Isomerizations between Nitrosyl Halides X–N=O and Isonitrosyl Halides X–O–N: A Matrix-Spectroscopic Study

Günther Maier,* Hans Peter Reisenauer, and Michael De Marco[a]

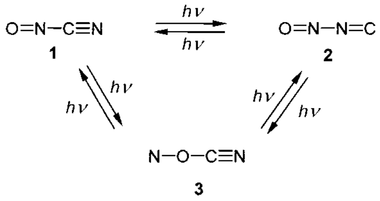
Dedicated to Professor Wolfgang Lüttke on the occasion of his 80th birthday

Abstract: Irradiation of nitrosyl bromide BrNO (**4**) with light of the wavelength $\lambda = 248$ nm and nitrosyl chloride ClNO (**6**) with $\lambda = 193$ nm in an argon matrix at 10 K leads to the corresponding isomers isonitrosyl bromide BrON (**5**) and isonitrosyl chloride ClON (**7**). Both new compounds **5** and **7** have been identified by comparison of the experimental and calculated (BLYP/6-311+G*) IR spectra. Nitrosyl fluoride FNO (**8**) could not be transferred into isonitrosyl fluoride FON (**9**). The back reactions **5** →**4** and **7** →**6** can be initiated by UV ($\lambda > 310$ nm), visible or IR light. The retransformation also occurs spontaneously in the matrix at 10 K under exclusion of any UV/Vis or IR radiation. Surprisingly, the reaction rates of these spontaneous back reactions are temperature independent between 8.5 and 25 K. The mechanism of these processes is discussed.

Keywords: ab initio calculations · isomerizations · matrix isolation · nitrosyl halides · photochemistry

Introduction

Recently, we[1] were able to demonstrate that the three isomers nitrosyl cyanide (**1**), nitrosyl isocyanide (**2**), and isonitrosyl cyanide (**3**) of the elemental composition CN_2O can be interconverted photochemically in an argon matrix at 10 K.



The relative ratios of the components depend on their different UV/Vis absorptions and the wavelengths used. The transformation of **1** into **2** was no surprise. However, the generation of **3** was important in so far, as to the best of our knowledge this species was the first example for an isonitrosyl compound. The three isomers **1**–**3** are probably linked to each other by the radical pair $[NO^{\bullet}+{}^{\bullet}CN]$. That means, it must be assumed that the formation of **3** upon irradiation of **1** or **2** should not be unique.

Indeed, it is even possible to photoisomerize the parent nitroso hydrogen H–N=O into isonitroso hydrogen H–O–N.[2] In addition, we mentioned already in our first paper[1] that nitrosyl chloride isomerizes to isonitrosyl chloride upon irradiation in argon at 10 K. Prompted by a recent publication of Hallou et al.[3] on the matrix photochemistry of nitrosyl chloride we give in this report the full account of our studies on rearrangements of nitrosyl halides.

Results and Discussion

Generation and identification of isonitrosyl bromide BrON (5): For the intended photoisomerization of nitrosyl bromide (**4**) it was essential to obtain the UV spectrum in argon matrix, because only the gas phase UV/Vis spectrum of **4** was described.[4] Therefore, **4** was prepared by reaction of potassium bromide with nitrosylsulfuric acid and condensed together with argon onto a spectroscopic window (CaF_2) at 10 K. Matrix-isolated **4** showed an intense absorption band at $\lambda_{max} = 220$ nm. This position is close to the reported[4] absorption in the gas phase spectrum (strong S_0 ($1^1A'$) $\rightarrow S_5$ ($4^1A'$) transition at $\lambda = 210$ nm, weak bands at wavelengths between 300 and 750 nm). Due to the low intensities the absorptions at longer wavelengths could not be detected in the matrix spectrum (Figure 1). It is also worth mentioning that the intense band of matrix-isolated **4** shows no vibrational fine structure. This is an indication that one is dealing with a dissociative transition, a good prerequisite for a photoisomerization of **4** via the radical pair $[NO^{\bullet}+{}^{\bullet}Br]$.

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Table 1. Comparison of the experimental IR spectrum of nitrosyl bromide (**4**) and isonitrosyl bromide BrON (**5**) (Ar, N_2, 10 K, [cm^{-1}]) with the calculated (BLYP/6–311 + G*; CCSD(T)/TZ2P[7]) absorptions of **4** and **5**. Relative intensities are given in parentheses.

	sym.		exptl, Ar[a]		exptl, N_2		BLYP		CCSD(T)	
BrNO (**4**)										
ν_1	A′	ν_{NO}	1800.3/1797.9	(1.0)	1822.8	(1.0)	1807	(1.0)[b]	1798	(1.0)[c]
ν_2	A′	δ_{BrNO}	536.1/534.7	(0.08)	528.4	(0.08)	530	(0.07)	545	(0.08)
ν_3	A′	ν_{NBr}	261.3	(0.05)	257.4	(0.05)	252	(0.04)	268	(0.05)
$2\nu_1$			3567.3/3561.5	(0.04)	3611.7	(0.03)				
$\nu_1+\nu_3$			2060.6/2058.7	(<0.01)	2080.0	(<0.01)				
$\nu_2+\nu_3$			794.1	(<0.01)	783.5	(<0.01)				
BrON (**5**)										
ν_1	A′	ν_{NO}	1820.0	(1.0)	1816.2	(1.0)	1902	(1.0)[f]	1827	(1.0)[g]
ν_2	A′	δ_{BrON}	ca. 350[d]	–	365.4	(<0.01)	373	(0.02)	348	(<0.01)
ν_3	A′	ν_{OBr}	–	–	ca. 190[e]	–	195	(0.01)	165	(<0.01)
$2\nu_1$			3615.0	(0.3)	3609.2	(0.17)				
$\nu_1+\nu_2$			2168.1	(<0.01)	2173.9	(<0.01)				
$\nu_1+\nu_3$					2007.4	(<0.01)				

[a] In argon band splitting occurs through a matrix effect. [b] Absolute intensity: 754 km mol^{-1}. [c] Absolute intensity: 741 km mol^{-1}. [d] Estimated from the combination $\nu_1+\nu_2$. [e] Estimated from the combination $\nu_1+\nu_3$. [f] Absolute intensity: 715 km mol^{-1}. [g] Absolute intensity: 1057 km mol^{-1}.

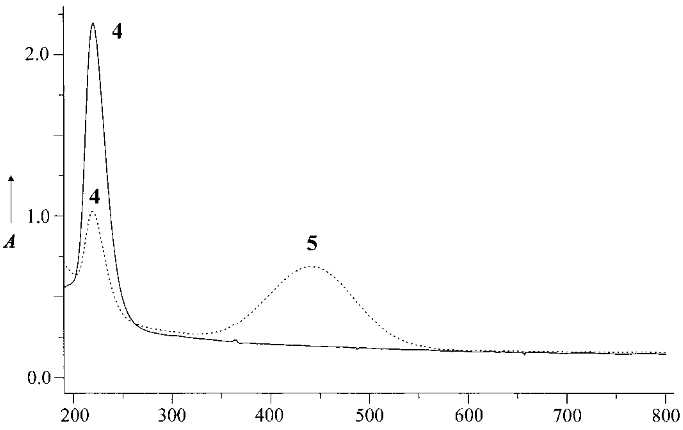
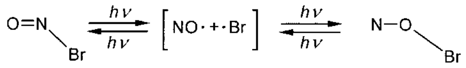


Figure 1. UV/Vis spectra of nitrosyl bromide BrNO (**4**) and isonitrosyl bromide BrON (**5**) in argon at 10 K. The spectrum of **5** was measured after 15 min irradiation of **4** with $\lambda = 248$ nm.

Upon irradiation in argon at 10 K either with a low pressure mercury lamp ($\lambda = 254$ nm) or a KrF laser ($\lambda = 248$ nm) the absorption band of **4** at 220 nm diminishes and a new broad band (ranging from 330 to 550 nm; $\lambda_{max} = 440$ nm) can be observed (Figure 1), which again shows no vibrational structure. As a result of this absorption the matrix now has a yellow-orange color, so consequently the matrix has to be protected from daylight in order to prevent the photochemical back reaction **5**→**4** (see below). We assign the band at $\lambda_{max} = 440$ nm to isonitrosyl bromide (**5**).



4 **5**

Parallel to the change in the UV spectrum the formation of isonitrosyl bromide (**5**) upon irradiation of nitrosyl bromide (**4**) in argon at 10 K with $\lambda = 248$ nm (KrF laser) can also be followed IR spectroscopically. The already known[5] bands of matrix-isolated **4** (Table 1, Figure 2) decrease and new absorptions, which can be contributed to isonitrosyl bromide (**5**), appear at 3615.0 and 1820.0 cm^{-1}, the latter having by far the highest intensity (Figure 2).

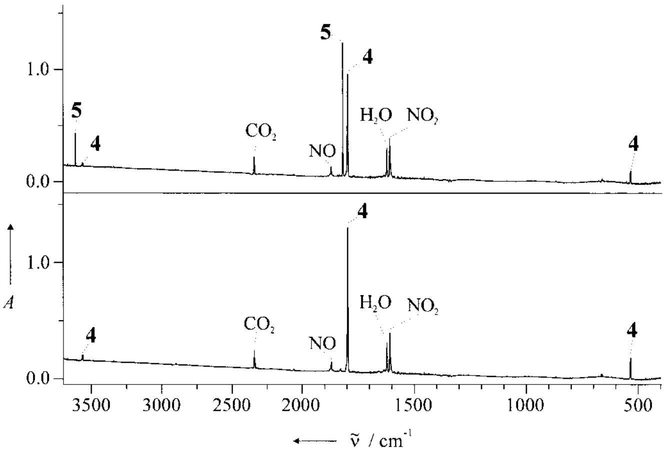


Figure 2. IR spectra taken before (bottom) and after (top) 15 min irradiation of nitrosyl bromide BrNO (**4**) in argon at 10 K with $\lambda = 248$ nm.

Abstract in German: *Die Belichtungen von Nitrosylbromid BrNO (**4**) mit Licht der Wellenlänge $\lambda = 248$ nm und Nitrosylchlorid ClNO (**6**) mit $\lambda = 193$ nm in einer Argonmatrix bei 10 K führen zu den entsprechenden Isomeren Isonitrosylbromid BrON (**5**) und Isonitrosylchlorid (**7**). Die beiden neuen Verbindungen **5** und **7** wurden durch den Vergleich der experimentellen mit den berechneten (BLYP/6–311 + G*) IR-Spektren identifiziert. Nitrosylfluorid FNO (**8**) konnte nicht in Isonitrosylfluorid FON (**9**) überführt werden. Die Rückreaktionen **5**→**4** und **7**→**6** können mit ultraviolettem ($\lambda >$ 300 nm), sichtbarem und infrarotem Licht initiiert werden. Die Rückbildung setzt in der Matrix bei 10 K allerdings auch spontan unter Ausschluß von ultravioletter, sichtbarer oder infraroter Bestrahlung ein. Überraschenderweise sind die Reaktionsgeschwindigkeiten dieser spontanen Rückreaktion zwischen 8.5 und 25 K nicht temperaturabhängig. Der Mechanismus dieser Prozesse wird diskutiert.*

The comparison between the experimental and calculated (BLYP/6-311+G*; Gaussian program package [6]) spectra shows good agreement for the NO stretching vibration ν_1 at 1820.0 cm^{-1} (Table 1, Figure 3). The two other fundamental vibrations ν_2 (bending vibration) and ν_3 (OBr stretching vibration) could not be detected, which is in accordance with the calculated low intensity or the position of the bands. The band at 3615.0 cm^{-1} has to be regarded as an astonishingly intense overtone of ν_1. From the combination band at 2168.1 cm^{-1} the wavenumber of the bending vibration of **5** is estimated to be 350 cm^{-1}.

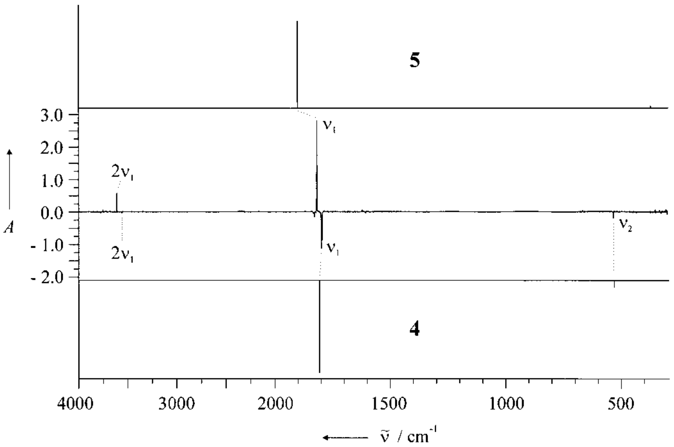


Figure 3. Comparison of the experimental (middle) and calculated (BLYP/6-311+G*) IR spectra of nitrosyl bromide BrNO (**4**) (bars at bottom) and isonitrosyl bromide BrON (**5**) (bars at top). The experimental spectrum is a difference spectrum (15 min irradiation of **4** in argon at 10 K with $\lambda = 248$ nm). The bands with negative values diminish, while those with positive values enhance upon irradiation.

In order to evaluate the quality of the theoretical spectra not only the IR absorptions of the photoisomers but also of the educt molecules were calculated and compared with the experimental spectra (Tables 1 and 2). It turned out that the BLYP method was sufficient for this purpose, since it gave wavenumbers and intensities very similar to the data calculated before by Lee[7-9] on a much higher level (CCSD(T)/TZ2P).

Additional information about isonitrosyl bromide (**5**) was achieved by using a N_2 matrix. In this case some additional bands can be observed, which have to belong to the photoisomer of nitrosyl bromide (**4**). Again the bands of **4** (Table 1) disappeared upon irradiation under the conditions mentioned above and new bands of **5** could be detected not only at 3609.2 ($2\nu_1$) and 1816.2 cm^{-1} (ν_1), but also at 2173.9, 2007.4, and 365.4 cm^{-1}. The absorption at 365.4 cm^{-1} can be assigned to the fundamental vibration ν_2. From the combination tone at 2007.4 cm^{-1} even the third fundamental vibration ν_3 can be indirectly determined (estimated to lie at about 190 cm^{-1}; Table 1). Figure 4 shows the relevant section of the IR spectrum observed during the photoisomerization $4 \rightarrow 5$ in a N_2 instead of an argon matrix.

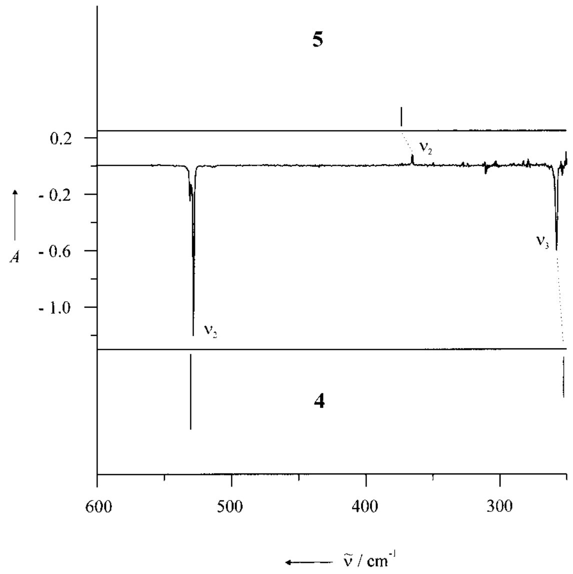


Figure 4. Comparison of a section of the experimental (middle) and calculated (BLYP/6-311+G*) IR spectra of nitrosyl bromide BrNO (**4**) (bars at bottom) and isonitrosyl bromide BrON (**5**) (bars at top). The experimental spectrum is a difference spectrum (15 min irradiation of **4** in N_2 at 10 K with $\lambda = 248$ nm). The bands with negative values diminish, while those with positive values enhance upon irradiation.

Upon irradiation into the long wavelength UV absorption (Figure 1) of **5** with light $\lambda > 310$ nm reformation of **4** occurs, as can be seen from the diminution of the IR bands of **5** and reappearance of the absorptions of **4**. Subsequent irradiation with the KrF laser ($\lambda = 248$ nm) initiates again the generation of **5**. These reversible photochemical transformations are accompanied by the appearance of small amounts of nitric oxide. This observation can be explained by the formation of radical pair $[NO^{\bullet}+{}^{\bullet}Br]$ upon irradiation of either **4** or **5**. Partial escape of $NO^{\bullet}$ from the matrix cage allows its detection, since it has no bromine atom in direct neighborhood and cannot recombine to **4** or **5**.

Generation and identification of isonitrosyl chloride ClON (7): Nitrosyl chloride (**6**), prepared analogous to **4** [10] by reaction of sodium chloride with nitrosylsulfuric acid, possesses a UV maximum at $\lambda = 200$ nm in an argon matrix (Figure 5). This position corresponds to the spectrum meas-

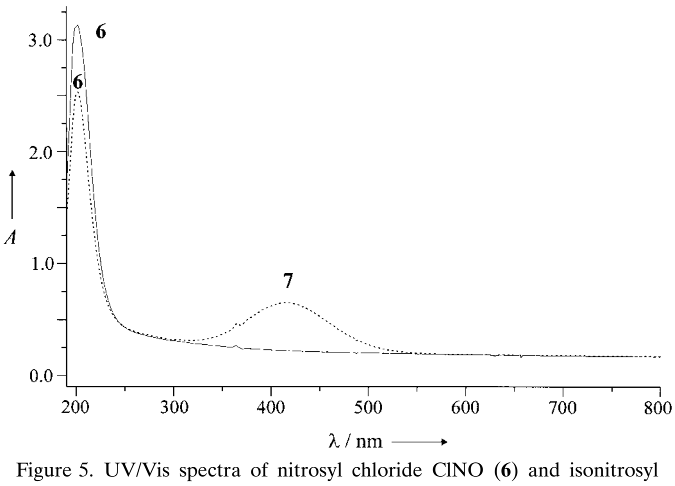
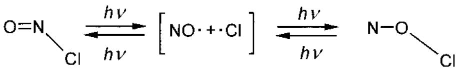


Figure 5. UV/Vis spectra of nitrosyl chloride ClNO (**6**) and isonitrosyl chloride ClON (**7**) in argon at 10 K. The spectrum of **7** was measured after 1 min irradiation of **6** with $\lambda = 193$ nm.

ured in the gas phase, which can be characterized—similar to the strongest UV band of nitrosyl bromide—as the S_0 ($1^1A'$)$\rightarrow S_5$ ($4^1A'$) transition.[11] Additional bands cannot be observed in the matrix UV spectrum, in spite of the fact that in the gas phase spectrum several weak absorptions in the long-wavelength region can be detected.[11] The strong UV band of matrix-isolated **6** shows, as is the case for the absorption band of nitrosyl bromide (**4**), no vibrational fine structure. This indicates that the corresponding transition of **6** is also dissociative. Therefore, we expected the fragmentation of nitrosyl chloride (**6**) into the radical pair [NO$^\bullet$+$^\bullet$Cl] upon irradiation into the 200 nm band. Indeed, excitation (ArF laser; $\lambda = 193$ nm) of **6** in argon at 10 K leads to a new strong absorption in the region 320–550 nm ($\lambda_{max} = 417$ nm), which turns the matrix to a yellow color. We assign this absorption to isonitrosyl chloride (**7**). Such a dissociative transition should allow an easy refragmentation of **7** into the radical pair. Indeed, isonitrosyl chloride (**7**) has a high sensitivity against daylight. The matrix has to be kept in dark in order to prevent a photochemical back reaction. Matrix-isolated **7** is transformed back to nitrosyl chloride (**6**) within 30–60 s upon irradiation with light of the wavelength $\lambda > 310$ nm. If one starts again to irradiate with 193 nm light the original photoreaction **6**→**7** recurs. The photoisomerization **6**→**7** can also be initiated with $\lambda = 248$ nm, but in this case the amount of the new isomer **7** is much lower. The two isomers **6** and **7** exist in a photoequilibrium, which can be influenced by the used wavelength.

An even better basis for the structural elucidation of isonitrosyl chloride (**7**) is its IR spectrum. Starting from nitrosyl chloride (**6**), whose argon matrix IR spectrum (Figure 6, Table 2) was identical with the reported matrix spectrum,[12] new bands were observed upon irradiation at 10 K with an ArF laser (193 nm; 1–45 min). The most prominent absorption is found at 1842.0 cm^{-1} and can be assigned to the NO stretching vibration of isonitrosyl chloride (**7**) (Figure 6, Table 2), as has been recently also claimed by Hallou et al.[3]



6 **7**

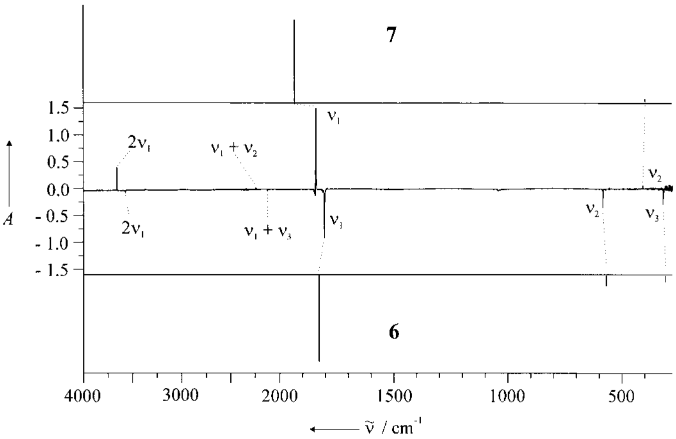


Figure 6. Comparison of the experimental (middle) and calculated (BLYP/6–311 + G*) IR spectra of nitrosyl chloride ClNO (**6**) (bars at bottom) and isonitrosyl chloride ClON (**7**) (bars at top). The experimental spectrum is a difference spectrum (15 min irradiation of **6** in argon at 10 K with λ = 193 nm). The bands with negative values diminish, while those with positive values enhance upon irradiation.

Besides this band (ν_1) another fundamental vibration of **7** can directly be detected at 409.4 cm^{-1}. Visualization of this normal mode showed that it is the bending vibration ν_2 (this band was assigned by Hallou et al.[3] to the OCl stretching

Table 2. Comparison of the experimental IR spectrum of ClNO (**6**) and ClON (**7**) (Ar, N_2, 10 K, [cm^{-1}]) with the calculated (BLYP/6–311 + G*; CCSD(T)/TZ2P[8]) absorptions of **6**. Relative intensities are given in parentheses.

	sym.		exptl, Ar		exptl, N_2		BLYP		CCSD(T)	
ClNO (**6**)										
ν_1	A′	ν_{NO}	1805.9	(1.0)	1830.8	(1.0)	1828	(1.0)[a]	1805	(1.0)[b]
ν_2	A′	δ_{ClNO}	585.2 (^{35}Cl)/ 584.3 (^{37}Cl)	(0.19)	575.9	(0.12)	569	(0.12)	602	(0.16)
ν_3	A′	ν_{NCl}	321.1 (^{35}Cl)/ 317.3 (^{37}Cl)	(0.09) (0.04)	–		309	(0.07)	338	(0.11)
$2\nu_1$			3574.6	(0.03)	3626.0	(<0.01)				
$\nu_1+\nu_2$			2390.5	(<0.01)	2407.1	(<0.01)				
$\nu_1+\nu_3$			2125.7 (^{35}Cl)/ 2121.9 (^{37}Cl)	(<0.01)	2147.2 (^{35}Cl)/ 2143.2 (^{37}Cl)	(<0.01)				
$\nu_2+\nu_3$			903.0 (^{35}Cl)/ 898.2 (^{37}Cl)	(<0.01)	889.4 (^{35}Cl)/ 884.7 (^{37}Cl)	(<0.01)				
ClON (**7**)										
ν_1	A′	ν_{NO}	1842.0	(1.0)	1852.0	(1.0)	1936	(1.0)[d]	1842	(1.0)[e]
ν_2	A′	δ_{ClON}	409.4	(0.03)	405.2	(0.03)	400	(0.04)	415	(<0.01)
ν_3	A′	ν_{OCl}	≈247[c]		–		238	(0.02)	250	(<0.01)
$2\nu_1$			3661.0	(0.2)	3682.5	(0.08)				
$\nu_1+\nu_2$			2244.4	(0.02)	2252.2	(<0.01)				
$\nu_1+\nu_3$			2090.8 (^{35}Cl)/ 2088.1 (^{37}Cl)	(<0.01)	2066.2	(<0.01)				
$\nu_2+\nu_3$			656.3 (^{35}Cl)/ 652.8 (^{37}Cl)	 (<0.01)						

[a] Absolute intensity: 618 km mol^{-1}. [b] Absolute intensity: 597 km mol^{-1}. [c] Estimated from the combinations $\nu_1+\nu_3$ and $\nu_2+\nu_3$. [d] Absolute intensity: 596 km mol^{-1}. [e] Absolute intensity: 1257 km mol^{-1}.

vibration ν_3). Additional bands at 3661.0, 2244.4, 2090.8/2088.1, and 656.3/652.8 cm^{-1} can be attributed to combination tones (Table 2). The third fundamental vibration ν_3 can be derived from the combination bands ($\nu_1+\nu_3$) at 2090.8/2088.1 cm^{-1} and ($\nu_2+\nu_3$) at 656.3/652.8 cm^{-1}. The identification of these combination modes follows from the comparison of the experimental and calculated isotopic splittings (due to ^{35}Cl and ^{37}Cl) in the spectra of **6** and **7** (Table 3). If this analysis is correct, the OCl stretching vibration ν_3 of **7** has to lie at about 247 cm^{-1}, in accordance with the calculated value of 238 cm^{-1}.

Table 3. Comparison of the experimental (Ar, 10 K, [cm^{-1}]) with the calculated (BLYP/6-311+G*) ^{35}Cl/^{37}Cl-isotopic shifts in the spectra of **6** and **7**.

		6		**7**	
		Δ_{exptl}	Δ_{calcd}	Δ_{exptl}	Δ_{calcd}
ν_1	ν_{NO}	0	0	0	0
ν_2	$\delta_{\text{ClNO/ClON}}$	0.9	1.0	–[a]	0.9
ν_3	$\nu_{\text{NCl/OCl}}$	3.8	3.7	–[a]	2.7
$\nu_1+\nu_2$		–[a]	1.0	0.8	0.9
$\nu_1+\nu_3$		3.8	3.7	2.7	2.7
$\nu_2+\nu_3$		4.8	4.7	3.5	3.6

[a] Not directly measurable because of too low intensity.

Attempts towards the generation and identification of isonitrosyl fluoride FON (9): When we began our studies on isonitrosyl compounds,[1] we were confronted with the report that isonitrosyl fluoride (**9**) had been isolated.[13] Today, we believe on the basis of our own experiments that **9** is still an elusive molecule.

We prepared matrix-isolated nitrosyl fluoride (**8**) by cocondensation of a $NO^{\bullet}$/Ar together with a $F^{\bullet}$/Ar gas mixture, generated by passing CF_4 in argon through a microwave discharge zone. This procedure is analogous to that described by Jacox,[14] in which NF_3 was used as the source for fluorine atoms. The matrix formed under these conditions contained a large amount of nitrosyl fluoride (**8**), as evident from the IR bands at 1850.1, 751.1, and 503.8 cm^{-1} (Figure 7),[15] together with a list of side products (HF, HNO, OCF, OCF_2, CF_4, CF_3, CF_2, CO, CO_2, NO, NO_2, N_2O_2). In addition the spectrum showed two bands at 492.4 and 735.4 cm^{-1} (marked as X in Figure 7) and another one at 1884.2 cm^{-1} (marked as Y). Three bands in these positions were assigned by Swardzewski and Fox[13] to isonitrosyl fluoride (**9**).

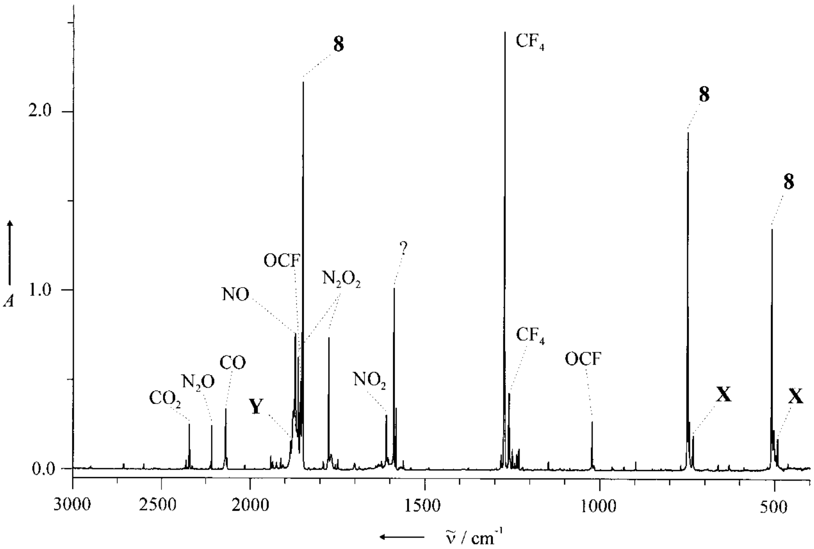
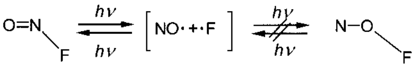


Figure 7. IR spectrum taken after cocondensation of a $NO^{\bullet}$/argon together with a $F^{\bullet}$/argon gas mixture.

The assumption that **9** might be, besides **8**, a recombination product of the radical pair [$NO^{\bullet}$+$^{\bullet}F$] seems reasonable. For instance, if CF_4 is replaced by CCl_4 in the experiment mentioned above, not only nitrosyl chloride (**6**) but also the isonitrosyl isomer **7** can be detected in the matrix spectrum. Nevertheless, there are four strong arguments, which indicate—as was argued before[9, 14, 16]—that the report[13] about the detection of isonitrosyl fluoride (**9**) should be revised:

a) Irradiation of the matrix containing nitrosyl fluoride (**8**) with wavelengths ranging from 185 to 700 nm gave no hint for any new bands close to the calculated absorptions. If light of the wavelength 313 nm was used, only the bands of **8** diminished and the absorption of $NO^{\bullet}$ became stronger. Perhaps **8** is split under these conditions into the radical pair [$NO^{\bullet}$+$^{\bullet}F$]. One partner can escape the matrix cage and is therefore not available for a recapture under formation of **8** (or **9**).



8 **9**

b) As shown in Table 4, the observed (own experiments) bands X and Y fit with the vibrations which were originally attributed to **9**, but not, especially as far as the relative intensities are concerned, with the calculated spectrum of **9**.

c) In addition, the bands marked X and Y do not belong to the same species. For instance, if the deposited matrix is irradiated with $\lambda = 248$ nm, the bands X decrease and at the same time the absorptions of **8** grow, whereas the band Y remains unchanged. In this context it should be mentioned, that Jacox[14] in her experiments registered the bands X as well, but only a very weak absorption at 1887 cm^{-1}.

d) In the case of the isotopomers (use of ^{15}N- and ^{18}O-labelled $NO^{\bullet}$) the reported[13] isotopic shifts of the observed bands X and Y can be compared with the calculated shifts for **8** and **9**. It turns out that the accordance is much better for nitrosyl fluoride (**8**) than for isonitrosyl fluoride (**9**) (Table 5).

Taking into account all these inconsistencies it is tempting to assume that the bands X and Y should not be assigned to isonitrosyl fluoride (**9**) but to FNO molecules, which differ

Table 4. Comparison of the observed bands X and Y (Figure 7) (Ar, 10 K, [cm^{-1}]) and of FNO (**8**) with the calculated (BLYP/6–311 + G*) IR spectra of FNO (**8**) and FON (**9**). Relative intensities are given in parentheses.

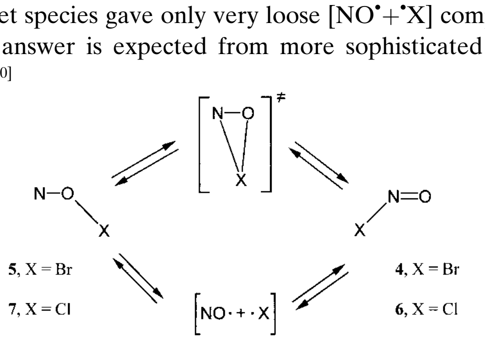
sym.	exptl, **8**	exptl, X+Y	calcd, **8**	calcd, **9**
ν_1 A′ ν_{NO}	1850.1 (1.0)	1884.2 (0.4)	1872 (1.0)	2022 (1.0)
ν_2 A′ $\delta_{FON/FNO}$	751.1 (0.72)	735.4 (1.0)	717 (0.5)	531 (0.23)
ν_3 A′ $\nu_{OF/NF}$	509.8 (0.5)	492.4 (0.5)	456 (0.3)	339 (0.05)

Table 5. Comparison of the reported[13] experimental (Ar, 8 K, [cm^{-1}]) isotopic shifts ($^{15}N^{16}O$ and $^{14}N^{18}O$ isotopomers relative to the $^{14}N^{16}O$ species) of the bands X+Y and of FNO (**8**) with the calculated (BLYP/6–311 + G*) shifts in the spectra of **8** and **9**.

	8 Δ_{exptl}[13]	X+Y Δ_{exptl}[13]	**8** Δ_{calcd}	**9** Δ_{calcd}
ν_1 ν_{NO}	32.5 (^{15}N)	–	33.1 (^{15}N)	36.1 (^{15}N)
	48.4 (^{18}O)	49.7 (^{18}O)	49.7 (^{18}O)	53.4 (^{18}O)
ν_2 $\delta_{FNO/FON}$	16.6 (^{15}N)	15.7 (^{15}N)	16.7 (^{15}N)	1.1 (^{15}N)
	8.1 (^{18}O)	8.3 (^{18}O)	6.3 (^{18}O)	18.3 (^{18}O)
ν_3 $\nu_{NF/OF}$	2.4 (^{15}N)	2.6 (^{15}N)	1.8 (^{15}N)	5.3 (^{15}N)
	7.3 (^{18}O)	7.2 (^{18}O)	8.4 (^{18}O)	2.7 (^{18}O)

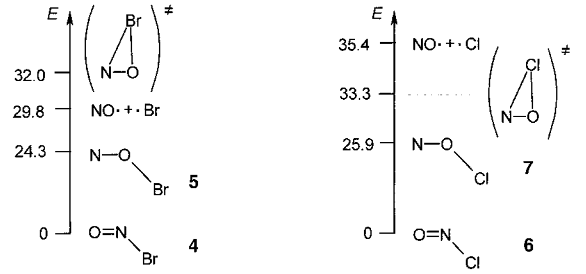
from the undisturbed nitrosyl fluoride (**8**) only by their varying matrix sites.

Stationary points on the potential-energy hypersurfaces of isonitrosyl bromide BrON (5) and isonitrosyl chloride ClON (7): Several theoretical contributions[7–9, 17–19] predict that not only nitrosyl halides like **4** and **6** but also their isonitrosyl isomers **5** and **7** represent minima on the singlet potential-energy hypersurface and should be candidates for matrix isolation. In order to evaluate the chance for realization it is, on the one hand, necessary to know their relative energies, on the other hand, to be aware of all the pathways of the energetically higher isomers for their stabilization. In case of the species representing the elemental composition N, O, X two alternative routes have to be considered. First, the dissociation into the radical pairs [NO$^•$+$^•$X], and second, a one-step isomerization via a cyclic transition state. As far as the isonitrosyl compounds are concerned, for which some nitrene character is expected,[2] it is also important to know their ground state multiplicity and the size of the singlet–triplet gaps. Our own calculations (B3LYP/6–311 + G*) on the triplet species gave only very loose [NO$^•$+$^•$X] complexes. A final answer is expected from more sophisticated calculations.[20]



Since all calculations show that the isonitrosyl isomers are higher in energy than the nitrosyl counterparts the main attention is directed towards the back reaction of the photochemically prepared isonitrosyl derivatives **5** and **7**.

For the transformation **5** →**4** and **7** →**6** the published[7–9, 17–19] and our own (B3LYP/6–311 + G*) calculations give a consistent picture. It is possible to find a transition state, which in the case of transition **5** →**4** is 2.2 kcal mol^{-1} higher and for reaction **7** →**6** is 2.1 kcal mol^{-1} lower than the energy of the two non-interacting fragments NO$^•$ and Br$^•$/Cl$^•$ (B3LYP/6–311 + G*). As shown in Scheme 1 the expected dissociation energy for **5** is 5.5 and for **7** is 9.5 kcal mol^{-1}. Calculations on a higher level, carried out by Lee,[9] had given similar barriers. So we conclude that the B3LYP method used by us is good enough in order to rationalize our experimental observations. This view is supported by the finding that B3LYP values for the dissociation energies of nitrosyl bromide (**4**) (exptl 27.9;[21] calcd 29.8 kcal mol^{-1}) and nitrosyl chloride (**6**) (exptl 37.1;[22] calcd 35.4 kcal mol^{-1}) agree quite well. A poorer conformity was achieved by using the BLYP method.



Scheme 1. Calculated relative energies (B3LYP/6–311 + G*, zero point vibrational energies are included in kcal mol^{-1}) of selected stationary points on the singlet potential-energy hypersurfaces of BrON (**5**) and ClON (**7**).

Structure of nitrosyl halides X–N=O and isonitrosyl halides X–O-N (X = Br, Cl): The geometry and bonding properties of nitrosyl and isonitrosyl halides (X = Br, Cl, F) have been treated theoretically by several authors.[7–9, 17–19] Therefore, only a few structural features calculated by Lee (CCSD(T)/TZ2P),[7–9] which are relevant for the new molecules **5** and **7**, will be discussed. Both compounds are not linear (angles of 122.3°[7] and 120.4°,[9]). The BrO distance in **5** is calculated[7] to be 2.476 Å, much longer than the calculated[7] value of 1.865 Å for Br_2O. The same prolongation is found in the calculated ClO distance of 2.273 Å[9] compared with 1.731 Å for Cl_2O.[9] On the other hand, the calculated NO distances are shorter in the isonitrosyl compounds **5**/**7** (1.135[7]/1.127 Å[9]) than in the nitrosyl isomers **4**/**6** (1.142[7]/1.141 Å[8]). If these values are compared with experimentally determined structural data it follows that the NO distances in **5**/**7** are between those of the NO^+ cation (1.063 Å)[23] and the NO$^•$ radical (1.151 Å).[23]

If the charge distribution is calculated,[7, 9] the halogen atom of **5**/**7** possesses the highest negative charge. At the same time the halogen is bound to an oxygen atom, which is also slightly negatively charged. This unfavorable charge distribution, which is different from the situation in the nitrosyl species, in which the positively charged atom sits in the center and is flanked by two negatively charged atoms, may be responsible for the reduced stability of the isonitrosyl compounds compared with the nitrosyl isomers.

IR induced isomerization of isonitrosyl bromide (5) and isonitrosyl chloride (7): During the measurement of the IR spectrum of **5** we observed that this compound is sensitive to

IR radiation: At the spot at which the IR beam of the spectrometer passed the matrix the yellow-orange color (caused by **5**) faded. If subsequently a second spectrum was taken the intensities of the IR bands of **5** had clearly decreased.

Being aware of this effect a glowing globar in combination with several filters was used in order to find out by which wavenumbers the back reaction **5**→**4** is initiated. Frequencies in the range 400–2000 (50% transmission at 1900 cm^{-1}) and 2300–3000 cm^{-1} (50% transmission at 2550 cm^{-1}) had no influence, whereas usage of filters with transmittances at 2120–2370 (50% transmission at 2250 cm^{-1}) and 2600–3750 cm^{-1} (40% transmission at 3580 cm^{-1}) caused an acceleration of the disappearance of **5**. These results indicate that **5** isomerizes to **4** upon IR irradiation within the ranges 2000–2300 and 3000–3700 cm^{-1}. This means, the reaction of **5** cannot occur by excitation of any fundamental vibrations (1820, ca. 350 and ca. 190 cm^{-1}), but has to originate from combination modes or overtones (e. g. 2168 or 3615 cm^{-1}).

The band at 2168 cm^{-1} corresponds to an energy difference of 6.2 $kcal\,mol^{-1}$. So the barrier for the isomerization **5**→**4** cannot be higher than this value. Indeed, as is shown above, the calculated (B3LYP/6–311 + G*) dissociation energy of **5** is 5.5 $kcal\,mol^{-1}$.

In case of isonitrosyl chloride (**7**) the influence of the IR radiation is much less pronounced. Only frequencies higher than 3500 cm^{-1} (> 10 $kcal\,mol^{-1}$) resulted in the disappearance of the IR bands of **7**. This observation indicates that the energy needed for the isomerization **7**→**6** is higher than for **5**→**4**. This is in agreement with the calculations (Scheme 1).

Examples for IR-induced reactions are rare. To the best of our knowledge this phenomenon has until now mostly been observed in rotational processes.[24–26] Sander et al.[27] described such an effect for the transformation of singlet bicyclo[3.1.0]hexa-3,5-dien-2-one into triplet 4-oxocyclohexa-2,5-dienylidene. The reactions of **5** and **7** may be the first cases, in which the energy of IR radiation is sufficient to initiate a transformation between structural isomers with different connectivities of the atoms.

Spontaneous isomerization of isonitrosyl bromide (5) and isonitrosyl chloride (7): The most astonishing property of **5** and **7** is their spontaneous thermal back reaction to **4** and **6** at a temperature as low as 10 K. If the calculated barriers are of any importance, **5** and **7** should be stable against thermal back reaction under matrix conditions.

We determined the rate constants for the reactions **5**→**4** and **7**→**6** by measuring the disappearance of the UV/Vis bands of **5** or **7** in Ar, Kr, and N_2 matrices (Table 6) and at various temperatures between 8.5 K and 25 K (argon only, Table 7). During all these experiments the matrix was kept in dark to exclude any influence of a photochemically induced reaction by visible light. The small contribution to the rate of isomerization by the UV light of the spectrometer during the UV measurement was taken into account in the determination of the rate constants. We also checked the influence of the black body radiation coming from outside by surrounding the matrix with a 30 K cold radiation shield during the experiment (except for the short intervals for taking the spectra). We found no effect. Furthermore, we measured the rate of the interconversion **7**→**6** in argon and N_2 at 10 K for the ^{15}N-isotopomers by IR spectroscopy (third column in Table 6).

Some peculiar aspects of the transformations of **5** and **7** deserve special comment. The surprising experimental facts are:

a) The spontaneous disappearances of the bands of **5** and **7** follow—as far as the special situation of matrix-isolated compounds allow such a conclusion—first-order kinetics (determined by measuring the decrease of the UV maxima of **5** or **7** and the increase of the UV maxima of **4** and **6** at temperatures between 8 and 25 K).

b) Isonitrosyl bromide (**5**) seems to isomerize slower than isonitrosyl chloride (**7**). The calculated barriers predict an opposite trend for a thermal effect.

c) The reaction rates are dependent on the matrix material (Table 6).

Table 6. Rate constants $k \times 10^4$ [s^{-1}] of the spontaneous isomerization BrON (**5**) → BrNO (**4**) and ClON (**7**) → ClNO (**6**) in different matrix materials (Ar, Kr, N_2, 12 K).

	BrON (**5**)	$ClO^{14}N$ (**7**)		$ClO^{15}N$ (**7**)
Ar	1.6[a]	2.7[b]	3.4[a]	3.4[b]
Kr	4.0[a]	–	11[a]	–
N_2	0.9[a]	54[b]	–	17[b]

[a] This value was determined on the basis of the behavior of the UV/Vis band. [b] This value was determined on the basis of the behavior of the NO stretching vibration in the IR spectrum.

d) Even an influence of the matrix material on the kinetic isotope effect can be measured. In case of $ClO^{15}N$ we observed in argon an increase from 2.7 to 3.4 × $10^{-4}\,s^{-1}$, and in N_2 a decrease from 54 to 17 × $10^{-4}\,s^{-1}$. This strange different dependence of the isotope effect in argon and N_2 was also observed by Hallou et al.[3]

e) The rate constants for the isomerization BrON (**5**) → BrNO (**4**) were practically temperature independent between 8.5 and 25 K (Table 7). The same phenomenon was observed for reaction ClON (**7**) → ClNO (**6**) (see also ref. [3]).

Table 7. Rate constants $k \times 10^4$ [s^{-1}] of the spontaneous isomerization BrON (**5**) → BrNO (**4**) in dependence of the temperature between 8.5 and 25 K.

T [K]	8.5	12	15	20	25
BrON (**5**)[a]	1.59	1.60	1.80	1.86	1.57

[a] All values were determined on the basis of the behavior of the UV/Vis band.

Is it possible to rationalize these experimental observations? Obviously the processes **5**→**4** and **7**→**6** do not follow classical rate theory. A rate constant of $1 \times 10^{-4}\,s^{-1}$ at 12 K would correspond to an activation energy of less than 1 $kcal\,mol^{-1}$. Such an extremely low barrier should cause a tremendous temperature dependence of the rate constant at the experimentally studied temperatures between 8 and 25 K. But this is not observed. In addition these low experimental enthalpies of activation are in full contrast to the calculated values (see above).

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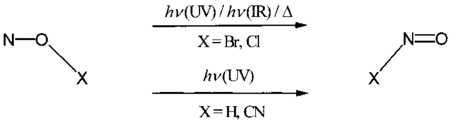
Under such circumstances normally a tunneling effect is discussed as the factor responsible for the unusual high rate constant and its independence from the raise in temperature. Such a proposal, which has also been made for the chlorine shift in **7**,[3] is even more problematic for **5**, in which the migration of such a heavy atom like bromine has to occur. But one should realize that in the transformation **5** →**4**, it may not be the bromine atom which changes its position. From a visualization of the IR deformation vibration of **4** or **5** we know that in this mode the position of the bromine remains practically the same and only the NO unit migrates. From this point of view one can derive that in the reaction **5** →**4** via a cyclic transition state it needs only a "rocking vibration" of the NO group with a high amplitude in order to transfer one isomer into the other.

Another point why we hesitate to assume a tunneling effect in the case of the isomerization of the isonitrosyl halides **5** and **7** is the observation that there are obviously two categories of isonitrosyl compounds X–O–N: If X is a hydrogen atom or a cyano group, the isomerization to the corresponding nitrosyl isomers can only be enforced by electronic excitation. If X is a bromine or chlorine atom, this reaction is also possible upon IR irradiation or by a spontaneous process, which is even active at 10 K. The reason, why isonitrosyl fluoride (**9**) cannot be detected may arise from the fact, that the back reaction to nitrosyl fluoride (**8**) is extremely fast.



Examples for hydrogen tunneling in matrix-isolated electroneutral molecules were discussed in several cases.[28–30] But it is difficult to substantiate such an assumption. Heavy atom (C atom) tunneling has also been proposed for matrix-isolated species (automerization of rectangular cyclobutadiene;[31, 32] ring closure of 1,3-cyclopentanediyl[33] and 1,3-cyclobutanediyl[34]). Since the tunneling rate has to decrease with a higher mass of the migrating unit experimental indications for tunneling of heavy atoms like chlorine or bromine are rare. Therefore, the intramolecular transformations **5** →**4** and **7** →**6** are of broader interest.

An intermolecular example at least for a $NO^{\bullet}$ transfer under matrix conditions is given by former work of Pimentel and Frei.[35] They studied the reaction $NO^{\bullet}+O_3 \rightarrow {}^{\bullet}NO_2$ in a matrix at 10 K and made similar observations as we did in the studies described above. The authors explained their experimental findings by quantum-mechanical tunneling.

So it is tempting to assume that the same explanation is also valid for the spontaneous isomerizations **5** →**4** and **7** →**6**. But if this is true, it is hard to understand why HON is stable under matrix conditions[2] and is not tunneling back to HNO. So we asked ourselves: Is heavy atom tunneling the only answer? In our opinion an alternative to tunneling could perhaps be the crossing of the singlet and triplet energy surfaces during the reactions of **5** and **7**. Sander et al.[27] have shown in the case of singlet bicyclo[3.1.0]hexa-3,5-dien-2-one that a thermally induced intersystem crossing can function as the rate-determining step. Perhaps **5** and **7** isomerize not exclusively on the singlet surface but follow a crossing to the triplet energy surface. It can be expected that the singlet–triplet gap between **S-5** and **T-4** or **S-7** and **T-6** may be small. In this case the transformation **5** →**4** could follow the reaction path **S-5** →**T-4** →**S-4** (each intersystem crossing step could per se be prone to tunneling). This sequence would be an example of a double "two-state reaction"[36] (Figure 8).

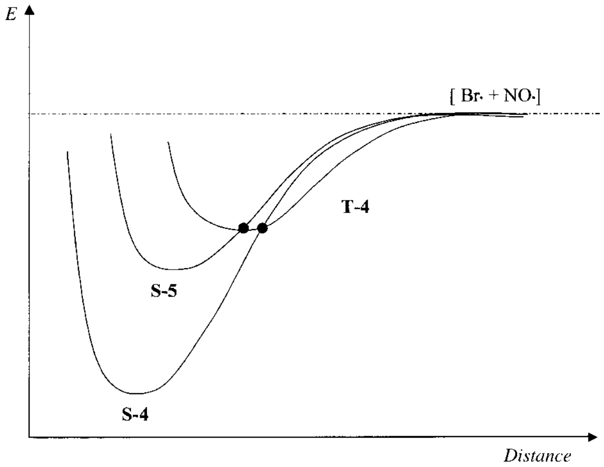


Figure 8. Expected crossings of the potential energy hypersurfaces of **S-4**, **S-5**, and **T-4**.

We hope that high level calculations[20] will give us an answer, whether heavy atom tunneling or a change in multiplicity causes the unexpected fast isomerizations found for isonitrosyl bromide (**5**) and isonitrosyl chloride (**7**).

Experimental Section

Matrix isolation spectroscopy: *Cryostat*: Displex closed-cycle refrigeration system CSA 202 from Air Products. *Temperature indicator/controller*: 3700-APD-E from Air Products, gold (0.07 % iron)/chromel thermo couple. *Matrix windows*: CsI for IR and CaF_2 for UV/Vis experiments. *Spectrometers*: FT-IR spectrometer IFS 55 from Bruker, resolution 0.7 cm^{-1}; diode array spectrometer HP 8453 from Hewlett–Packard (190–1100 nm, resolution 1 nm). *Microwave generator*: Raytheon PGM 10X1 (2466 MHz and 130 W with 100 %). *Light sources*: Mercury high-pressure lamp HBO 200 from Osram with a cutoff filter KG 1 (if only $\lambda > 310$ nm was required); mercury low-pressure spiral lamp from Gräntzel with interference filters (185 and 254 nm); excimer laser from Lambda Physik LPX 105; globar in combination with several filters from Laser Components for IR irradiation.

Kinetic measurements: Kinetic data have been determined by integrating the intense NO stretching vibration of **7** and by measuring the relative absorbance values of the absorption maxima of **5** and **7** in the UV/Vis spectra.

Nitrosyl bromide (4): Nitrosyl bromide (**4**) was prepared by reaction of potassium bromide with nitrosylsulfuric acid (Aldrich) at room temperature. The compound was purified by sublimation at −80 °C (10^{-3} Torr). Matrix-isolated samples were prepared by sublimation of **4** at −100 °C through a capillary (in order to reduce the speed of evaporation) and deposition on a matrix window at 10 K together with a large excess of inert gas.

Nitrosyl chloride (6): Nitrosyl chloride (**6**) was prepared according to the literature.[10] Matrix-isolated samples were prepared by sublimation of **6** at −115 °C (according to the procedure given above) and deposition on a matrix window at 10 K together with a large excess of inert gas.

Nitrosyl fluoride (8): Matrix-isolated nitrosyl fluoride (**8**) was prepared by cocondensation of a NO$^{\bullet}$/Ar together with a F$^{\bullet}$/Ar gas mixture, generated by passing CF_4 in argon (ratio 0.7:1000) through a microwave discharge zone.

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