Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Hydrogen-atom tunneling through a very high barrier; spontaneous thiol → thione conversion in thiourea isolated in low-temperature Ar, Ne, H_2 and D_2 matrices

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Electronic Supplementary Information

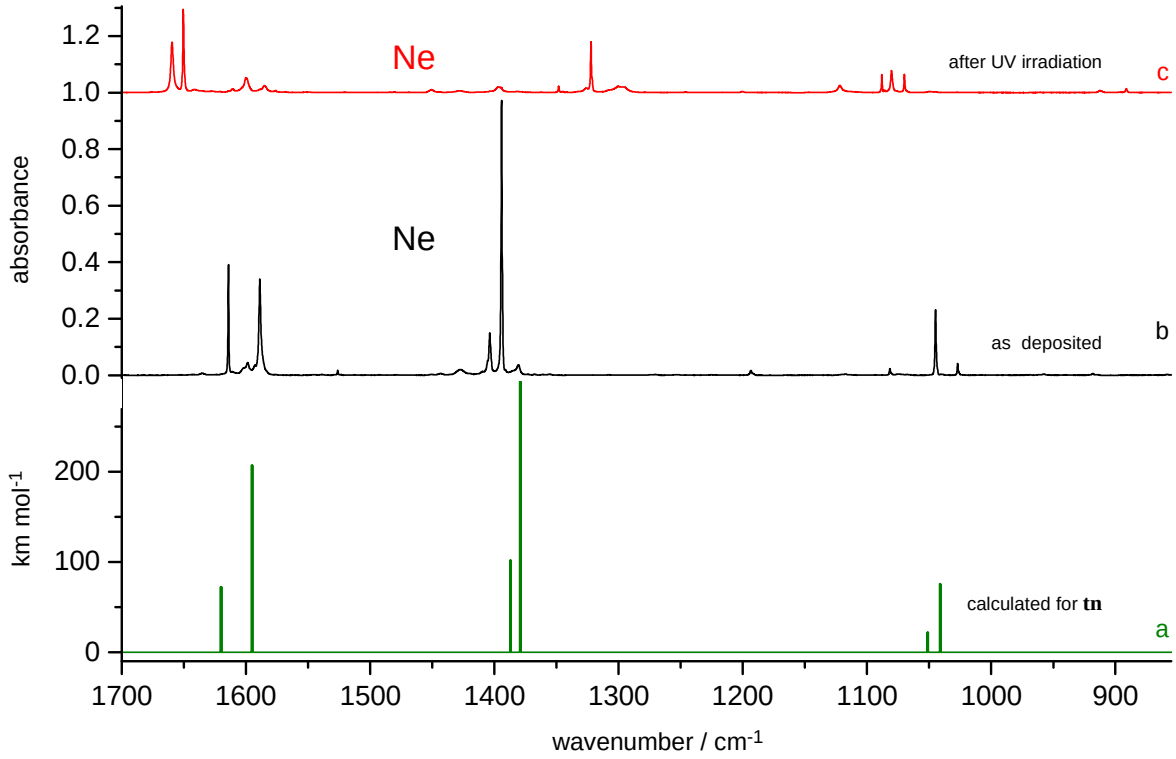

Fig. S1 Infrared spectra of thiourea monomers isolated in a Ne matrix. The spectra were recorded: (b) after deposition of the matrix, the spectrum of the thione tautomer; (c) after UV (λ > 270 nm) irradiation of the matrix, when the thiol tautomers were generated. The experimental spectra are compared with (a) theoretical spectrum calculated at the DFT(B3LYP)/6-311++G(2d,p) level for **tn** thione form of thiourea. The calculated wavenumbers were scaled by 0.98.

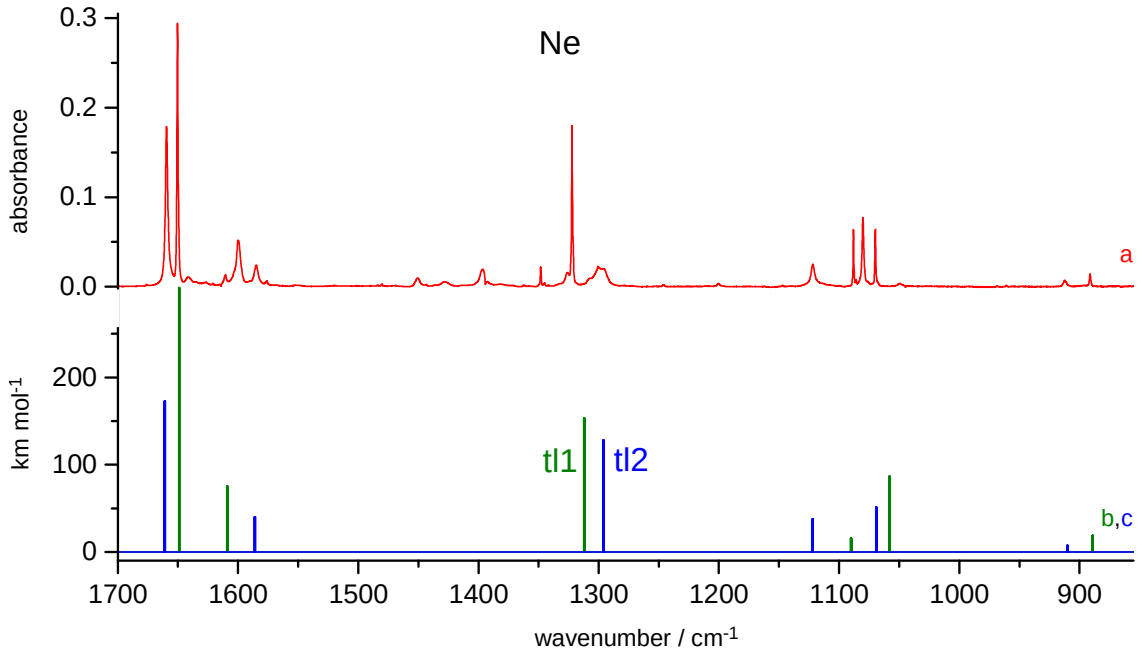

Fig. S2 Infrared spectrum of the photoproducts generated (see Fig. S1) upon UV(λ > 270 nm) irradiation of monomers of thiourea isolated in a Ne matrix. The experimental spectrum (a) is compared with theoretical spectra calculated at the DFT(B3LYP)/6-311++G(2d,p) level for **tl1** (b, green) and **tl2** (c, blue) thiol conformers of thiourea. The calculated wavenumbers were scaled by 0.98.

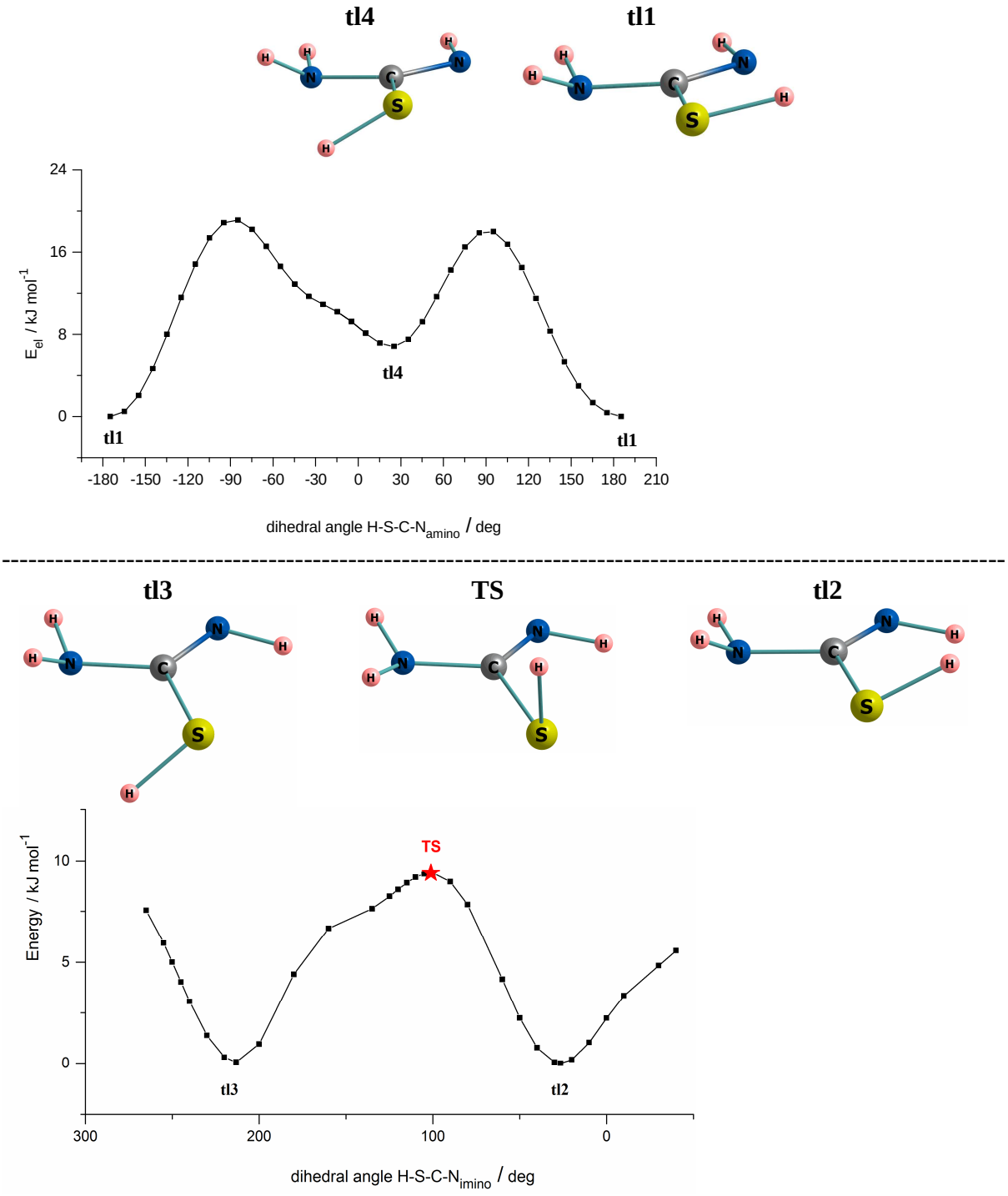

Fig. S3 The barriers for the **tl4** → **tl1** and **tl3** → **tl2** rotamerization, calculated at the MP2/6-311++G(2d,p) level. The calculated energy of **tl4** form is 6.8 kJmol^{-1} higher than **tl1**, and the height of the barrier for **tl4** → **tl1** transition is 11.2 kJmol^{-1}. The Red asterisk shows the position of the optimized **tl3**→**tl2** transition state TS. The calculated energy of TS is higher by 9.4 kJmol^{-1} than the energy of **tl2** form.

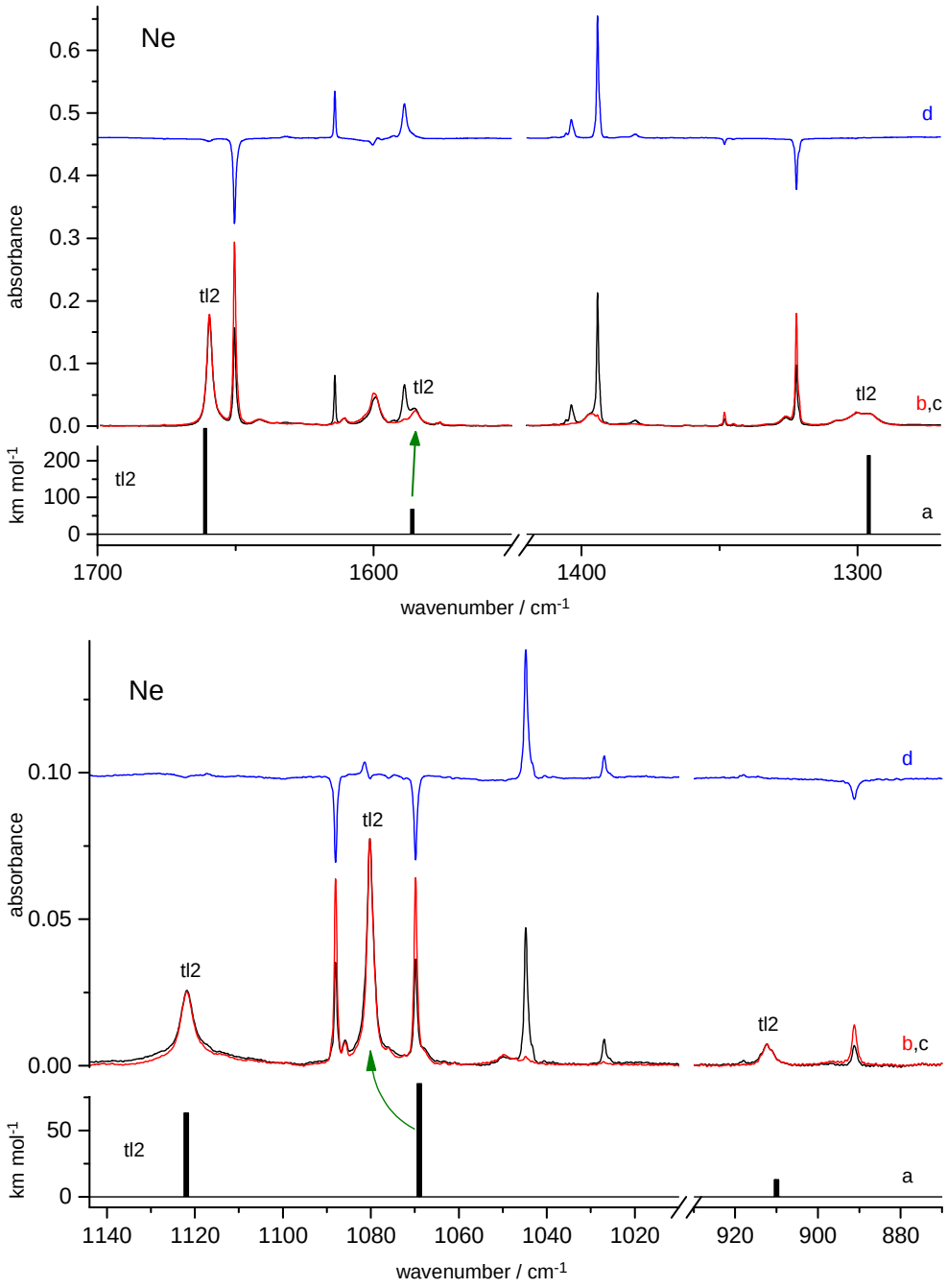

Fig. S4 Thiol → thione (**tl1** → **tn**) tunneling transformation observed for monomers of thiourea isolated in a Ne matrix. The thiol **tl1** and **tl2** forms of the compound were prepared upon UV (λ > 270 nm) irradiation. The IR spectrum of the UV-irradiated matrix is shown as trace (b, red). The matrix was then kept for 48 hours at 3.5 K and in the dark. The IR spectrum recorded after this long period is presented in trace (c, black). The tunneling process revealed itself as intensity decrease of IR bands due to **tl1** and intensity increase of the bands due to **tn**, see trace (d, blue) where the difference spectrum: trace c *minus* trace b is shown. The experimental bands assigned to UV-generated thiol form **tl2** did not change their intensities proving that this conformer was not involved in any spontaneous structural alterations. Fragments of the IR spectrum of **tl2**, calculated at the DFT(B3LYP)/6-311++G(2d,p) level, are shown in trace (a). The calculated wavenumbers were scaled by 0.98.

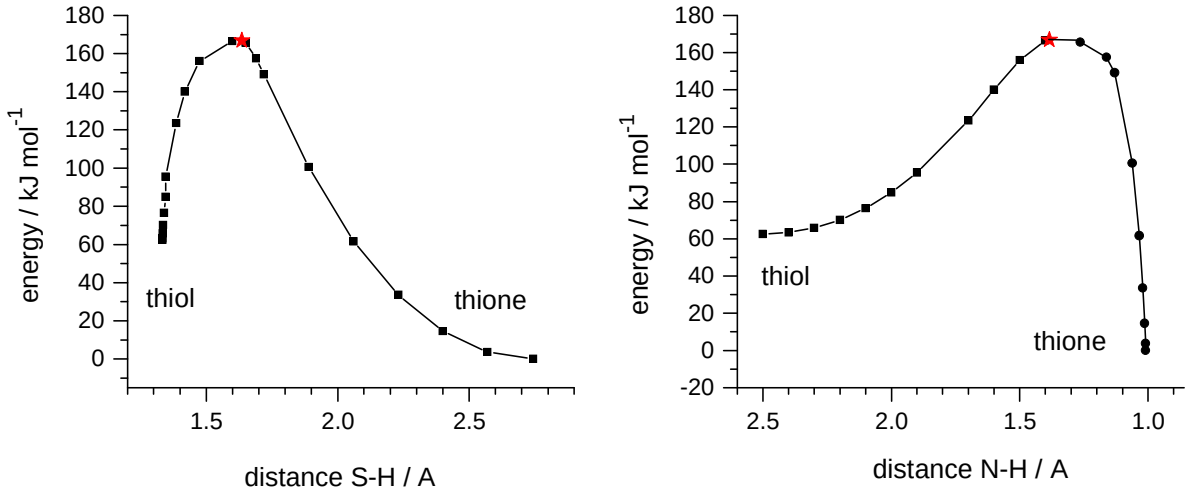

Fig. S5 Barrier for the thiol → thione (**tl1** → **tn**) transition in thiourea. The barrier was calculated, at the MP2//6-311++G(2d,p) level, as a relaxed scan. At each point of this scan the S-H distance (left panel) or N-H distance (right panel) was fixed at a chosen value and all other parameters determining the geometry of the molecule were fully optimized. The highest-energy point of the barrier (marked with an asterisk) corresponds to the optimized transition state. Zero on the ordinate scale corresponds to the energy calculated for the **tn** tautomer. The calculated energy of **tl1** is higher by 62 kJ mol^{-1} and the energy of the transition state is higher by 166 kJ mol^{-1} than the energy of **tn**,

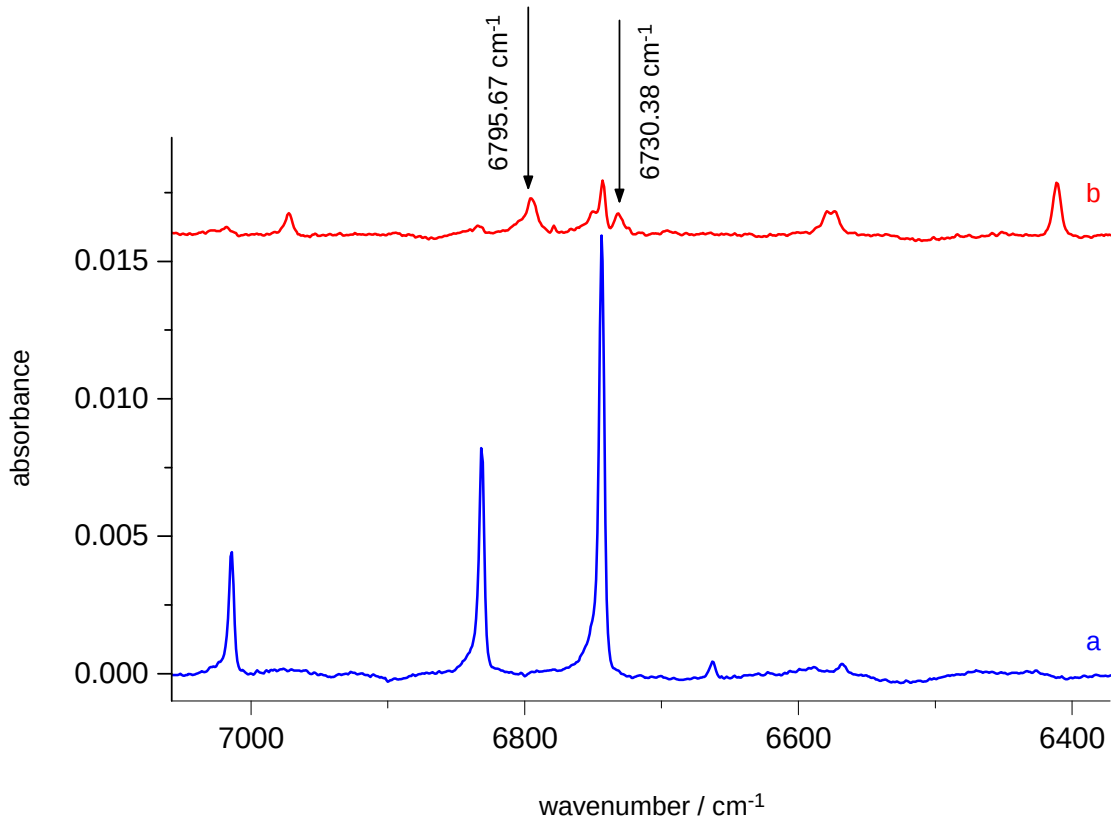

Fig. S6 Fragment of the near-IR spectra of thiourea isolated in an Ar matrix: (a) recorded after deposition of the matrix; (b) recorded after UV(λ > 270 nm) irradiation of the matrix. After exposure to UV light the matrix was additionally irradiated with monochromatic near-IR light from a tunable diode laser at wavenumbers indicated by the arrows.

Table S1. Experimental wavenumbers ($\tilde{\nu}$) and relative integrated intensities (***I***) of the IR absorption bands in the spectrum of thiourea isolated in Ar, D_2, H_2 and Ne matrices and the tentative assignment to the normal modes calculated for thione form **tn**.

Ar matrix		**D_2 matrix**		**H_2 matrix**		**Ne matrix**		**Mode number** [a]
$\tilde{\nu}$ / cm^{-1}	***I*** / rel.	$\tilde{\nu}$ / cm^{-1}	***I*** / rel.	$\tilde{\nu}$ / cm^{-1}	***I*** / rel.	$\tilde{\nu}$ / cm^{-1}	***I*** / rel.	
3539	172	3545	122	3546	118	3557	124	$Q_{tn}1$, $Q_{tn}2$
3424	47	3431	23	3432	28	3443	36	$Q_{tn}3$
3418	67	3424	64	3425	79	3437	86	$Q_{tn}4$
1610	71	1613	72	1612	83	1614	90	$Q_{tn}5$
<u>1590</u>, 1581	152	1592	247	1593	224	1589	243	$Q_{tn}6$
1518	6	1517	4	1518	6	1526	4	
1401	96	1413	80	1412	84	1404	87	$Q_{tn}7$
1389, <u>1385</u>	384	1391	352	1391	352	1394	306	$Q_{tn}8$
1273	1	1282, 1274	2	1282, 1274	3	1270	1	
1192	9	1210	7	1204	6	1194	11	
1078	7	1091	3	1088	3	1081	8	
1043	74	1051	63	1050	68	1045	77	$Q_{tn}10$
1024	12	1036	10	1032	13	1027	13	$Q_{tn}9$
760	16	759	16	759	16	764	17	$Q_{tn}11$
712	28	743	7	749	20	721	20	$Q_{tn}13$
645	29	~700		688	12	640	4	$Q_{tn}14$
578	22	574	10	567	7	561	11	

Wavenumbers of more intense components of split bands are underline.

[a] Frequencies and intensities of normal modes calculated at the DFT(B3LYP)/6-311++G(2d,p) level for the thione tautomer **tn** of thiourea are given in Table S4 of the ESI.

Table S2. Experimental wavenumbers ($\tilde{\nu}$) and relative integrated intensities (*I*) of the IR absorption bands in the spectrum of the photoproduct generated upon UV irradiation of thiourea isolated in low-temperature matrices, tentatively assigned to the normal modes calculated for the thiol **tl1** isomer of thiourea.

Ar matrix		**D_2 matrix**		**H_2 matrix**		**Ne matrix**		**Mode number[a]**
$\tilde{\nu}$ / cm^{-1}	*I* / rel.	$\tilde{\nu}$ / cm^{-1}	*I* / rel.	$\tilde{\nu}$ / cm^{-1}	*I* / rel.	$\tilde{\nu}$ / cm^{-1}	*I* / rel.	
3520	68	3527	39	3529	18	3540	60	$Q_{tl1}1$
3419	27	3426	13	3427	35	3439	57	$Q_{tl1}2$
2625	13	2620	10	2619	10	2620	4	$Q_{tl1}4$
1641	293	1642	312	1642	324	1650	265	$Q_{tl1}5$
1597	68	1599	72	1599	69	1600	151	$Q_{tl1}6$
		1398	10	1399	20			
1342	26	1348	24	1348	18	1348	15	
1318	187	1325	145	1325	146	1322	123	$Q_{tl1}7$
1086	44	1092	43	1092	52	1088	39	$Q_{tl1}8$
1067	48	1073	54	1073	60	1070	51	$Q_{tl1}9$
890, <u>888</u>	16	894	20	894	19	891	14	$Q_{tl1}10$
807	34					809	42	$Q_{tl1}11$
772	25	784	55	783	44	775	43	
671	53	674	65	674	43	674	11	$Q_{tl1}12$
586	8					586	123	$Q_{tl1}13$

Wavenumbers of more intense components of split bands are underlined.

[a] Frequencies and intensities of normal modes calculated at the DFT(B3LYP)/6-311++G(2d,p) level for the thiol **tl1** isomer of thiourea are given in Table S5 of the ESI.

Table S3. Experimental wavenumbers ($\tilde{\nu}$) and relative integrated intensities (***I***) of the IR absorption bands in the spectrum of the photoproduct generated upon UV irradiation of thiourea isolated in low-temperature matrices, tentatively assigned to the normal modes calculated for the thiol **tl2** isomer of thiourea.

Ar matrix		**D_2 matrix**		**H_2 matrix**		**Ne matrix**		**Mode number**[a]
$\tilde{\nu}$ / cm^{-1}	**I** / rel.	$\tilde{\nu}$ / cm^{-1}	***I*** / rel.	$\tilde{\nu}$ / cm^{-1}	***I*** / rel.	$\tilde{\nu}$ / cm^{-1}	***I*** / rel.	
3522	84	3522	134	3525	80	3540	55	$Q_{tl2}1$
3415	39					3433	59	$Q_{tl2}2$
2623	6	2618	3					$Q_{tl2}4$
1649	327	1651	192	1652	235	1659	323	$Q_{tl2}5$
1580	40					1585	64	$Q_{tl2}6$
1445	2	1451	28	1451	147	1451	22	
1294	149	1300	78	1300	106	1301, 1297	104	$Q_{tl2}7$
1121, 1112	80					1122	55	$Q_{tl2}8$
1077	59	1084	59	1084	186	1080	108	$Q_{tl2}9$
909	16	913	16	913	26	912	13	$Q_{tl2}10$
829	6					818	43	
						755	39	$Q_{tl2}11$
658	35					661	104	$Q_{tl2}12$

[a] Frequencies and intensities of normal modes calculated at the DFT(B3LYP)/6-311++G(2d,p) level for the thiol **tl2** isomer of thiourea are given in Table S6 of the ESI.

TableS4. Normal mode frequencies ($\tilde{\nu}$) and absolute intensities (A^{th}) of the IR bands predicted at the DFT(B3LYP)/6-311++G(2d,p) level for the thione tautomer **tn** of thiourea**.**

DFT(B3LYP)/6-311++G(2d,p)		
mode number	$\tilde{\nu}$ (x0.98) / cm^{-1}	A^{th} / km mol^{-1}
$Q_{tn}1$	3611	24
$Q_{tn}2$	3610	67
$Q_{tn}3$	3490	12
$Q_{tn}4$	3482	43
$Q_{tn}5$	1620	72
$Q_{tn}6$	1595	207
$Q_{tn}7$	1387	102
$Q_{tn}8$	1379	300
$Q_{tn}9$	1051	22
$Q_{tn}10$	1041	75
$Q_{tn}11$	749	11
$Q_{tn}12$	627	6
$Q_{tn}13$	565	90
$Q_{tn}14$	488	45
$Q_{tn}15$	450	4
$Q_{tn}16$	392	2
$Q_{tn}17$	381	308
$Q_{tn}18$	333	126

TableS5. Normal mode frequencies ($\tilde{\nu}$) and absolute intensities (A^{th}) of the IR bands predicted at the DFT(B3LYP)/6-311++G(2d,p) level for the thiol **tl1** isomer of thiourea**.**

DFT(B3LYP)/6-311++G(2d,p)		
mode number	$\tilde{\nu}$ (x0.98) / cm^{-1}	A^{th} / km mol^{-1}
$Q_{tl1}1$	3586	25
$Q_{tl1}2$	3484	25
$Q_{tl1}3$	3386	5
$Q_{tl1}4$	2646	4
$Q_{tl1}5$	1649	303
$Q_{tl1}6$	1609	75
$Q_{tl1}7$	1312	154
$Q_{tl1}8$	1090	16
$Q_{tl1}9$	1058	87
$Q_{tl1}10$	888	19
$Q_{tl1}11$	774	81
$Q_{tl1}12$	648	66
$Q_{tl1}13$	589	5
$Q_{tl1}14$	474	231
$Q_{tl1}15$	448	9
$Q_{tl1}16$	375	14
$Q_{tl1}17$	350	10
$Q_{tl1}18$	184	24

TableS6. Normal mode frequencies ($\tilde{\nu}$) and absolute intensities (A^{th}) of the IR bands predicted at the DFT(B3LYP)/6-311++G(2d,p) level for the thiol **tl2** isomer of thiourea**.**

DFT(B3LYP)/6-311++G(2d,p)		
mode number	$\tilde{\nu}$ (x0.98) / cm^{-1}	A^{th} / km mol^{-1}
$Q_{tl2}1$	3594	34
$Q_{tl2}2$	3483	30
$Q_{tl2}3$	3472	16
$Q_{tl2}4$	2637	1
$Q_{tl2}5$	1661	288
$Q_{tl2}6$	1586	67
$Q_{tl2}7$	1296	214
$Q_{tl2}8$	1122	63
$Q_{tl2}9$	1068	85
$Q_{tl2}10$	910	13
$Q_{tl2}11$	765	30
$Q_{tl2}12$	641	39
$Q_{tl2}13$	624	117
$Q_{tl2}14$	516	181
$Q_{tl2}15$	433	16
$Q_{tl2}16$	404	37
$Q_{tl2}17$	349	1
$Q_{tl2}18$	216	15