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Chemical Physics 237 (1998) 265–271

Chemical Physics

Infrared spectra and theoretical calculations of HCl complexed with NO

L. Krim, M.E. Alikhani

Laboratoire de Spectrochimie Moléculaire (UMR CNRS 7614), Université P. et M. Curie, Boîte 49, bâtiment F74, 4 Place Jussieu, Paris Cedex 05, France

Received 3 March 1998; revised 13 July 1998

Abstract

The vibrational spectra of NO:HCl trapped in argon matrix have been reinvestigated. In the high frequency region, two stretching modes of N-O and H-Cl have been observed in agreement with a recent paper [Chem. Phys. 185 (1994) 365]. In the low frequency region, two bands (N-H stretch and out of plane bend) have been identified. From a theoretical study, it has been shown that the four experimental frequencies of the complex are well reproduced only for a bent structure in which H-bonding takes place between the nitrogen atom of NO and the hydrogen atom of HCl. The calculated frequency shifts of the N-O and H-Cl stretching modes upon complexation agree well with the experimental values.

1. Introduction

Recently, Saxce et al. [1] reported a combined experimental and theoretical investigation of hydrogen chloride and hydrogen bromide complexed with nitric oxide monomer. They experimentally identified two bands corresponding to H-X and N-O stretching modes of the NO:HX complexes (X = Cl or Br) isolated in argon matrix. They showed that, upon complexation the H-Cl stretching mode is red shifted, while the N-O one is blue shifted. In the theoretical calculations, performed at the UHF-SCF (unrestricted Hartree-Fock self consistent field), UMP2 (second order Møller-Plesset perturbation method), and CASSCF (multiconfiguartion method) levels of theory, they studied three different geometries, one linear with H-bonding between N and H (ON...HCl) and two bents with H-bonding between O and H (NO...HCl). A vibrational analysis (with UMP2) indicated that the linear geometry corresponds to a transition state structure. The calculated frequency shifts of both donor and acceptor (with CASSCF method) are not in satisfactory agreement with the experimental data.

In order to complete the analysis of vibrational frequencies of the NO:HCl complex particularly in the low frequency region, an experimental investigation in solid argon was performed. The structural and vibrational study of the complex has also been carried out using the density functional theory approach (DFT).

2. Experimental techniques

^{14}NO gas was provided by ''L'Air Liquide'' with a stated chemical purity of 99.9%, ^{15}NO gas by ''Isotec'' with an isotopical purity of 97.8%, HCl gas by Matheson (99.9%). DCl gas was prepared in the laboratory by addition of D_2O onto solid PCl_5.

PII: S0301-0104(98)00283-3

Argon gas, was also furnished by ‘‘L’Air Liquide’’ with a purity of 99.9995%.

The NO (or HCl) gas was first trapped in a liquid nitrogen, then a small amount was allowed to evaporate and the partial pressure so obtained was mixed with argon gas in order to obtain the desired concentration ratios NO/Ar, HCl/Ar and NO: HCl /Ar. In the present work different values of these ratios were used :

Pure NO/Ar and pure HCl/Ar: 1/3000, 1/1000, 1/400, 1/300, 1/100 ;

Mixture NO:HCl/Ar: 1:1/3000, 1:1/300, 1:1/100, 1/2/400, 2/1/400, 5/1/1000, 1/5/1000.

Typically, 35 mMole of the gaseous mixture were deposited onto a window cooled down to 20 K. Deposition took around 90 min. In order to check the pressure effect, spectra were recorded every deposited 5 mMole.

Spectra were recorded using a FTIR Bruker spectrometer (IFS 120HR) at resolutions of 0.5 cm^{-1} in the 20–500 cm^{-1} range and 0.1 cm^{-1} in the 500–6000 cm^{-1} range. An Hg lamp was used for the domain located below 100 cm^{-1} and Globar lamp above 100 cm^{-1}.

A bolometer detector was used for the low frequency region, typically from 20 to 500 cm^{-1} and a MCT detector from 500 to 6000 cm^{-1}. No signal was observed beyond 3750 cm^{-1} under the present conditions.

Three kinds of spectra were recorded at a series of different temperatures and pressures:

- spectra recorded for pure NO in argon matrix NO/Ar.
- spectra recorded for pure HCl in argon matrix HCl/Ar.
- spectra recorded for mixtures of NO and HCl in argon matrix NO:HCl /Ar.

All spectra presented in this paper were recorded at the temperature of deposition, 20 K. But in order to study the temperature effect on complex formation, some annealing of the matrix at several temperatures up to 35 K were performed.

3. Experimental results

The frequencies of all the absorptions measured with ^{14}NO:HCl, pure ^{14}NO, and pure HCl are listed in Table 1. Spectra of NO and $(NO)_2$ [2–4], HCl and $(HCl)_2$ [5–10] isolated in argon matrix are well known, and therefore their IR bands can easily be identified (Table 1). Some vibrational frequencies of NO:HCl and $(NO)_2$:HCl have been measured from spectra of the mixture of NO and HCl in argon matrix .

In our spectra, two regions can be distinguished as following : low frequency region and high frequency region.

3.1. Low frequency region (20–500 cm^{-1})

Two bands with frequencies lower than 100 cm^{-1} have been detected. The lowest one located at 32.4 cm^{-1} is as a strong signal (Fig. 1). This frequency can not be assigned to a mode of an NO:HCl complex, because it depends on neither NO nor HCl gas concentrations. On the other hand, it has the same behaviour that two other observed bands assigned to the water molecule located at 1590 cm^{-1} and 3727 cm^{-1} regions. Therefore, the band at 32.4 cm^{-1} may be attributed to water molecule [11,12]. The

Table 1
All the observed frequencies in cm^{-1} (relative intensities [a] in parentheses) in argon matrix, for ^{14}NO and HCl

Frequency (relative intensity)	Species	Mode
32.4 (0.13)	H_2O	Rotation
72.8 (0.23)	HCl	Translation
146.5 (0.09)	NO:HCl	
179.6 (0.08)	NO:HCl	
231 (0.1)	$(HCl)_2$	Bending
243.5 (0.08)	$(NO)_2$	Bending
1776.5 (0.73)	$(NO)_2$	N-O asymm. stretch
1802.8 (0.01)	$(NO)_2$:HCl	N-O asymm. stretch
1863.5, 1865.5 (0.28)	$(NO)_2$	N-O symm. stretch
1867.4 (0.11)	$(NO)_2$:HCl	N-O symm. stretch
1872.2, 1874.5 (0.30)	NO in two sites	
1880.3 (0.10)	NO:HCl	N-O stretch
2816.1 (0.02)	$(NO)_2$:HCl	H-Cl stretch
2818.0 (0.013)	$(HCl)_2$	H-Cl stretch
2827.5 (0.49)	NO:HCl	H-Cl stretch
2854.5 (0.19)	HCl	P(1) line
2863.6	N_2:HCl	H-Cl stretch
2870.7 (0.05)	HCl	Q branch
2888.1 (1)	HCl	R(0) line

[a] The relative IR intensity are calculated with respect to the R(0) band intensity of HCl.

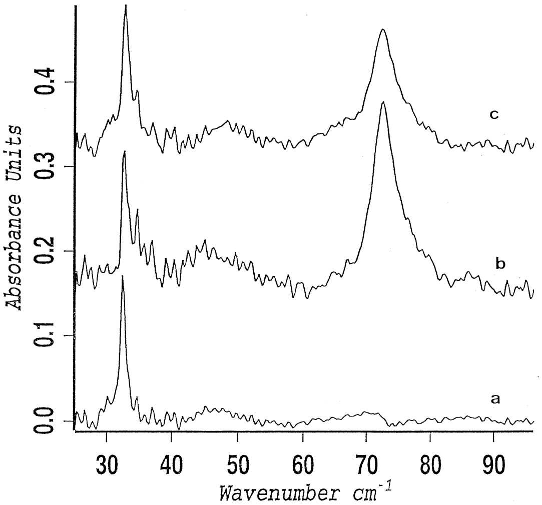

Fig. 1. NO and HCl trapped in argon matrix at 20 K. 0–100 cm^{-1} region (a) ^{14}NO in Ar, 1/200, (b) HCl in Ar, 1/400, (c) ^{14}NO:HCl/Ar , 2:1/400.

presence of this band probably does not allow the lowest fundamental mode of NO:HCl to be observed. The second band located at 72.8 cm^{-1} is relatively wide (fwhm = 5.4 cm^{-1}), and its intensity depends only on the HCl concentration (Fig. 1). It can easily be attributed to the translation of HCl monomer in argon matrix [13]. It could also hide a fundamental mode of NO:HCl complex.

In the 100–200 cm^{-1} region, two bands with same intensity, separated by 30 cm^{-1}, were observed. The first one located at 146.5 cm^{-1} is relatively wide (fwhm = 17 cm^{-1}), and its intensity depends on both NO and HCl concentrations (Fig. 2). It is also sensitive to a change in the isotopic composition of HCl/DCl (Fig. 3). Its infrared intensity remains constant after a warming of the matrix. It can then be attributed to a mode of the NO:HCl complex. The second band was observed at 179.6 cm^{-1}, with a width as large as that of the first one (fwhm = 16 cm^{-1}). Its dependence on both NO and HCl concentrations and also on the isotopic composition of HCl indicates that it should be attributed to another fundamental mode of the NO:HCl complex. Spectra obtained with the NO:HCl:DCl/Ar// 2:1:1/400 mixture exhibit four bands in 100-200 cm^{-1} region (Fig. 3). In addition of the two bands located at 146.5 and 179.6 cm^{-1}, the two other bands were located at 96.0 and 125.0 cm^{-1} which correspond to two modes of the NO:DCl complex.

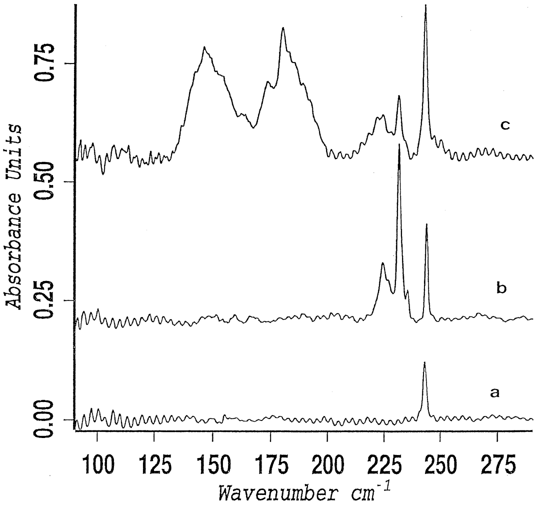

Fig. 2. NO and HCl trapped in argon matrix at 20 K. 100–300 cm^{-1} region (a) ^{14}NO in Ar, 1/200, (b) HCl in Ar, 1/400, (c) ^{14}NO:HCl/Ar, 2:1/400.

3.2. High frequency region (1700–3000 cm^{-1})

3.2.1. NO region (1700–2000 cm^{-1})

As it is shown in Fig. 4, ^{14}NO molecule perturbed by HCl presents a strong band located at 1880.3

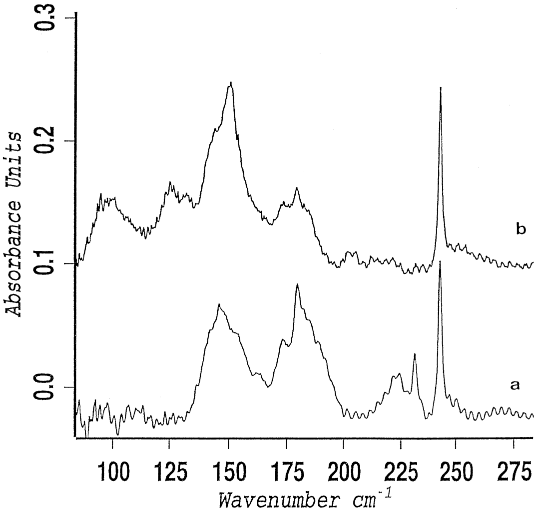

Fig. 3. NO, HCl and DCl trapped in argon matrix at 20 K. Far infrared region (a) ^{14}NO:HCl/Ar, 2:1/400, (b) ^{14}NO:HCl:DCl/ Ar, 2:1:1/400.

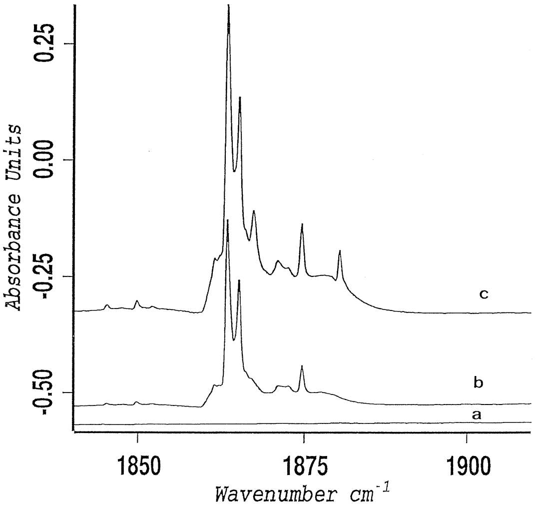

Fig. 4. NO and HCl trapped in argon matrix at 20 K. NO region (a) HCl in Ar, 1/400, (b) ^{14}NO in Ar, 1/200, (c) NO:HCl/Ar, 2:1/400.

cm^{-1}. Its infrared intensity remains constant after matrix warming. In agreement with Ref. [1], this band can be attributed to the N-O stretching mode of ^{14}NO:HCl. The bands located at 1847.1 and 1882.8 cm^{-1} (Fig. 5) correspond to ^{15}NO:HCl, and ^{14}NO:DCl, respectively.

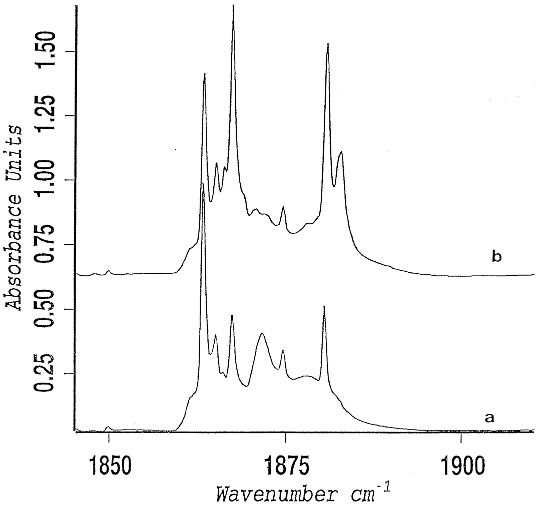

Fig. 5. NO, HCl and DCl trapped in argon matrix at 20 K. NO region (a) ^{14}NO:HCl/Ar, 2:1/400, (b) ^{14}NO:HCl:DCl/Ar, 2:1:1/400.

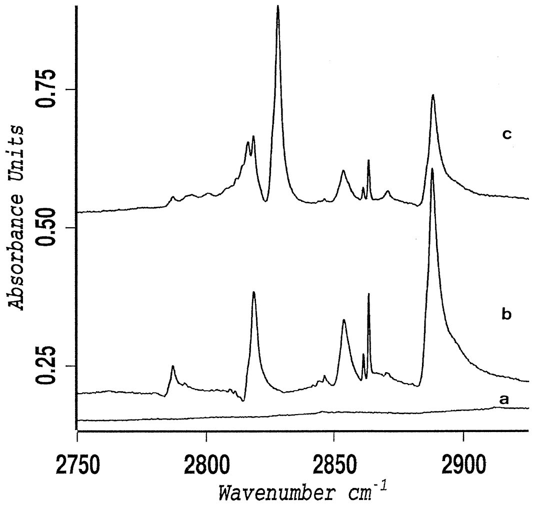

Fig. 6. NO and HCl trapped in argon matrix at 20 K. HCl region (a) ^{14}NO in Ar, 1/200, (b) HCl in Ar, 1/400, (c) NO:HCl/Ar, 2:1/400.

The ν_1 and ν_5 modes of $(NO)_2$ perturbed by HCl are also observed at 1867.4 and 1802.3 cm^{-1}, respectively [1]. The isotopic effects of the ν_1 mode are observed at 1871.0, 1854.0, and 1834.5 cm^{-1}, for $(^{14}NO)_2$:DCl, (^{14}NO-^{15}NO):HCl, and $(^{15}NO)_2$:HCl, respectively.

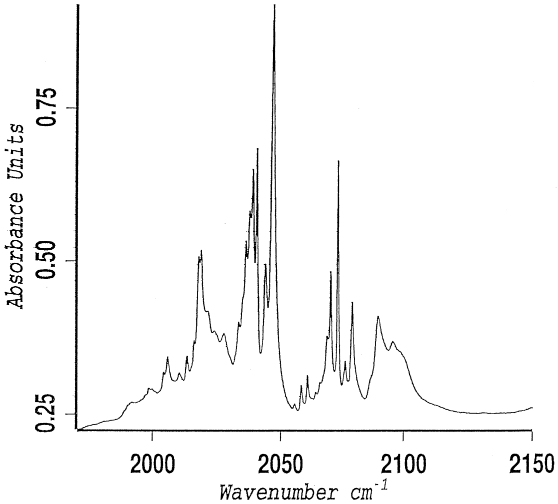

Fig. 7. NO, HCl and DCl trapped in argon matrix at 20 K. DCl region NO:HCl:DCl/Ar, 2:1:1/400.

3.2.2. HCl region (2000–3000 cm^{-1})

Two bands which depend on both NO and HCl concentrations as well as on the HCl isotopic substitution are observed in this region (Fig. 6). For the strongest one located at 2827.5 cm^{-1}, there is no change when ^{14}NO is substituted by ^{15}NO, while it is observed at 2046.8 cm^{-1} for the DCl/HCl isotopic effect (Fig. 7). In agreement with Ref. [1], this band can be assigned to the H-Cl stretching mode of ^{14}NO:HCl. The second band located at 2816.1 cm^{-1} depends on the $(NO)_2$ concentration, and its IR intensity increases when the matrix is warmed. There is no change on the frequency of this band after an NO isotopic substitution, while it is largely red shifted (777 cm^{-1}) after the DCl/HCl isotopic change (Fig. 7). This band can be assigned to the H-Cl stretching mode of $(^{14}NO)_2$:HCl [1].

Table 3
Geometrical and vibrational properties of NO:HCl using B3LYP

Parameters	Linear ClH...NO	Bent ClH...NO
r_{HCl} (Å)	1.2824	1.2874
r_{NO}	1.1452	1.1444
r_{HN}	2.4802	2.2963
∠(ClHN) (deg.)	0.0	177.5
∠(HNO)	0.0	124.8
E (au)	−590.774637	−590.775429
D_e (kcal.mol^{-1}) [a]	0.7	1.2
μ (D)	1.59	1.73
ω_{HCl} (cm^{-1})	2908 (127)	2826 (298)
ω_{NO}	1968 (44)	1966 (57)
$\delta_{\omega_{HCl}}$ [b]	14	96
$\delta_{\omega_{NO}}$ [b]	−15	−13
Elec. state	$^2\Sigma$	$^2A'$

[a] D_e = E (submolecules) − E (complex).
[b] δ_ω = ω (isolated molecule) − ω (complexated molecule).

4. Theoretical study of the NO...HCl complex

Several extensive studies on hydrogen-bonded complexes, using DFT theory, have shown that, in contrast to the local density approximation (LDA) which is incapable of describing the properties of the hydrogen bond, the nonlocal functionals (particularly the hybride functional B3LYP [14,15]) have been noted to result in a closer agreement with experimental and traditional *ab-initio* results [16–21]. Recently, Latajka et al. [22,23] have evidenced that an increase of the exact exchange part of B3LYP from 0.20 to 0.35 improves the agreement between the DFT results and the experimental ones. They have shown that the energetic and structural results obtained from the new parametrized hybrid functional are very close to those calculated from sophisticated approaches as MP4 (fourth-order) and QCISD(T) (quadratic CI calculations). The reparametrized functional is denoted as B3LYP(M). In the present paper, we use both hybride functionals (B3LYP(M) and B3LYP) to study the NO:HCl complex and their submolecules. All calculations have been performed using the Gaussian94 quantum chemical package [24]. As it has already been shown [22,23], the 6-311++G(2d,2p) basis set of Pople et al. [25] is suitable to study the H-bonded systems. Here, this basis set is used for all atoms.

As shown in Table 2, the geometrical and vibrational properties of isolated HCl and NO obtained

Table 2
Geometrical and vibrational properties of HCl and NO

Parameters	HCl		NO	
	B3LYP	B3LYP(M)	B3LYP	B3LYP(M)
r (Å)	1.2811 1.274 [a]	1.2739	1.1472 1.151 [a]	1.1391
E (au)	−460.837686	−461.161413	−129.935841	−130.137637
μ (D)	1.17 1.09 [a]	1.17	0.13 0.15 [a]	0.08
ω(cm^{-1})	2922 (42)	2982 (43)	1953 (43)	2018 (50)
ν_{exp}	2885.98 [a] (2870.7 [b])		1876 [a] (1872.2 [b])	

[a] Ref. [26]. [b] This work.

Table 4
Optimized geometrical properties of NO:HCl using B3LYP(M)

Parameters	Bent ClH...NO	Bent ClH...ON
r_{HCl} (Å)	1.2769	1.2753
r_{NO}	1.1372	1.1397
r_{HN}	2.5000	2.5315
∠(ClHN) (deg.)	177.3	
∠(ClHO)		177.1
∠(HNO)	127.4	
∠(HON)		128.2
E (au)	−591.300175	−590.299712
D_e (kcal.mol^{-1}) [a]	0.7	0.4
μ (D)	1.54	1.35
Elec. state	$^2A'$	$^2A'$

[a] $D_e = E$ (submolecules) − E (complex).

from both functionals are in a satisfactory agreement with the experimental data [26]. In Table 3 are listed the geometrical and some vibrational properties of two structures of NO:HCl obtained using the B3LYP functional. In concordance with some recent calculations [1], the linear geometry appears to be a transition structure with one imaginary frequency (75i cm^{-1}) corresponding to the inversion isomerization of the bent structure. The bent geometry of the ClH...NO isomer is found to be very slightly bound, whose inversion barrier height is about 0.5 kcal/mol. Only the bent structures of the two possible isomers (ClH...NO and ClH...ON) have been studied with the B3LYP(M) functional (Tables 4 and 5). It has been shown that the ClH...NO isomer is more stable than the ClH...ON one. A similar energetic property has been found for the XY:HF (XY = CO or NO) complexes [27]. One can see that the H-O distance in the ClH...ON complex is calculated larger than the H-N distance in the ClH...NO isomer. The same trend was seen for the FH...ON and FH...NO complexes [27].

The calculated vibrational frequencies using B3LYP(M) for both bent isomers as well as the experimental values are presented in Table 5. The calculated vibrational analysis has been performed in the harmonic approximation. One can readily note that the experimental frequencies are well reproduced by the B3LYP(M) techniques. The frequency shifts of the H-Cl and N-O stretching modes upon complexation, denoted as δ_{ν_1} and δ_{ν_2} respectively, are listed in Table 5. It should be noted that the experimental value of δ_{ν_1} is positive (red shift), while that of δ_{ν_2} is negative (blue shift). The theoretical value of δ_{ν_1} is positive for both isomers, but only its value for the bent ClH...NO structure agrees well with the experimental one. Furthermore, the δ_{ν_2} value is negative for the ClH...NO structure and positive for the ClH...ON one. As shown in Tables 3 and 5, the agreement between the theoretical δ_{ν_1} and δ_{ν_2} values and the experimental ones is well improved in going from B3LYP to B3LYP(M).

Inspecting the calculated infrared intensities (Table 5) shows that the experimental detection of the two ν_4 and ν_5 bands should be difficult because they are found to be very weak. Moreover, if we calculate the relative IR intensities of the fundamen-

Table 5
Vibrational properties of the NO:HCl complex using B3LYP(M) [a]

	Symm. mode	Bent ClH...NO	Bent ClH...ON	Exp.
A′	ν_1 (HCl str.)	2937.2 (170)	2963.7 (115)	2827.5 [b] (0.49 [d])
	ν_2 (NO str.)	2029.0 (56)	2012.0 (56)	1880.3 [c] (0.10 [d])
	ν_3 (NH str.)	204.8 (8)	169.9 (29)	179.6 (0.08 [d])
	ν_4 (HNO bend)	69.4 (3)	58.6 (2)	
	ν_5 (ClHN bend)	36.1 (0.5)	33.2 (0.5)	
A″	ν_6 (O.P. bend)	165.9 (32)	132.0 (33)	146.5 (0.09 [d])
	δ_{ν_1} [e]	44.7	18	43.2
	δ_{ν_2} [e]	−10.6	+6.4	−8.1

[a] Frequencies are in cm^{-1}. Calculated IR intensities are the absolute intensities and are given in km.mol^{-1}.

[b] Located at 2827.0 cm^{-1} in Ref. [1].

[c] Located at 1880.5 cm^{-1} in Ref. [1].

[d] The relative IR intensities (see Table 1).

[e] $\delta_\nu = \nu$ (isolated molecule) − ν (complexated molecule).

tal modes of the ClH...NO isomer with respect to the ν_1 band intensity, we obtain a good agreement between the theoretical and experimental values.

We can thus deduce that the experimentally observed species is a bent structure in which the H-bonding takes place between the nitrogen and hydrogen atoms. In order to verify the reability of this conclusion, a calculation has been performed for the NO:FH complex at the same level of theory as the NO:HCl complex. It has been shown that the experimental red shift of the H-F submolecule (-23.1 cm^{-1}) and blue shift of the N-O subunit (84 cm^{-1}) [8] are only well calculated for a bent structure of the FH...NO isomer, while for the NO...HF bent isomer, the two frequencies are calculated to be red shifted.

5. Conclusions

From a codeposition of HCl with nitric oxide in an argon matrix, the NO:HCl hydrogen bonded complex has been isolated. Two bands in the far infrared region were experimentally observed. The $^{15}NO:HCl$ and $^{14}NO:DCl$ isotopic bands were also recorded.

Using DFT aproach, four geometries (two linear and two bent structures) have been optimized for the NO:HCl complex. It was shown that the experimental data are well reproduced only for the ClH...NO bent structure in which the H-bonding occurs between the hydrogen atom of HCl and the nitrogen atom of nitric oxide. It has been shown that the same feature holds for the NO:HF complex.

Acknowledgements

One of us (L.K.) thanks D. Carrère for her help during the experiments. We thank Prof. N. Lacome for corrections to the English text.

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