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Infrared and Raman spectra and vibrational analyses calculated with Moeller–Plesset perturbation theory of second order of nitrosoethylene and its chloro-derivatives

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Abstract The conformational and structural stabilities of nitrosoethylene $\text{CH}_2=\text{CH}-\text{N}=\text{O}$, chloronitrosoethylene $\text{CH}_2=\text{CCl}-\text{N}=\text{O}$, and Dichloronitrosoethylene $\text{CCl}_2=\text{CH}-\text{N}=\text{O}$ were investigated by ab initio Moeller–Plesset perturbation theory of second order (MP2) calculations using the 6–311+G** basis set to include electron correlation. From the calculations all three were predicted to exist predominantly in the planar *trans* structure (C=C and N=O bonds are *trans* to each other) with high *trans-cis* rotational barriers of about 9 kcal mol^{-1} as a result of pronounced conjugation between C=C and N=O bonds. The vibrational frequencies were computed for the three molecules, and also the d_1 and d_2 deuterated variants for the parent molecule at the MP2 level. Normal coordinate analyses were carried out and the potential energy distributions (PED), among the symmetry coordinates of the normal modes of the molecule were computed. Complete vibrational assignments were made on the basis of normal coordinate analyses for the molecules. The two chlorinated derivatives of nitrosoethylene were also investigated in the same way. As expected, we then find high Raman and infrared intensities in all modes that contain a high content of chlorine movements because vibrations of C–Cl bonds lead to large changes in polarizability, as well as to a large change in dipole moment. However, modes involving double bonds also have quite large intensities. An appreciable number of modes in these molecules are more or less pure symmetry coordinates.

Keywords Conformational equilibria · Normal coordinate analyses · Rotational barriers · Nitrosoethylene · Chlorinated nitrosoethylenes

Introduction

The interesting properties of nitroso and nitro compounds [1–19] have attracted attention to investigate the structural and conformational stabilities of several nitroso R–N=O and nitro R–NO₂ compounds [20–22]. Nitroisocyanate $\text{O}_2\text{N}-\text{N}=\text{C}=\text{O}$, nitrosoisocyanate $\text{ON}-\text{N}=\text{C}=\text{O}$ [20], nitroketene $\text{O}_2\text{N}-\text{CH}=\text{C}=\text{O}$ and nitrosoketene $\text{ON}-\text{CH}=\text{C}=\text{O}$ [21] were predicted from theoretical calculations to exist exclusively in the planar conformations. The NO rotational barrier in nitrosoketene was calculated to be about 18 kcal mol^{-1} , and that of the NO₂ group in nitroketene to be about 10 kcal mol^{-1} [21]. These barriers were calculated to be about 6 and 2 kcal mol^{-1} for nitrosoisocyanates and nitroisocyanates, respectively [20]. The significant differences between the aforementioned barriers were attributed to the decrease in the partial π -character of the N–N bond in the isocyanate as compared to that of the C–N bond in the ketene [20, 21].

Additionally, the stability of cyclopropene $\text{c-C}_3\text{H}_4$ and many of its reactive derivatives [23–29] especially perfluorocyclopropene $\text{c-C}_3\text{F}_4$ [25] has led to the investigation of the structural stability of 3-nitrosocyclopropane and 3-nitrocyclopropene [22]. From the calculations, 3-nitrosocyclopropene was predicted to exist predominantly in the *trans* conformation (the N=O bond is *trans* to the ring and eclipses a hydrogen of the ring) with a relatively high *trans-cis* rotational barrier of about 8 kcal mol^{-1} . The NO₂ rotational barrier in 3-nitrocyclopropene was predicted from the symmetric potential scan to be about $4.4 \text{ kcal mol}^{-1}$.

In the present study, the interest in organonitrogen compounds is continued and the structures of nitrosoethylene $\text{CH}_2=\text{CH}-\text{N}=\text{O}$ together with its chlorinated derivatives were investigated. The energies of the molecules in their possible structures were optimized at the ab initio MP2 level using the 6–311+G** basis set. The vibrational frequencies were computed for the molecules and, in the case of the parent molecule, also for its

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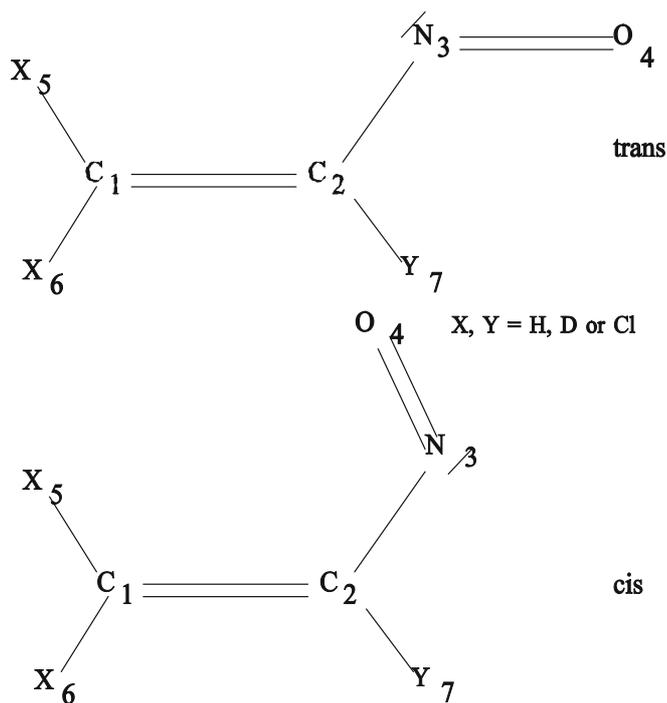


Fig. 1 Atom numbering for *cis* (upper) and *trans* (lower) conformers of the different nitrosoethylene derivatives (X and Y denote H or Cl)

*d*₁-deuterated and *d*₂-deuterated species. Then normal coordinate analyses were carried out to calculate the potential energy distributions (PED) among the symmetry coordinates of the normal modes for the stable forms of the molecules. The vibrational assignments of the normal modes were made on the basis of the calculated PED values and isotopic substitution and the results of the work are presented herein.

The molecules studied are of considerable interest because the investigations are expected to shed some light on the effects of an NO group bound to a vinyl group and also on those of chlorine substitution in such molecules. We expect that such effects can be explained on the basis of electronegativity changes, but this must be checked by actual calculations, the results of which are given herein.

Ab initio calculations

The GAUSSIAN 98 program [30], running on an IBM RS/6000 43P model 260 workstation, was used to carry out the MP2 calculations. The 6-311+G** basis set was employed to optimize the structures and predict the energies and dipole moments of nitrosoethylene CH₂=CH-N=O [31] and its chlorinated derivatives in their stable structures (Fig. 1).

The optimized energies and structural parameters of the chlorinated molecules are listed in Tables 1 and 2.

Note that, for the case of the parent molecule, the structural data have already been published [31] and are not reproduced here, while the energies are all given for

Table 1 Structural parameters, total dipole moments and rotational constants calculated on the MP2/6-311+G** level for *trans* monochloro-nitrosoethylene (mono-CINE, X=H, Y=Cl) and for *trans* dichloro-nitrosoethylene (di-CINE, X=Cl, Y=H)

Parameter	Mono-CINE	di-CINE	Microwave ^a
Bond lengths (Å)			
r(C ₁ =C ₂)	1.344	1.355	1.335 ^b
r(C ₂ -N ₃)	1.447	1.412	1.439
r(N ₃ =O ₄)	1.222	1.238	1.220 ^b
r(C ₁ -X ₅)	1.085	1.704	1.070 ^b
r(C ₁ -X ₆)	1.083	1.713	1.070 ^b
r(C ₂ -Y ₇)	1.717	1.087	1.070 ^b
Bond angles (degree)			
(C ₁ C ₂ N ₃)	115.3	118.9	117.1
(C ₂ N ₃ O ₄)	115.2	112.4	112.7
(C ₂ C ₁ X ₅)	117.7	123.7	120.0 ^b
(C ₂ C ₁ X ₆)	122.1	120.2	120.0 ^b
(C ₁ C ₂ Y ₇)	125.1	122.0	120.0 ^b
Torsional angle (degree)			
(C ₁ C ₂ N ₃ O ₄)	180.0	180.0	180.0
Dipole moment (Debye)			
μ _r	3.47	2.59	2.77
Rotational constants (GHz)			
A	5.59679	3.58007	
B	4.12471	1.48291	
C	2.37365	1.04858	

^a Structural parameters from microwave data on nitrosoethylene in Ref. [6]

^b Assumed parameters

the sake of comparison. The optimized structural parameters of the chlorinated forms were compared to the corresponding parameters obtained from microwave data of nitrosoethylene [6]. Note that some of the parameters had to be guessed because they could not be found in the relevant literature. Further, the experimental data is from the parent molecule only because we could not find data for the chlorinated forms.

Asymmetric torsional potential scans

Potential scans for the internal rotation about the C-N single bond were obtained by allowing the CCNO dihedral angles (Φ) in the molecule to vary from 0° (*cis* position) to 180° (*trans* position). Full geometry optimizations at each of the fixed dihedral angles (Φ) of 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, and 165° were carried out at the MP2/6-311+G** level. The torsional potential was represented as a Fourier cosine series in the dihedral angle (Φ):

$$E(\phi) = V_0 + \sum_{n=1}^6 \frac{V_n}{2} [1 - \cos(n\phi)] \quad (1)$$

where the potential coefficients from *V*₁ to *V*₆ are considered adequate to describe the potential function. The results of the energy optimizations at the MP2 level were used to calculate the six coefficients by least squares fitting for the three systems (Table 3).

Table 2 The MP2 total energies, E_t in Hartree, and MP2 relative energies, E_r in kcal mol⁻¹, for the *cis* and *trans* structures and the optimized transition states (*TS*) for nitrosoethylene (*NE*), monochloro-nitrosoethylene (*mono-CINE*) and dichloro-nitrosoethylene (*di-CINE*) together with the dihedral angles, given as Φ in degrees

Structure	NE			Mono-CINE			di-CINE		
	Φ	E_t	E_r	Φ	E_t	E_r	Φ	E_t	E_r
<i>cis</i>	0.0	-207.374476	4.305	0.0	-666.430627	4.955	0.0	-1125.480587	5.406
<i>trans</i>	180.0	-207.381337	0.000	180.0	-666.438523	0.000	180.0	-1125.489203	0.000
<i>TS</i>	90.6	-207.367301	8.808	92.3	-666.423833	9.218	88.7	-1125.473684	9.738

Note that the data are given for all the molecules in the table, although those for the parent molecule have already been published [31]. The three potential curves in the molecule are shown in Fig. 2.

Although the curve for the parent molecule has already been published, it is shown here again to emphasize the expected similarities between the potentials for the parent and those for the chlorinated derivatives. This is necessary because in the chlorinated molecules some slight linear dependencies in the wavefunctions appear, which do not show up in the parent molecules. The reasons are the larger basis sets in case of Cl atoms. The curve for the parent molecule might suggest a minimum about 15° away from the actual *cis* form, however, this is only an artifact of the fit and not due to the ab initio calculations. Note that the calculations for the *cis* form were not started at the exact dihedral angle. Even if so, if *cis* were a maximum or a saddle point, then there would be imaginary frequencies, which is not the case. The similarity of the curves indicates that these linear dependencies do not have drastic consequences in the results. Especially for the spectra, it seems to be more practical to turn to the MP2 spectra instead of the DFT ones [31], because it is known that all MP2 frequencies are too high and thus can be scaled, while for the DFT ones some are usually too high and others too low, and thus no scaling can be done.

Table 3 Calculated potential constants in kcal mol⁻¹ (see equation in the text) for the asymmetric torsion in nitrosoethylene (NE), monochloro-nitrosoethylene (mono-CINE) and dichloro-nitrosoethylene (di-CINE), together with the root mean square deviations, rms in kcal mol⁻¹, and the maximum (“maximum” refers not to *trans* where the relative deviation of the fit is infinite due to the division by 0, being the exact value for *trans*) deviations d_m relative to the calculated point in %, for the fits, as well as E_0 in Hartree to which the relative energies refer (all on MP2 level)

Quantity	NE	mono-CINE	di-CINE
V_0	4.309	4.957	5.406
V_1	-2.823	-3.264	-4.146
V_2	6.684	6.765	7.022
V_3	-1.331	-1.639	-1.202
V_4	-0.6982	-0.4589	-0.2611
V_5	-0.1579	-0.6198×10^{-1}	-0.6114×10^{-1}
V_6	-0.3215×10^{-1}	-0.4019×10^{-1}	0.1180×10^{-2}
RMS	0.2911×10^{-2}	0.6016×10^{-2}	0.4481×10^{-2}
d_m	0.8012	1.392	0.5882
E_0	-207.381344	-666.438537	-1125.489217

The rotational barriers increase when going from the parent molecule to monochlorinated and dichlorinated derivatives. This is relatively easy to explain and in line with expectations. When going from butadiene to nitroso ethylene, one substitutes the CH=CH₂ group in butadiene by the more electronegative N=O group and thus increases the double bond character in the C–N bond as compared to the C–C one because the more electronegative N=O group attracts electrons out of the vinyl group partially into the C–N bond, but also into the NO group itself. Thus, the rotational barrier in

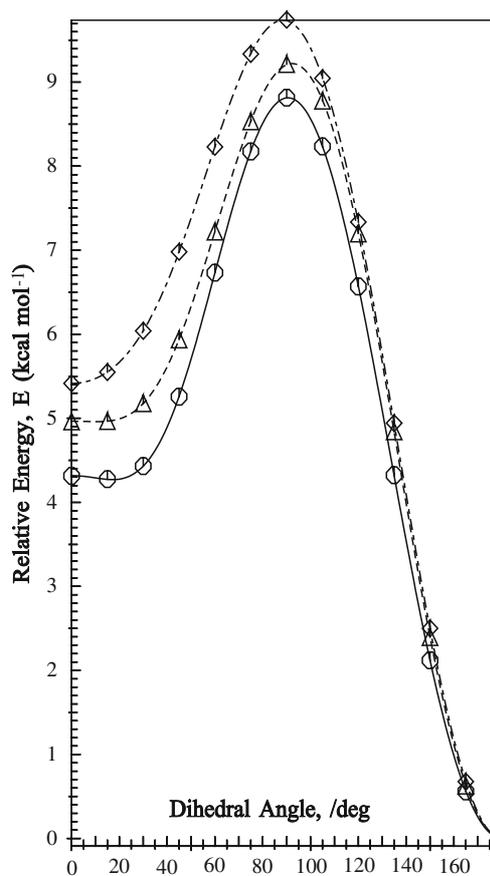


Fig. 2 Calculated potential curves for the asymmetric torsion in nitrosoethylenederivatives at MP2/6-311+G** level: parent molecule (solid line, MP2 numbers highlighted by hexagons), monochloroderivative (dashed line, MP2 numbers highlighted by triangles), dichloroderivative (dashed-pointed line, MP2 numbers highlighted by diamonds)

Table 4 Internal coordinate definitions for nitrosoethylene (X, Y = H), monochloro-nitrosoethylene (X = H, Y = Cl) and dichloro-nitrosoethylene (X = Cl, Y = H)

No.	Coordinate	Definition	
1	C ₁ -C ₂	Stretch	R
2	C ₂ -N ₃	Stretch	X
3	N ₃ -O ₄	Stretch	S
4	C ₁ -X ₅	Stretch	P ₁
5	C ₁ -X ₆	Stretch	P ₂
6	C ₂ -Y ₇	Stretch	T
7	C ₁ C ₂ N ₃	Bend	β ₁
8	N ₃ C ₂ Y ₇	Bend	β ₂
9	C ₁ C ₂ Y ₇	Bend	β ₃
10	C ₂ N ₃ O ₄	Bend	γ
11	X ₅ C ₁ X ₆	Bend	α ₁
12	C ₂ C ₁ X ₅	Bend	α ₂
13	C ₂ C ₁ X ₆	Bend	α ₃
14	C ₂ -Y ₇	Wag (out-of-plane bend)	ω
15	X ₅ C ₁ C ₂ N ₃ -X ₆ C ₁ C ₂ N ₃	Torsion	ξ ₁
16	X ₅ C ₁ C ₂ N ₃ +X ₆ C ₁ C ₂ N ₃	Torsion	ξ ₂
17	C ₁ C ₂ N ₃ O ₄ +Y ₇ C ₂ N ₃ O ₄	Asymmetric torsion	τ

Note that they hold also for *d*₁-nitrosoethylene (X = H, Y = D) and for *d*₂-nitrosoethylene (X = D, Y = H). For atom denotation see Fig. 1

nitrosoethylene is expected to be higher than that in butadiene, which we found to be 5.44 kcal mol⁻¹ at MP2/6-311+G**, and about 7 kcal mol⁻¹ at the DFT/6-311+G** level. When on the other side of the C-N bond hydrogens are replaced by chlorines, the electronegativity is increased and thus the double bond character of the C-N bond increased, thus increasing the rotational barriers when going from a CH₂=CH group to a CH₂=CCl and on to a CCl₂=CH group. The more electronegative groups prevent to some extent the attraction of electrons into the NO group itself, leaving a higher electron density in the C-C bond. In fluorinated and brominated derivatives one expects the same trend, but the corresponding increases in barriers to be larger in the former and lower in the latter ones.

Table 5 Symmetry coordinates (not normalized) for nitrosoethylenes (denotation as in Table 4)

Species	Description	Symmetry coordinate
A'	CX ₂ Anti-symmetric stretch	S ₁ = P ₁ -P ₂
	CX ₂ Symmetric stretch	S ₂ = P ₁ +P ₂
	C-Y Stretch	S ₃ = T
	N=O Stretch	S ₄ = S
	C=C Stretch	S ₅ = R
	C-N Stretch	S ₆ = X
	CX ₂ Scissor deformation	S ₇ = 2α ₁ -α ₂ -α ₃
	CX ₂ Wag	S ₈ = α ₂ -α ₃
	C-Y In-plane bend	S ₉ = β ₂ -β ₃
	C=C-N In-plane bend	S ₁₀ = 2β ₁ -β ₂ -β ₃
A''	CNO In-plane bend	S ₁₁ = γ
	C-Y Wag (out-of-plane bend)	S ₁₂ = ω
	CX ₂ Deformation I	S ₁₃ = ξ ₁
	CX ₂ Deformation II	S ₁₄ = ξ ₂
	Asymmetric torsion	S ₁₅ = τ

The potentials are rather flat around *cis*. A reason for this might be that the NO group could attract enough electron density into the C-N bond to simulate some amount of conjugation even in slightly non-planar structures. However, if not for steric effects, this should be the same in the *trans* conformer. However, *cis*, as opposed to *trans*, is somewhat destabilized by steric effects, which could lead to the flatter potential around *cis*.

Normal coordinate analyses and vibrational spectra

The optimized structural parameters of nitrosoethylene were used to calculate the vibrational frequencies of the *d*₀, *d*₁ and *d*₃ deuterated species of the molecule as well as the chlorinated derivatives at the MP2/6-311+G** level of calculation. Nitrosoethylene in its *trans* conformation has C_s symmetry and the 15 vibrational modes span the irreducible representations: 11 A' and 4 A''. The A' modes should be polarized whereas the A'' modes be depolarized in the Raman spectrum of the liquid. Normal coordinate analyses were carried out for the stable *trans* conformers of the molecules as described previously [32, 33]. The internal and symmetry coordinates of the molecule are listed in Tables 4 and 5.

The PED for each normal mode among the symmetry coordinates of the molecules were calculated and are given in Table 6.

A complete assignment of the fundamentals was proposed based on the calculated PED values, infrared band intensities, Raman line activities, depolarisation ratios and isotopic substitution in case of the *d*₁ and *d*₂ species of the parent molecule. The data of the vibrational assignments are listed in Table 6.

The vibrational infrared and Raman spectra were calculated using the computational methods described previously [33, 34]. To calculate the Raman spectra, the wavenumbers *k*_{*j*}, the scattering activities *S*_{*j*}, and the depolarisation ratios ρ_{*j*} were obtained from MP2/6-311+G** calculations. The calculated vibrational Raman and infrared spectra of the parent molecule are shown in Figs. 3 and 4, using scaled wavenumbers.

Results and discussion

Nitrosoethylene CH₂=CH-NO [4-6, 15, 23] has been the subject of many studies over the past few years. The microwave spectra of *trans*-nitrosoethylene and its ¹⁵N isotopic species generated by pyrolysis of chloroacetaldehyde oxime-¹⁵N were observed and its rotational constants, nuclear quadrupole coupling constants due to the nitrogen atom, dipole moments and lowest vibrational frequencies were all determined [5, 6]. More recently, *ab initio* [15] and DFT [23] studies of nitrosoethylene and its derivatives have been reported. From the theoretical calculations, the structural parameters of the molecule were reported to be strongly affected by the substitution groups in the nitrosoethylene

Table 6 Symmetry species, s_i , MP2 wavenumbers, k_i in cm^{-1} , scaled wavenumbers, k'_i in cm^{-1} , infrared intensities, I_i in km mol^{-1} , Raman activities, S_i in $\text{\AA}^4 \text{amu}^{-1}$, depolarization ratios ρ_i and distribution of the potential energy of a normal mode in the symmetry coordinates, PED (only values larger than 10% are given), for the normal modes i in d_0 , d_1 , and d_2 -nitrosoethylene

s_i	k_i	k'_i	I_i	S_i	ρ_i	PED
<i>d</i> ₀ -nitrosoethylene (X, Y = H)						
A''	159	159	0.2	0.4	0.75	87% S_{15} , 13% S_{12}
A'	351	333	1.0	0.3	0.66	71% S_{10} , 21% S_{11}
A'	616	585	0.7	6.4	0.13	57% S_{11} , 21% S_6 , 11% S_{10}
A''	678	643	0.9	1.5	0.75	81% S_{14} , 10% S_{15}
A'	906	859	23.2	0.7	0.73	52% S_8 , 36% S_6
A''	952	903	27.0	2.4	0.75	93% S_{13}
A''	998	946	40.4	0.2	0.75	71% S_{12} , 19% S_{14}
A'	1165	1105	60.6	28.1	0.47	38% S_6 , 17% S_8 , 16% S_9 , 12% S_{11} , 11% S_{10}
A'	1292	1226	1.4	8.8	0.26	56% S_9 , 20% S_8 , 13% S_5
A'	1426	1352	18.7	20.8	0.41	75% S_7 , 12% S_9
A'	1491	1415	36.7	37.9	0.43	94% S_4
A'	1664	1579	2.4	36.6	0.11	68% S_5 , 19% S_7
A'	3189	2991	0.6	25.3	0.24	70% S_2 , 30% S_3
A'	3207	3008	3.9	151.2	0.16	69% S_3 , 29% S_2
A'	3303	3099	0.2	52.3	0.68	99% S_1
<i>d</i> ₁ -nitrosoethylene (X = H, Y = D)						
A''	157	157	0.3	0.3	0.75	88% S_{15} , 11% S_{12}
A'	345	328	1.0	0.3	0.63	72% S_{10} , 21% S_{11}
A'	590	559	0.6	4.9	0.14	50% S_{11} , 19% S_6 , 12% S_9 , 12% S_{10}
A''	645	612	2.2	1.5	0.75	48% S_{14} , 39% S_{12} , 12% S_{15}
A''	840	797	9.4	0.3	0.75	50% S_{12} , 49% S_{14}
A'	867	823	8.0	1.8	0.15	35% S_8 , 33% S_9 , 26% S_6
A''	954	905	43.0	2.1	0.75	100% S_{13}
A'	994	943	34.9	13.7	0.37	41% S_9 , 25% S_6 , 19% S_{11} , 10% S_8
A'	1198	1136	35.4	10.7	0.73	44% S_8 , 26% S_6 , 13% S_{10}
A'	1411	1338	26.6	36.0	0.35	73% S_7 , 17% S_5
A'	1489	1413	35.0	37.7	0.40	93% S_4
A'	1640	1556	1.6	35.3	0.08	65% S_5 , 23% S_7
A'	2375	2228	2.8	34.1	0.34	95% S_3
A'	3194	2996	0.4	97.6	0.10	99% S_2
A'	3303	3098	0.1	54.5	0.71	100% S_1
<i>d</i> ₂ -nitro soethylene (X = D, Y = H)						
A''	154	154	0.1	0.1	0.75	86% S_{15} , 13% S_{12}
A'	314	298	1.2	0.2	0.73	68% S_{10} , 16% S_8 , 16% S_{11}
A''	542	514	0.0	0.4	0.75	97% S_{14}
A'	597	566	1.2	6.4	0.12	61% S_{11} , 16% S_6
A''	759	720	25.8	3.3	0.75	99% S_{13}
A'	765	726	7.6	0.4	0.29	61% S_8 , 24% S_6
A''	941	893	22.6	1.2	0.75	94% S_{12}
A'	1046	992	7.1	6.8	0.51	88% S_7
A'	1136	1078	76.2	25.9	0.51	55% S_6 , 15% S_{11} , 12% S_{10} , 11% S_8
A'	1279	1214	1.4	6.7	0.20	76% S_9
A'	1490	1414	41.4	45.2	0.42	93% S_4
A'	1612	1529	2.6	48.8	0.12	72% S_5 , 10% S_9
A'	2334	2189	0.7	31.1	0.14	94% S_2
A'	2462	2310	0.1	25.3	0.73	99% S_1
A'	3202	3004	4.2	79.6	0.23	99% S_3

The scale factors are $(0.88)^{1/2}$ for CH and CD stretches above 2000 cm^{-1} , $(0.90)^{1/2}$ for bendings between 200 and 2000 cm^{-1} and 1.00 for modes below 200 cm^{-1}

molecule [23]. Furthermore, the π -electron donor groups NH_2 , $\text{N}(\text{CH}_3)_2$, OH and OCH_3 were predicted to transfer the charges through the central transmission group $-\text{CH}=\text{CH}-$, which is very effective in modifying the NO bond length [23].

In our previous study, a comprehensive analysis of the vibrational spectra of nitrosoethylenes was provided, calculated at the DFT level [31]. At present, from energy optimization at MP2/6-311+G** level, chlorinated nitrosoethylenes were found to exist predominantly in

the *trans* conformation with high *trans* to *cis* rotational barriers of more than 9 kcal mol^{-1} . Furthermore, the *cis* forms were predicted to be about 5 kcal mol^{-1} higher in energy than the *trans* conformers of the molecules and thus, do not need to be included in the spectra calculations.

The vibrational wavenumbers of *trans* nitrosoethylene $\text{CH}_2-\text{CH}-\text{N}=\text{O}$ are given in Table 6 together with those of the *d*₁-deuterated and *d*₂-deuterated species. Then the potential energy distributions among the

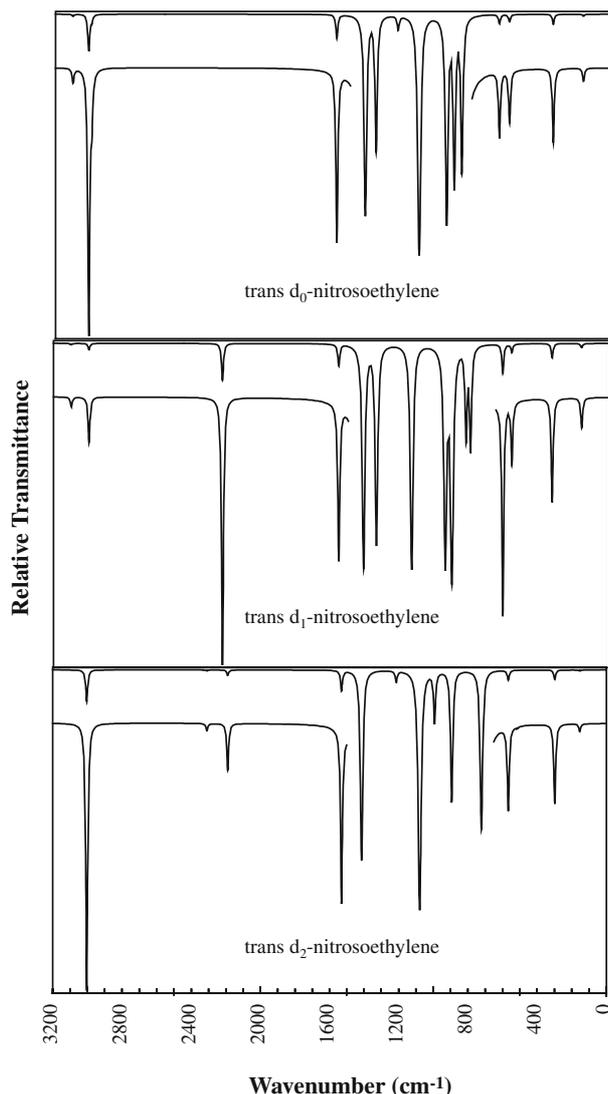


Fig. 3 Vibrational infrared spectra of *trans* d_0 -nitrosoethylene (upper panel), *trans* d_1 -nitrosoethylene (centre panel) and *trans* d_2 -nitrosoethylene (lower panel) using scaled wavenumbers from the MP2/6-311+G** calculations

symmetry coordinates of the normal modes were calculated for the three d_0 -species, d_1 -species, and d_2 -species of the parent (Table 6). The vibrational modes that are associated with the vinyl group were compared with the corresponding ones observed for propenoyl fluoride [35]. The vibrational assignments of most of the fundamental vibrations of nitrosoethylene were straightforward based on the calculated PED as shown in Table 6. Several of the calculated modes, especially those associated with the bending ones, were predicted to mix with other modes and could not be assigned based only on calculated PED values. It is important to repeat these calculations at the MP2 level in the present study, because we feel that scaled MP2 wavenumbers are more reliable than the DFT ones published earlier [31], because the latter cannot be scaled.

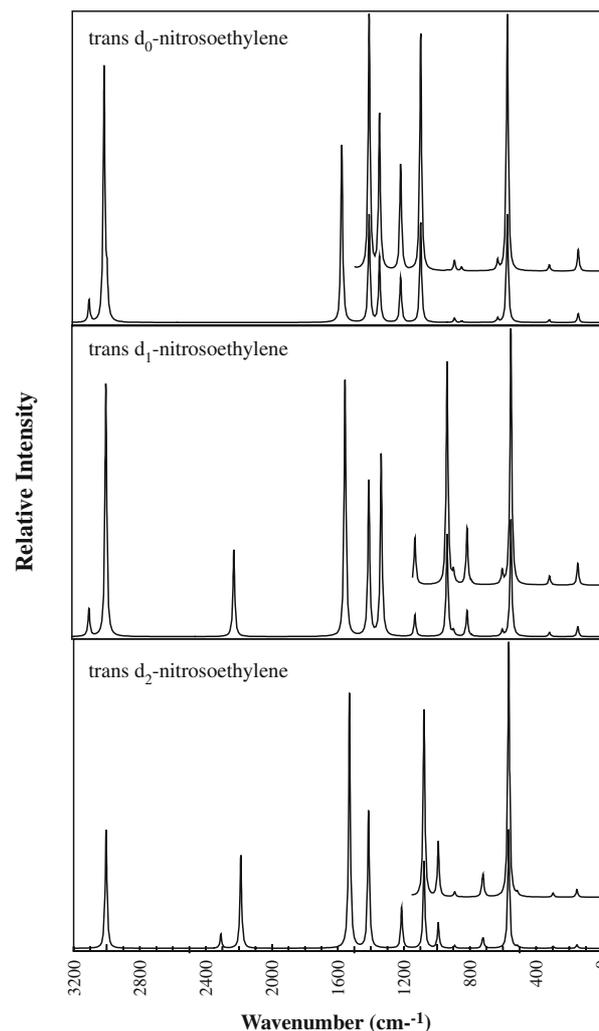


Fig. 4 Vibrational Raman spectra of *trans* d_0 -nitrosoethylene (upper panel), *trans* d_1 -nitrosoethylene (centre panel) and *trans* d_2 -nitrosoethylene (lower panel) using scaled wavenumbers from the MP2/6-311+G** calculations

There are three stretches that are associated with the C-H modes (S_1 , S_2 , and S_3) of the vinyl $\text{CH}_2=\text{CH}$ group and all were predicted to have little mixing with other vibrations (Table 6). These three modes were calculated at 3099, 3008, and 2991 cm^{-1} in the spectrum of d_0 , at 3098, 2996, and 2229 cm^{-1} in the spectrum of d_1 , and at 3004, 2310, and 2189 cm^{-1} in the spectrum of d_2 -nitrosoethylene (Table 6), respectively. The C=C stretching mode was calculated at 1579 cm^{-1} (PED of 68% S_5) in the spectrum of d_0 -nitrosoethylene (Table 6), considerably mixed with S_7 (19% PED). This mode was observed at 1630 cm^{-1} in the Raman spectra of the *trans* conformation of propenoyl fluoride [35].

The C-N stretching mode was calculated to mix considerably with other vibrations of the molecule (Table 6). The N=O stretch was calculated at 1415 cm^{-1} (PED of 94% S_4) with high infrared intensity in the spectrum of nitrosoethylene (Fig. 3). Several of the bending modes in the spectra of the molecule were

Table 7 Symmetry species, s_i , MP2 wavenumbers, k_i in cm^{-1} , scaled wavenumbers, k'_i in cm^{-1} , infrared intensities, I_i in km mol^{-1} , Raman activities, S_i in $\text{\AA}^4 \text{amu}^{-1}$, depolarization ratios ρ_i and distribution of the potential energy of a normal mode in the

symmetry coordinates, PED (only values larger than 10% are given), for the normal modes i in monochloro-nitrosoethylene and dichloro-nitrosoethylene

s_i	k_i	k'_i	I_i	S_i	ρ_i	PED
Monochloro-nitrosoethylene (X = H, Y = Cl)						
A''	158	158	1.2	0.3	0.75	89% S_{15}
A'	255	241	0.5	3.5	0.67	50% S_9 , 24% S_{11} , 21% S_{10}
A'	374	355	0.1	3.4	0.72	57% S_{10} , 32% S_9
A''	474	450	0.3	0.8	0.75	96% S_{12}
A'	657	623	25.2	9.7	0.12	46% S_3 , 32% S_6
A'	697	661	10.3	5.3	0.55	55% S_{11} , 26% S_3
A''	724	686	1.8	0.7	0.75	100% S_{14}
A'	889	843	42.1	4.6	0.35	42% S_8 , 40% S_6 , 11% S_{11}
A''	914	867	42.6	2.5	0.75	100% S_{13}
A'	1180	1120	90.4	16.2	0.42	49% S_8 , 23% S_6 , 12% S_{10}
A'	1410	1338	24.3	29.3	0.39	80% S_7 , 13% S_5
A'	1504	1426	72.7	35.3	0.44	92% S_4
A'	1653	1568	37.5	35.5	0.13	71% S_5 , 17% S_7
A'	3203	3005	1.9	98.7	0.10	99% S_2
A'	3319	3113	1.0	55.0	0.75	100% S_1
Dichloro-nitrosoethylene (X = Cl, Y = H)						
A''	137	137	0.8	0.0	0.75	68% S_{15} , 12% S_{12} , 10% S_{13}
A'	164	164	3.3	2.1	0.71	47% S_8 , 46% S_{10}
A''	234	226	5.7	1.3	0.75	85% S_{14} , 15% S_{15}
A'	292	277	0.2	4.4	0.66	86% S_7
A'	426	404	8.4	1.2	0.51	24% S_{10} , 23% S_8 , 22% S_2 , 13% S_1 , 13% S_6
A''	486	461	4.1	0.6	0.75	90% S_{13}
A'	491	466	1.4	5.9	0.08	43% S_{11} , 30% S_2 , 12% S_8
A'	759	720	37.0	3.7	0.59	36% S_2 , 29% S_{11} , 11% S_1
A''	844	801	18.1	1.6	0.75	100% S_{12}
A'	965	916	103.8	2.2	0.49	69% S_1 , 17% S_6
A'	1124	1066	273.5	102.6	0.36	60% S_6 , 12% S_{11}
A'	1285	1220	35.8	11.0	0.29	77% S_9
A'	1443	1369	71.2	119.0	0.32	86% S_4
A'	1609	1527	128.4	78.0	0.20	74% S_5
A'	3217	3018	2.0	72.9	0.20	100% S_3

The scale factors are $(0.88)^{1/2}$ for stretches above 2000 cm^{-1} , $(0.90)^{1/2}$ for bendings between 200 and 2000 cm^{-1} and 1.00 for modes below 200 cm^{-1}

calculated to have a small degree of mixing with other vibrations. For example, the CH_2 scissoring, CH, and C=C-N bending modes could be assigned with confidence on the basis of their PED values (Table 6) with, however, some small degree of mixing with other symmetry coordinates. The lowest vibrational torsional mode in the spectra of nitrosoethylene was calculated to have a non-negligible but small degree of mixing, as shown in Table 6.

Let us turn now to the vibrational spectra of the chlorinated derivatives. Their wavenumbers are given in Table 7 and their infrared and Raman spectra plots are shown in Figs. 5 (mono-CINE) and 6 (di-CINE).

The table shows, that in the mono-chloro derivative the lowest mode is pure asymmetric torsion at 158 cm^{-1} . The next higher band at 242 cm^{-1} appears to be substantially mixed, containing 50% C-Cl bend, 24% CNO bend and 21% C=C-N bend. The latter is contained to 57% in the next mode at 355 cm^{-1} mixed with 32% C-Cl bend. Then at 450 cm^{-1} we find purely the C-Cl wag (96% PED). At 623 and 661 cm^{-1} the C-Cl stretch appears, in the former (46%) mixed with 32% C-N

stretch, while in the latter (26%) it is mixed with 55% CNO bend. The line at 686 cm^{-1} is pure CH_2 deformation II. While the next higher one is again mixed, the CH_2 deformation I appears purely at 867 cm^{-1} . At 1426 cm^{-1} the pure NO stretch shows up, then at 1526 cm^{-1} a mixture of 71% C=C stretch with 17% CH_2 scissor motion follows. All these lines, also the highly mixed ones at lower wavenumbers, show a high intensity both in the Raman and in the infrared spectrum. The two CH_2 stretches appear at 3005 and 3113 cm^{-1} with a high intensity in the Raman spectrum, but a low-one in the infrared one.

In the case of the di-chloro compound, the lowest wavenumber at 137 cm^{-1} is not the pure torsion alone, but 68% of the torsion is mixed with 12% C-H wag and 10% CCl_2 deformation I. At 164 cm^{-1} CCl_2 wag appears in an equal mix with C=C-N bend, while at 226 cm^{-1} CCl_2 deformation II (85%) is mixed again with the asymmetric torsion (15%). The CCl_2 scissor appears pure (86%) at 277 cm^{-1} . The following band of relatively low intensity is a highly mixed one, followed by CCl_2 deformation I pure (90%). Then two mixed bands followed by

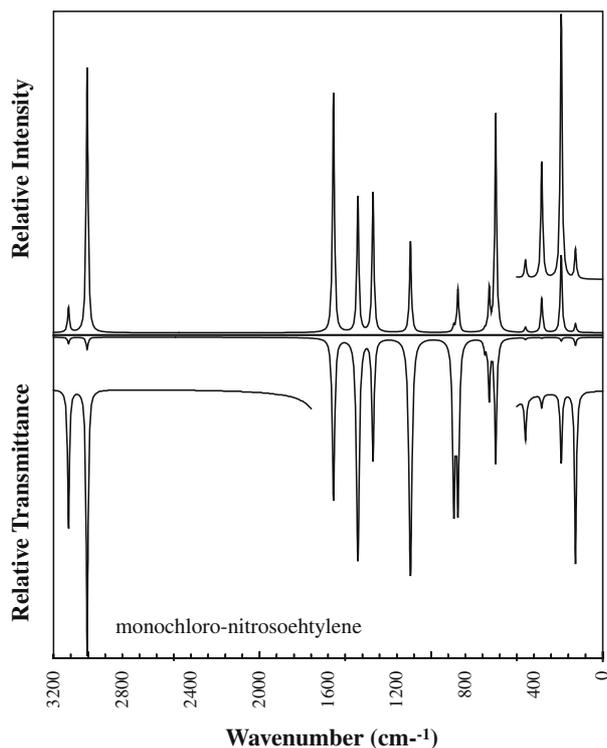


Fig. 5 Vibrational Raman (*upper panel*) and infrared (*lower panel*) spectra of *trans* monochloro-nitrosoethylene using scaled wavenumbers from the MP2/6-311+G** calculations

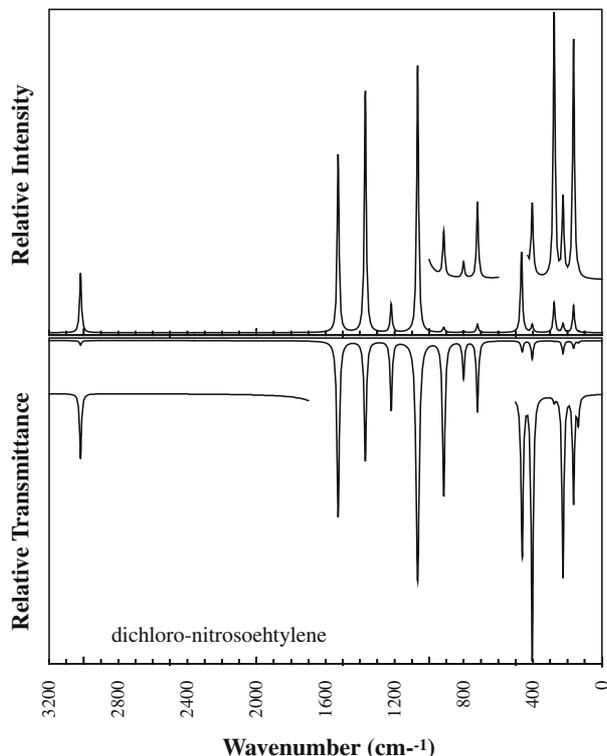


Fig. 6 Vibrational Raman (*upper panel*) and infrared (*lower panel*) spectra of *trans* dichloro-nitrosoethylene using scaled wavenumbers from the MP2/6-311+G** calculations

pure CH wag show up. In this region there are appreciable infrared transmittances, while the Raman intensities are low. The next bands are of higher intensity in both spectra and considerably mixed then follow some pure motions, i.e. 77% CH bend at 1220 cm^{-1} , 86% NO stretch at 1369 cm^{-1} , 74% C=C stretch at 1527 cm^{-1} , and finally 100% CH stretch at 3018 cm^{-1} .

A comparison of the predicted spectra with experiment would be highly desirable, but we were not able to find experimental spectra of these highly reactive molecules in the literature. Finally it turned out that most of the effects of an NO group and chlorine substitution of potential curves and on spectra are due to electronegativity, besides some steric influences.

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