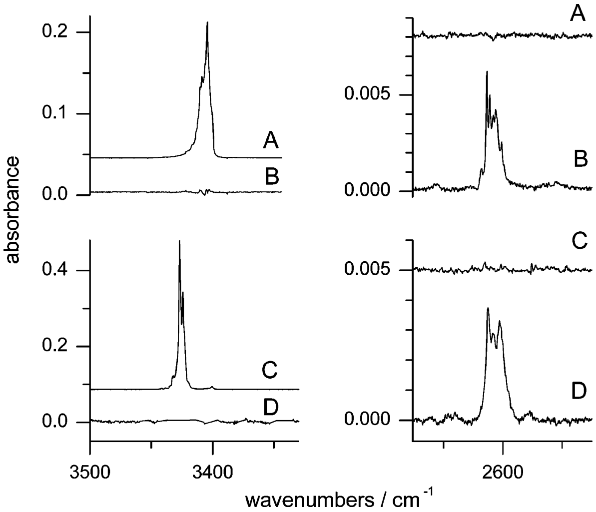


Figure 2. IR spectra of trithiocyanuric acid isolated in (A) N_2 matrix, (C) Ar matrix. IR spectra of the photoproduct generated after 3 h of irradiation of the matrixes with UV (λ > 270 nm) light: (B) N_2 matrix, (D) Ar matrix. The presented bands are due to νNH (at ca. 3400 cm^{-1}) and νSH (at ca. 2600 cm^{-1}) vibrations.

The obvious exception to the general similarity of the IR spectra of the compound isolated in Ar and N_2 matrixes is the pair of bands observed at ca. 700 cm^{-1}. The band at 687 cm^{-1} in the spectrum of TCA isolated in an Ar matrix has its counterpart in the spectrum of the compound in an N_2 matrix positioned at the significantly higher wavenumber of 729 cm^{-1} (see Figure 4). Such a shift to higher wavenumbers is characteristic of bands attributed to the wagging vibrations of NH groups.[27,28] Also, the broadening of the band observed in the spectrum of TCA in solid nitrogen is usually observed for bands due to γNH modes. This experimental effect caused by the matrix environment is in full agreement with the interpretation of these absorptions resulting from comparison with the theoretically predicted spectrum (Table 4).

TABLE 7: Wavenumbers ($\tilde{\nu}$/cm^{-1}) and Relative Intensities (I_{rel}) of the IR Bands in the Spectra of the Photoproduct Generated from Trithiocyanuric Acid Isolated in Ar and N$_2$ Matrixes Assigned to the Normal Modes Predicted Theoretically for the Trithol C_{3h} Isomer (form II)[a]

Ar matrix		N$_2$ matrix		calculated			approximate description
$\tilde{\nu}$	I_{rel}	$\tilde{\nu}$	I_{rel}	modes[b]	$\tilde{\nu}$[c]	A^{th}	
2612, 2607, 2602	30	2612, 2610, 2605	44	Q2, Q2*	2639	0.4	νSH
1505, *1499*, 1496[d]	1338	1502, *1499*, 1496	1550	Q3, Q3*	1507	1546	νR
1287, 1282, 1280, 1276, 1263	636	1290, 1280, 1267	646	Q4, Q4*	1282	748	νR
852, 836	222	856, 840	176	Q10, Q10*	837	254	βR, νCS
797	11	798	8	Q11	787	9	τR, γCS

[a] The theoretically calculated wavenumbers ($\tilde{\nu}$/cm^{-1}) and absolute intensities (A^{th}/km mol^{-1}) of the corresponding bands are also listed. [b] Detailed PED descriptions of the normal modes are given in Table 6. [c] Theoretical frequencies were scaled by 0.98. [d] The most intense components of the split bands are in italics.

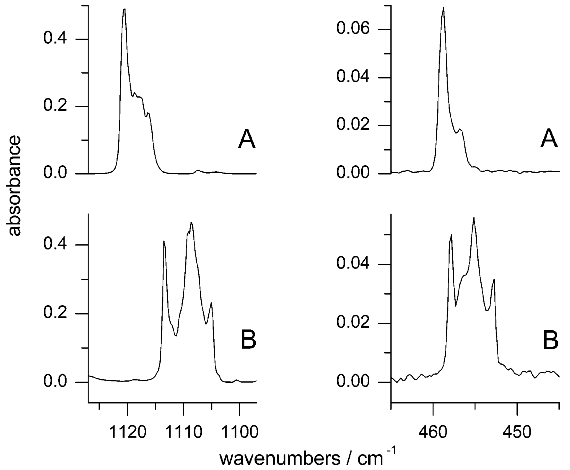


Figure 3. Comparison of band shapes in the IR spectra of trithiocyanuric acid isolated in (A) nitrogen matrix and (B) argon matrix.

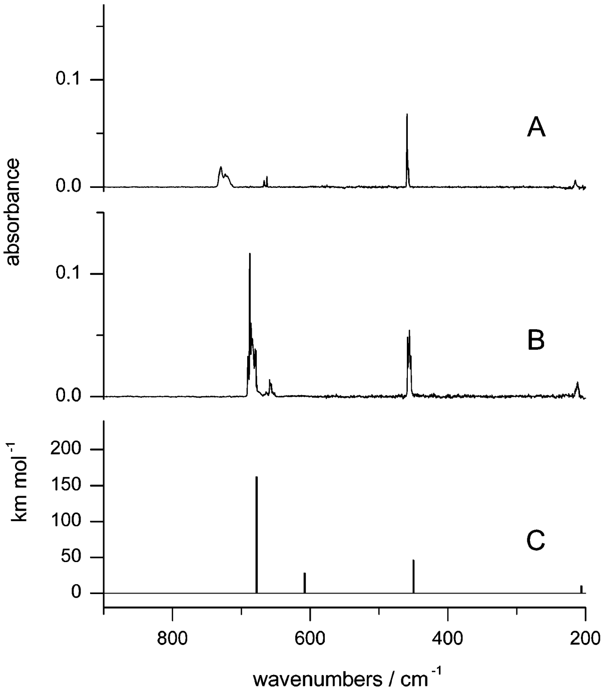
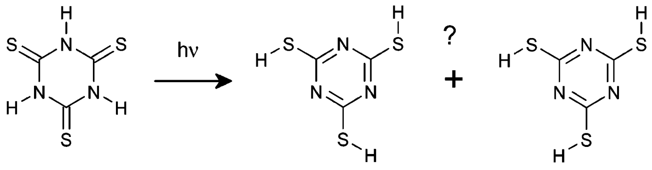


Figure 4. Low-frequency fragments of the IR spectra of trithiocyanuric acid isolated in (A) nitrogen matrix and (B) argon matrix. (C) The corresponding fragment of the spectrum of trithione tautomer **I** of the compound theoretically calculated at the DFT(B3LYP)/6-31++G(d,p) level. Theoretical wavenumbers were scaled by a single factor of 0.98. The baselines of the experimental spectra were corrected.

SCHEME 4 UV-Induced Triple Proton Transfer



I **II** **III**

The structured band at about 450 cm^{-1}, whose shape is more complex in the spectrum of the compound isolated in an Ar matrix and somewhat simpler in the spectrum of an N$_2$ matrix (see Figure 3), has been assigned to the bending vibrations of the ring, coupled with the stretching vibrations of C=S groups.

Effect of UV Irradiation: The Triple Proton Transfer. Upon irradiation of TCA isolated in low-temperature matrixes with UV light (λ > 270 nm), the IR spectrum of the compound changed significantly. The bands of the initial spectrum decreased in intensity, whereas a set of completely new bands appeared. Monitoring of the IR spectra during the progress of the photoreaction revealed a continuous decrease of the population of the substrate accompanied by an increase of the population of the photoproduct. No bands that would behave in a different manner than the IR absorptions due to the substrate and the final photoproduct were observed at any stage of the photoprocess.

The new band emerging upon UV irradiation at 2612, 2607, and 2602 cm^{-1} (that is in the frequency range typical of the bands due to SH stretching modes) and the disappearance of the absorption bands in the NH stretching region (Figure 2) suggest that the product of the photoreaction is the trithiol tautomeric form of TCA (Scheme 4).

The spectra of the photoproduct are very well reproduced (see Figure 5) by the DFT(B3LYP)/6-31++G(d,p) theoretical spectrum predicted for trithiol isomer **II** with C_{3h} symmetry (Table 6). The one-to-one correspondence between the bands in the experimental and theoretical spectra, as well as the good agreement between the observed and predicted wavenumbers and the relative intensities of the IR bands (see Table 7), leave no doubt that trithiol form **II** was photogenerated. However, the possibility that some minor quantity of the photoproduced trithiol tautomer adopts the rotameric form (**III**) cannot be excluded. The spectra of forms **II** and **III** are quite similar, but the clear presence of the band at 852 and 836 cm^{-1} in the spectrum emerging after UV irradiation (Figure 5) shows that the main photoproduced species has structure **II**.

Both the experimental spectrum of the photoproduct(s) and the theoretically predicted spectrum of form **II** are very simple. Similarly to the case for the trithione form **I**, the experimental bands due to degenerate normal modes belonging to the E′ representation are split into several components. The only observed band that was due to the nondegenerate normal mode Q11 of A″ symmetry (Tables 6 and 7) appeared in the spectra of the photoproduct in both matrixes as a single sharp peak at 797 cm^{-1} (Ar) and 798 cm^{-1} (N$_2$); see the insert in Figure 5.

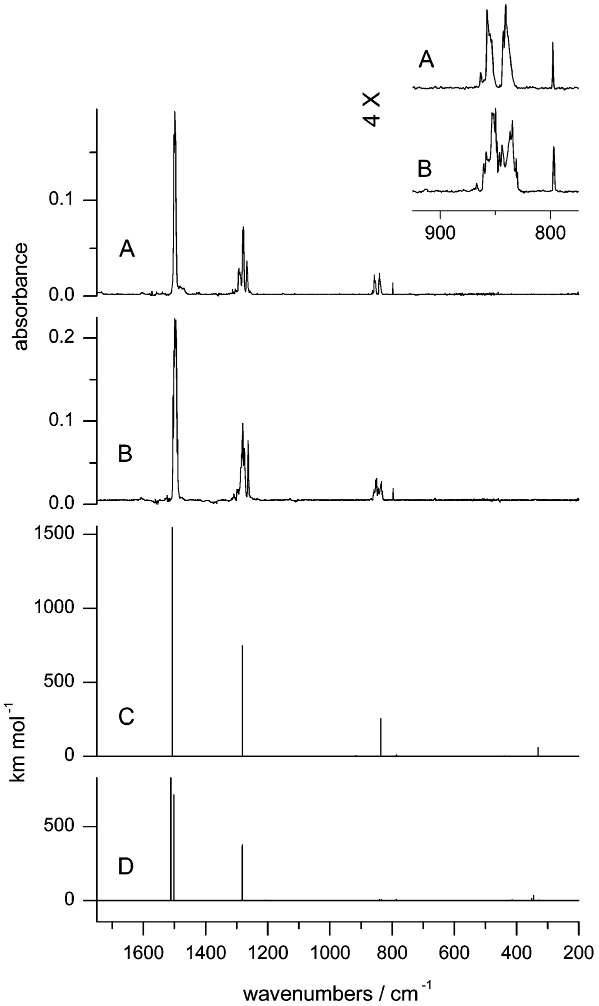


Figure 5. IR spectra of photoproduct(s) generated from matrix-isolated trithiocyanuric acid upon UV (λ > 270 nm) irradiation: (A) nitrogen matrix and (B) argon matrix. Theoretical spectra of (C) trithiol isomer **II** and (D) trithiol isomer **III** calculated at the DFT(B3LYP)/6-31++G-(d,p) level. Theoretical wavenumbers were scaled by a single factor of 0.98. The baselines of the experimental spectra were corrected.

Conclusions

In this work, monomers of trithiocyanuric acid isolated in low-temperature Ar and N_2 matrixes were studied using FTIR spectroscopy. Upon UV irradiation, trithione form **I** of the compound, exclusively populated after deposition of the matrixes, was converted into the trithiol tautomer. No spectral signatures of any intermediate photoproducts were observed at any stage of the photoreaction. The main trithiol photoproduct (**II**) has C_{3h} symmetry; however, we cannot exclude the possibility that small amounts of the other planar conformer (**III**) of the trithiol tautomer were also produced (see Scheme 4).

At present, the mechanism of intramolecular photoreactions transforming the thione forms of thiocarbonyl compounds into the corresponding thiol tautomers is not known. For the oxo analogues of these compounds,[29,30] a photoinduced dissociation−association of hydrogen atom (PIDA) mechanism was proposed by Sobolewski et al.[31−33] However, it still remains unclear if the PIDA mechanism could also govern the phototautomeric processes in thiocarbonyl compounds.

The structures of the substrate and the product of the photoreaction were positively identified on the basis of good agreement between the experimental IR spectra and the spectra theoretically calculated at the DFT(B3LYP)/6-31++G(d,p) level. As far as we are aware, the trithione → trithiol UV-induced conversion, observed in the present work, is the first described case of an intramolecular triple proton-transfer photoreaction.

References and Notes

(1) Muller, A., Junge, W., Ratajczak, H., Diemann, E., Eds.; *Studies in Physical and Theoretical Chemistry Vol. 78: Electron and Proton Transfer in Chemistry and Biology*; Elsevier Science Ltd.: Amsterdam, 1992.

(2) Chou, P. T. *J. Chin. Chem. Soc.* **2001**, *48*, 651.

(3) Waluk, J. In *Conformational Analysis of Molecules in Excited States*; Waluk, J., Ed.; Wiley VCH: New York, 2000; p 57.

(4) Lapinski, L.; Nowak, M. J.; Les, A.; Adamowicz, L. *J. Am. Chem. Soc.* **1994**, *116*, 1461.

(5) Nowak, M. J.; Lapinski, L.; Rostkowska, H.; Les, A.; Adamowicz, L. *J. Phys. Chem.* **1990**, *94*, 7406.

(6) Lapinski, L.; Nowak, M. J.; Kwiatkowski, J. S.; Leszczynski, J. *J. Phys. Chem. A* **1999**, *103*, 238.

(7) Prusinowska, D.; Lainski, L.; Nowak, M. J.; Adamowicz, L. *Spectrochim. Acta, Part A* **1995**, *51*, 1809.

(8) Rostkowska, H.; Lapinski, L.; Nowak, M. J. *J. Phys. Chem. A* **2003**, *107*, 804.

(9) Rostkowska, H.; Lapinski, L.; Khvorostov, A.; Norwak, M. J. *Chem. Phys.* **2003**, *298*, 223.

(10) Rostkowska, H.; Nowak, M. J.; Lapinski, L.; Adamowicz, L. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3012.

(11) Lapinski, L.; Rostkowska, H.; Khvorostov, A.; Nowak, M. J. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1524.

(12) Rostkowska, H.; Lapinski, L.; Khvorostov, A.; Nowak, M. J. *J. Phys. Chem. A,* **2003**, *107*, 6373.

(13) Nowak, M. J.; Lapinski, L.; Fulara, J.; Les, A.; Adamowicz, L. *J. Phys. Chem.* **1991**, *95*, 2404.

(14) Lapinski, L.; Nowak, M. J.; Kolos, R.; Kwiatkowski, J. S.; Leszczynski, J. *Spectrochim. Acta, Part A* **1998**, *54*, 685.

(15) Armstrong, D. R.; Davies, J. E.; Feeder, N.; Lamb, E.; Longridge, J. J.; Rawson, J. M.; Snaith, R.; Wheatley, A. E. H. *J. Mol. Model.* **2000**, *6*, 234.

(16) Pedireddi, V. R.; Chatterjee, S.; Ranganathan, A.; Rao, C. N. R. *J. Am. Chem. Soc.* **1997**, *119*, 10867.

(17) Møller, M.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(18) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(19) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(20) Nowak, M. J.; Lapinski, L.; Kwiatkowski, J. S.; Leszczynski, J. In *Computational Chemistry: Reviews of Current Trends*; Leszczynski, J., Ed.; World Scientific: Singapore, 1997; Vol. 2, Chapter 4.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(22) Schachtschneider, J. H. Technical Report No. 57-65; Shell Development Co.: Emeryville, CA, 1966.

(23) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra*; McGraw-Hill: London, 1955.

(24) Keresztury, G.; Jalsovszky, G. *J. Mol. Struct.* **1971**, *10*, 304.

(25) Rostkowska, H.; Szczepaniak, K.; Nowak, M. J.; Leszczynski, J.; KuBulat, K.; Person, W. B. *J. Am. Chem. Soc.* **1990**, *112*, 21.

(26) Alpert, N. E.; Keiser, W. E.; Szymanski, H. A. *IR. Theory and Practice of Infrared Spectroscopy*; Plenum Press: New York, 1964.

(27) Lapinski, L.; Prusinowska, D.; Nowak, M. J.; Bretner, M.; Felczak, K.; Maes, G.; Adamowicz, L. *Spectrochim. Acta, Part A* **1996**, *52*, 645.

(28) Fulara, J.; Nowak, M. J.; Lapinski, L.; Les, A.; Adamowicz, L. *Spectrochim. Acta, Part A* **1991**, *47*, 595.

(29) Lapinski, L.; Fulara, J.; Nowak, M. J. *Spectrochim. Acta, Part A* **1990**, *46*, 61.

(30) Nowak, M. J.; Lapinski, L.; Fulara, J.; Les, A.; Adamowicz, L. *J. Phys. Chem.* **1992**, *96*, 1562.

(31) Sobolewski, A. L.; Adamowicz, L. *Chem. Phys.* **1996**, *213*, 193.

(32) Sobolewski, A. L.; Adamowicz, L. *J. Phys. Chem.* **1996**, *100*, 3933.

(33) Sobolewski, A. L.; Domcke, W.; Dedonder-Lardeux, C.; Jouvet, C. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1093.