

Vibrational Spectra and Structure of CH₃Cl:H₂O, CH₃Cl:HDO, and CH₃Cl:D₂O Complexes. IR Matrix Isolation and *ab initio* Calculations

Nadia Dozova, Lahouari Krim,* M. Esmail Alikhani, and Nelly Lacombe

LADIR/CNRS UMR 7075, Université Pierre et Marie Curie, Bat F74, case 49, 4 place Jussieu, 75252 Paris, Cedex 05, France

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The infrared spectra of CH₃Cl + H₂O isolated in solid neon at low temperatures have been investigated. The CH₃Cl + H₂O system is remarkable because of its propensity to form CH₃Cl:H₂O and CH₃Cl:(H₂O)_n (*n* ≥ 2) complexes. We focus here on the CH₃Cl:H₂O species. Low concentration studies (0.01–0.5%) and subsequent annealing lead to formation of the 1:1 CH₃Cl:H₂O complex with O–H···Cl–C or O···H–C intermolecular hydrogen bonds. Vibrational modes of this complex have been detected. In addition, spectra of D₂O + CH₃Cl and HDO + CH₃Cl have also been recorded. A detailed vibrational analysis of partially deuterated species shows that HDO is exclusively D bonded to CH₃Cl. This is a consequence of the preference for HDO to form a deuterium bonding complex rather than a hydrogen bonding one.

Introduction

The water vapor content of the stratosphere varies¹ and thus determines the balance of chemical reactions in the stratosphere. This implies that the future chemical composition of the stratosphere is dependent on any interaction (weak or strong) between water and the reagents present. Studies on bound molecular complexes^{2–4} where H₂O interacts with other molecules of the stratosphere can improve our understanding of stratospheric reactions. Ideally, in the laboratory, such reactions should be carried out in the gas phase to make sure that the complex partners are moving free of any external perturbation. Such experiments, although they can be performed, are difficult to achieve, while the matrix isolation technique is an easier, more powerful tool for studying molecular complexes.

In the present study, the structure of the CH₃Cl:H₂O complex was investigated by neon matrix isolation combined with infrared absorption spectroscopy. Detailed vibrational assignments were made from the observed spectra of the CH₃Cl:H₂O complex. Using *ab initio* calculations, geometrical and vibrational properties of the complex have been estimated. In addition, spectra of D₂O + CH₃Cl and HDO + CH₃Cl samples have also been recorded and the vibrational wavenumbers for the four isotopic complexes CH₃Cl:H₂O, CH₃Cl:DOH, CH₃Cl:HOD, and CH₃Cl:D₂O were calculated and compared with the observed values. All the wavenumbers of the observed bands on the partially deuterated complex are consistent with the calculated values of CH₃Cl:DOH, which proves the existence of the CH₃Cl:DOH complex (HDO is D bonded to CH₃Cl), rather than CH₃Cl:HOD.

Experimental Technique

CH₃Cl + H₂O samples were prepared by co-condensing CH₃Cl/H₂O/Ne mixtures onto a cryogenic metal mirror maintained at 5 K. Molar ratios (X/Ne, X = CH₃Cl or H₂O) ranged from 0.001 to 1%. The experimental method and setup have

been previously described in detail.⁵ We shall recall only the main points. The deposition times were around 60 min. Neon and CH₃Cl gases were obtained from “L’Air liquide” with purities of 99.9995 and 99.8%, respectively. CH₃Cl was purified by using trap-to-trap vacuum distillations. D-Isotopic water (Euriso-top 99.90%) as well as natural water was degassed in a vacuum line. The purity of the samples was confirmed spectroscopically.

Infrared spectra of the resulting samples were recorded in the transmission-reflection mode between 4500 and 500 cm⁻¹ using a Bruker 120 Fourier transform infrared (FTIR) spectrometer equipped with a KBr/Ge beam splitter and a liquid-N₂-cooled narrow band HgCdTe photoconductor. A resolution of 0.1 cm⁻¹ was used. Bare mirror backgrounds, recorded from 4500 to 500 cm⁻¹ prior to sample deposition, were used as references in processing the sample spectra. Absorption spectra in the mid-infrared were collected on samples through a KBr window mounted on a rotatable flange separating the interferometer vacuum (10⁻³ mbar) from that of the cryostatic cell (10⁻⁷ mbar). The spectra were subsequently subjected to baseline correction to compensate for infrared light scattering and interference patterns. All spectra were recorded at 5 K.

The samples could be irradiated using a 200 W mercury–xenon high pressure arc lamp and either interference narrow (5 nm full width at half-maximum (fwhm)) or broad band filters in order to find if some photoprocesses could be initiated by UV–visible or near-infrared light. Next, or after sample annealing up to 12 K in several steps, infrared spectra of the samples were recorded again between 4500 and 500 cm⁻¹ as outlined above.

Experimental Results

CH₃Cl in Ne Matrix. Spectra of pure CH₃Cl isolated in neon matrices have been recorded at 5 K at different concentrations of CH₃Cl and have been previously described.⁶ Briefly, the C–Cl stretching region (Figure 1a) has two sets of bands belonging to the two isotopomers CH₃³⁵Cl and CH₃³⁷Cl. Each band consists of three sharp peaks due to splitting by the matrix

* To whom correspondence should be addressed. E-mail: krim@ccr.jussieu.fr.

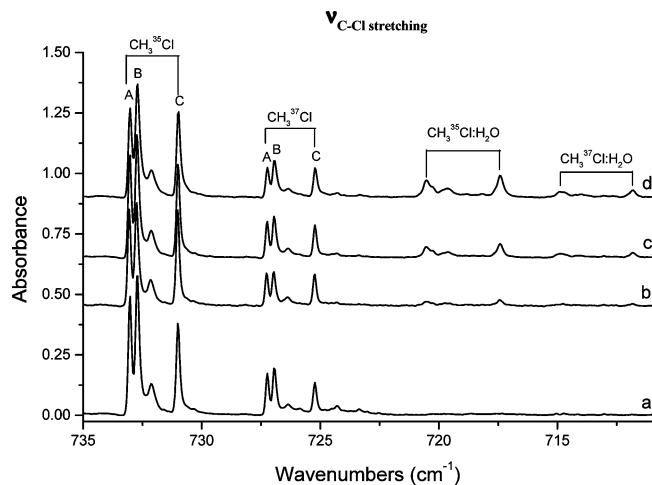


Figure 1. C–Cl stretching (ν_3 CH_3Cl) region of CH_3Cl and the $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ complex after deposition at 5 K: (a) $\text{CH}_3\text{Cl}/\text{Ne} = 5:10\ 000$; (b) $\text{CH}_3\text{Cl}/\text{H}_2\text{O}/\text{Ne} = 5:2.5:10\ 000$; (c) $\text{CH}_3\text{Cl}/\text{H}_2\text{O}/\text{Ne} = 5:5:10\ 000$; (d) $\text{CH}_3\text{Cl}/\text{H}_2\text{O}/\text{Ne} = 5:10:10\ 000$.

cage. For the $\text{CH}_3^{35}\text{Cl}$ isotopomer, they are situated at $733.0\ \text{cm}^{-1}$ (peak A), $732.7\ \text{cm}^{-1}$ (peak B with a shoulder at $732.1\ \text{cm}^{-1}$), and $731.0\ \text{cm}^{-1}$ (peak C), while, for the other isotopomer, they are located at $727.2\ \text{cm}^{-1}$, $726.9\ \text{cm}^{-1}$ (with a shoulder at $726.3\ \text{cm}^{-1}$), and $725.2\ \text{cm}^{-1}$, respectively. The shift between two corresponding peaks in the two isotopomers is $5.8\ \text{cm}^{-1}$. Upon annealing (11–12 K), only the band of site B remains intense, which characterizes the most stable site of CH_3Cl trapped in the neon matrix.

In the region of C–H symmetric stretching (and also for other vibrational modes of CH_3Cl), three peaks are observed; each of them is correlated with one of peaks A, B, and C in the C–Cl stretching mode region. Vibrational mode frequencies of CH_3Cl trapped in the most stable site in the neon matrix (site B) are given in Table 1. In the following, we will take the C–Cl stretching spectral region as a characteristic domain of the specific vibrational modes of the CH_3Cl monomer and $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ complex.

H_2O in Ne Matrix. Rovibrational spectra of water monomers trapped in solids have been the subject of several studies.^{7–11} H_2O rovibrational transitions are labeled $J''_{K''_a K''_c} \rightarrow J'_{K'_a K'_c}$, where J is the quantum number associated with the total rotational angular momentum and K_a and K_c are the quantum numbers of the components of J on the principal axes a and c , respectively.^{11–13} Due to the symmetry point group of water (C_{2v}), the hydrogen atoms are equivalent and may possess antiparallel ($p\text{-H}_2\text{O}$) or parallel ($o\text{-H}_2\text{O}$) nuclear spins. The ground state for

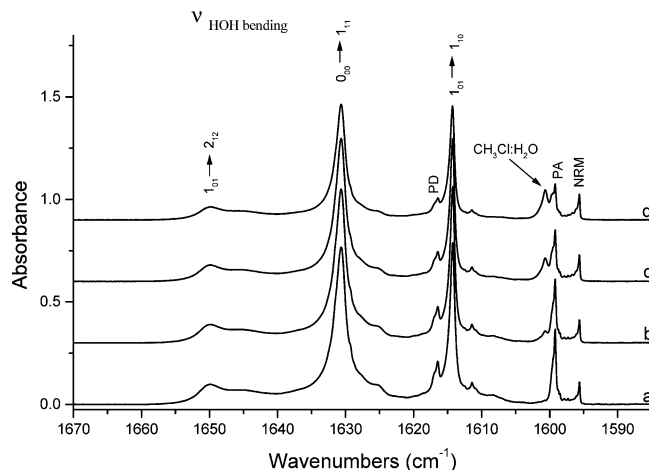


Figure 2. HOH bending (ν_2) region of H_2O and the $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ complex after deposition at 5 K: (a) $\text{H}_2\text{O}/\text{Ne} = 5:10\ 000$; (b) $\text{CH}_3\text{Cl}/\text{H}_2\text{O}/\text{Ne} = 1.5:5:10\ 000$; (c) $\text{CH}_3\text{Cl}/\text{H}_2\text{O}/\text{Ne} = 5:5:10\ 000$; (d) $\text{CH}_3\text{Cl}/\text{H}_2\text{O}/\text{Ne} = 10:5:10\ 000$.

the para and ortho molecules are the 0_{00} and 1_{01} levels, respectively. A nuclear spin conversion (NSC) process occurs between the 1_{01} rotational level (metastable level) and the 0_{00} ground level.¹³

Isolation in rare gas solids such as argon and neon shows that two kinds of water molecules are spectroscopically distinguishable: the rotating monomer (RM) which gives rise to several rovibrational lines starting from $J'' = 0$ or 1 and the nonrotating monomer (NRM) for which rotation is hindered either by the matrix inhomogeneity or by weak interactions between non-nearest neighbors and which gives rise to a transition close to the pure vibrational frequencies.^{7–9} It should be noticed that water monomers trapped in molecular solids, such as N_2 and normal -D_2 , do not rotate with the exception of solid H_2 .¹³ The three vibrational fundamentals are labeled ν_2 (HOH bending), ν_1 (symmetric stretching), and ν_3 (antisymmetric stretching).

ν_2 Mode. Figure 2a shows the infrared absorption spectrum of a $\text{H}_2\text{O}/\text{Ne}$ sample deposited at 5 K in the ν_2 region (HOH bending). The three most intense peaks of rotating H_2O molecules are situated at $1614.2\ \text{cm}^{-1}$ (rovibrational transition $1_{01} \rightarrow 1_{10}$), $1630.6\ \text{cm}^{-1}$ ($0_{00} \rightarrow 1_{11}$), and $1649.9\ \text{cm}^{-1}$ ($1_{01} \rightarrow 2_{12}$). The NRM peak is located at $1595.6\ \text{cm}^{-1}$ (characterized by an intensity increase with concentration and by an intensity decrease upon annealing). The other two intense peaks belong to the H_2O dimer: the one at $1599.2\ \text{cm}^{-1}$ belongs to the proton acceptor (PA) and the other at $1616.4\ \text{cm}^{-1}$ to the proton donor (PD).¹⁴

TABLE 1: Vibrational Mode Frequencies (in cm^{-1}) of CH_3Cl (Site B), H_2O (Nonrotating Monomer (NRM)), and the $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ Complex in a Neon Matrix

mode		monomer/Ne	$\text{CH}_3\text{Cl}:\text{H}_2\text{O}/\text{Ne}$	shift ^a
CH_3Cl				
C–Cl stretching	ν_3 CH_3Cl	726.9 (^{37}Cl)	714.8	–12.1
		732.7 (^{35}Cl)	720.5	–12.2
C–Cl rocking	ν_6 CH_3Cl	1019.4	1022.2	2.8
C–H symmetric bending	ν_2 CH_3Cl	1354.8	1357.3	2.5
C–H antisymmetric bending	ν_5 CH_3Cl	1451.5	1455.2	3.7
C–H symmetric stretching	ν_1 CH_3Cl	2967.5	2972.2	4.7
C–H antisymmetric stretching	ν_4 CH_3Cl	3036.7	3044.2	7.5
H_2O				
O–H bending	ν_2 H_2O	1595.6	1600.5	4.9
O–H symmetric stretching	ν_1 H_2O	3665.5	3625.9	–39.6
O–H antisymmetric stretching	ν_3 H_2O	3761.1	3738.8	–22.3

^a shift = $\nu_{\text{complex}} - \nu_{\text{free molecule}}$.

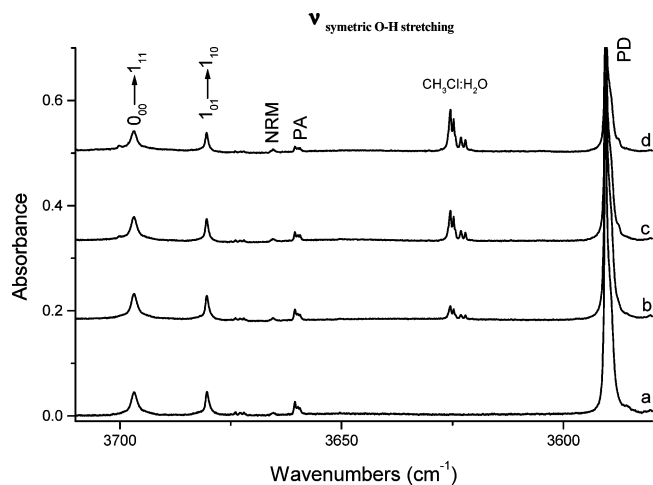


Figure 3. O–H symmetric stretching (ν_1) region of H₂O and the CH₃Cl:H₂O complex after deposition at 5 K: (a) H₂O/Ne = 5:10 000; (b) CH₃Cl/H₂O/Ne = 1.5:5:10 000; (c) CH₃Cl/H₂O/Ne = 5:5:10 000; (d) CH₃Cl/H₂O/Ne = 10:5:10 000.

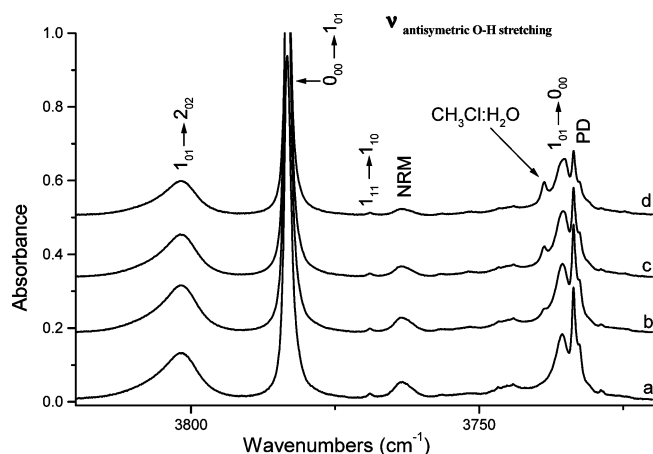


Figure 4. O–H antisymmetric stretching (ν_3) region of H₂O and the CH₃Cl:H₂O complex after deposition at 5 K: (a) H₂O/Ne = 5:10 000; (b) CH₃Cl/H₂O/Ne = 1.5:5:10 000; (c) CH₃Cl/H₂O/Ne = 5:5:10 000; (d) CH₃Cl/H₂O/Ne = 10:5:10 000.

ν_1 Mode. Figure 3a shows the symmetric O–H stretching region (ν_1). Two bands of the rotating monomer are observed at 3680.4 cm⁻¹ ($1_{01} \rightarrow 1_{10}$) and 3696.9 cm⁻¹ ($0_{00} \rightarrow 1_{11}$). The PA band of the water dimer is situated at 3660.5 cm⁻¹ and the PD band (very intense) at 3590.5 cm⁻¹. The nonrotating monomer (NRM) band is detected at 3665.5 cm⁻¹. The NRM band (in solid neon) has been observed by Nelander et al.⁹ and Forney et al.¹⁰ at 3664.8 and 3660.6 cm⁻¹, respectively. Our observation is comparable with that reported by Nelander et al.⁹ The band at 3660.6 reported by Forney et al.¹⁰ could not be due to the water monomer but to (H₂O)₂. Indeed, the intensity of this band increases upon annealing. This result is confirmed by the recent work of Perchard et al.¹⁴ who attributed this band to the ν_1 mode of the (H₂O)₂ proton acceptor.

ν_3 Mode. Figure 4a shows the antisymmetric O–H stretching region. The three most intense peaks of rotating H₂O molecules are situated at 3735.7 ($1_{01} \rightarrow 0_{00}$), 3783.3 ($0_{00} \rightarrow 1_{01}$), and 3801.7 cm⁻¹ ($1_{01} \rightarrow 2_{02}$). The PA band of the water dimer situated at 3750.0 cm⁻¹ and the PD band at 3733.7 cm⁻¹ have been largely studied by Perchard et al.¹⁴ The band of the nonrotating water monomer (NRM) is situated at 3761.1 cm⁻¹. The NRM band (in solid neon) has been observed by Nelander et al.⁹ and Perchard et al.¹⁴ at 3760.9 and 3760.8 cm⁻¹, respectively, which is comparable with our observation.

TABLE 2: Frequencies (cm⁻¹) and Assignments of Absorption Lines of Monomeric H₂O

transition	gas phase ¹⁵	solid argon ^{7,8}	solid neon (this work)	solid neon ¹⁰
ν_2 Region				
NRM ^a		1589.2	1595.6	1595.6
101 → 110 ortho	1616.714	1607.9	1614.2	1614.2
000 → 111 para	1634.970	1623.8	1630.6	1630.6
101 → 212 ortho	1653.268	1636.5	1649.9	1649.8
ν_1 Region				
NRM ^a		3638.3	3665.5	3660.6
101 → 110 ortho	3674.697	3653.5	3680.4	3680.6
000 → 111 para	3693.294	3669.7	3696.9	3696.9
ν_3 Region				
101 → 000 ortho	3732.135	3711.3	3735.7	3735.6
NRM ^a		3736.0	3761.1	
000 → 101 para	3779.493	3756.6	3783.3	3783.3
101 → 202 ortho	3801.420	3776.4	3801.7	3801.7

^a NRM: nonrotating molecule.

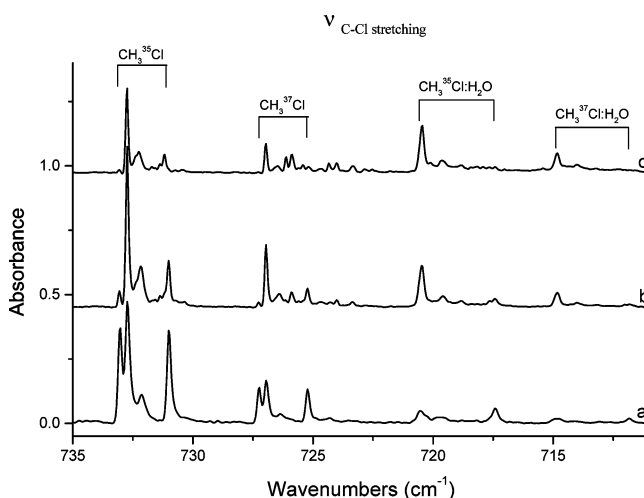


Figure 5. Annealing effects on CH₃Cl:H₂O bands in the C–Cl stretching mode (ν_3 CH₃Cl) region for a sample with CH₃Cl/H₂O/Ne = 5:1:10 000: (a) after deposition at 5 K; (b) after annealing to 11 K; (c) after annealing to 12 K. All spectra are recorded at 5 K.

The transition frequencies attributed to the rotating and nonrotating H₂O are given in Table 2 and compared to data in the literature.

CH₃Cl:H₂O in Ne Matrix. When CH₃Cl and H₂O are co-deposited in a neon matrix, new bands appear in the vibrational regions of both CH₃Cl and H₂O. Bands that grow linearly with the concentrations of both CH₃Cl and H₂O are assigned to the complex CH₃Cl:H₂O. Experiments are carried out at very low concentrations of H₂O and CH₃Cl in neon matrix to limit the aggregation processes. Under these conditions, CH₃Cl:H₂O bands become predominant.

C–Cl Region. The evolution of these new bands as a function of H₂O concentration in the region of the C–Cl stretching is shown in Figure 1, and their evolution upon annealing is shown in Figure 5. Absorption frequencies of the new bands are characterized by set I—720.5, 720.2 (shoulder), 719.6, and 717.4 cm⁻¹—and set II—714.8, 714.6 (shoulder), 714.0, and 711.8 cm⁻¹. The relative intensity of 3:1 between sets I and II indicates that set I belongs to the CH₃³⁵Cl:H₂O isotopomer, while set II belongs to CH₃³⁷Cl:H₂O. The shift between the bands of the two isotopomers is 5.6 cm⁻¹. The four bands for each CH₃Cl:H₂O isotopomer are probably due to the fact that different sites are occupied by the complex in the Ne matrix (similar to what is observed in the case of CH₃Cl monomer). This is confirmed

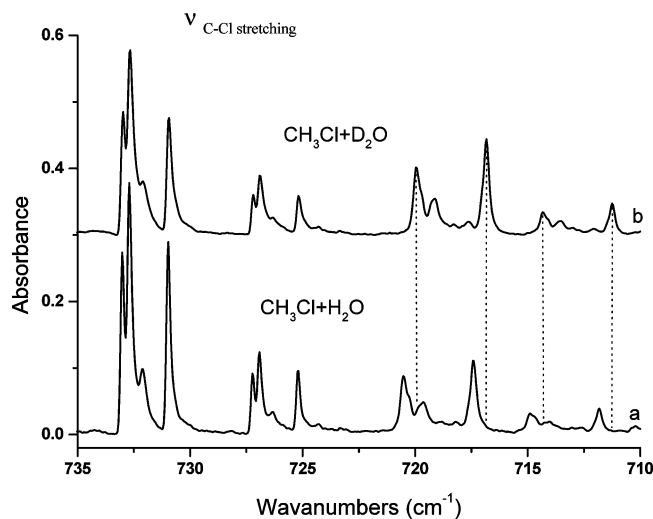


Figure 6. C–Cl stretching (ν_3 CH_3Cl) region of $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ and $\text{CH}_3\text{Cl}:\text{D}_2\text{O}$ after deposition at 5 K: (a) $\text{CH}_3\text{Cl}:\text{H}_2\text{O}:\text{Ne} = 5:5:10\ 000$; (b) $\text{CH}_3\text{Cl}:\text{D}_2\text{O}:\text{Ne} = 5:5:10\ 000$.

by the annealing effects shown in Figure 5. Upon annealing to 11 K, like in the case of CH_3Cl monomer bands, only the two bands at 720.5 and 714.8 cm^{-1} increase considerably (Figure 5b), showing that they correspond to the most stable site of the complex for the two isotopes ($\text{CH}_3^{35}\text{Cl}:\text{H}_2\text{O}$ and $\text{CH}_3^{37}\text{Cl}:\text{H}_2\text{O}$). Finally, $\text{CH}_3^{35}\text{Cl}:(\text{H}_2\text{O})_2$ and $\text{CH}_3^{37}\text{Cl}:(\text{H}_2\text{O})_2$ bands have also been observed at 706.9 and 701.4 cm^{-1} , respectively, but they will not be discussed in this paper ($\text{CH}_3\text{Cl}:(\text{H}_2\text{O})_2$ has been left for future study). All vibrational mode frequencies of CH_3Cl and $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ are listed in Table 1.

H_2O Region. The evolution of the bands of the $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ complex with respect to the concentration of CH_3Cl in the HOH bending (ν_2), O–H symmetric stretching (ν_1), and O–H antisymmetric stretching (ν_3) regions is given in Figures 2, 3, and 4, respectively. The ν_2 , ν_1 , and ν_3 bands of the complex are situated at 1600.5, 3625.9, and 3738.8 cm^{-1} , respectively. The symmetric stretching ν_1 band consists of four peaks at 3625.9, 3624.8, 3623.1, and 3622.1 cm^{-1} . These peaks are probably due to site splitting and are related to the different peaks of $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ in the C–Cl stretching region. Upon annealing between 7 and 11 K, $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ bands increase. They remain constant or slightly decrease at 12 K. All $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ vibrational mode frequencies and shifts ($\nu_{\text{complex}} - \nu_{\text{monomer}}$) are summarized in Table 1.

Finally, the $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ complex has been irradiated by UV–visible or near-infrared light in order to initiate some photochemical processes, but no photochemical reactions were observed.

$\text{CH}_3\text{Cl}:\text{D}_2\text{O}$ and $\text{CH}_3\text{Cl}:\text{HDO}$ in Ne Matrix. C–Cl Region. Infrared spectra for different samples with $\text{CH}_3\text{Cl}:\text{H}_2\text{O}:\text{Ne}$ and $\text{CH}_3\text{Cl}:\text{D}_2\text{O}:\text{Ne}$ in the C–Cl stretching region are shown in Figure 6. As already reported, the bands for the most stable site of the $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ complex are situated at 720.5 cm^{-1} ($\text{CH}_3^{35}\text{Cl}:\text{H}_2\text{O}$) and 714.8 cm^{-1} ($\text{CH}_3^{37}\text{Cl}:\text{H}_2\text{O}$), as shown in Figure 6a. The bands of $\text{CH}_3\text{Cl}:\text{D}_2\text{O}$ have the same structure as the bands of $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ but are slightly red shifted (Figure 6b); thus, the bands of the most stable site of $\text{CH}_3\text{Cl}:\text{D}_2\text{O}$ are located at 719.9 cm^{-1} ($\text{CH}_3^{35}\text{Cl}:\text{D}_2\text{O}$) and 714.3 cm^{-1} ($\text{CH}_3^{37}\text{Cl}:\text{D}_2\text{O}$). In contrast with the C–Cl stretching mode, H/D isotopic substitutions in H_2O monomer have no influence on the vibrational mode frequencies of the complex in the other spectral regions of CH_3Cl . In samples where HDO predominates, vibrational mode frequencies of $\text{CH}_3\text{Cl}:\text{HDO}$, in the area of CH_3Cl , are equal to those measured for $\text{CH}_3\text{Cl}:\text{D}_2\text{O}$.

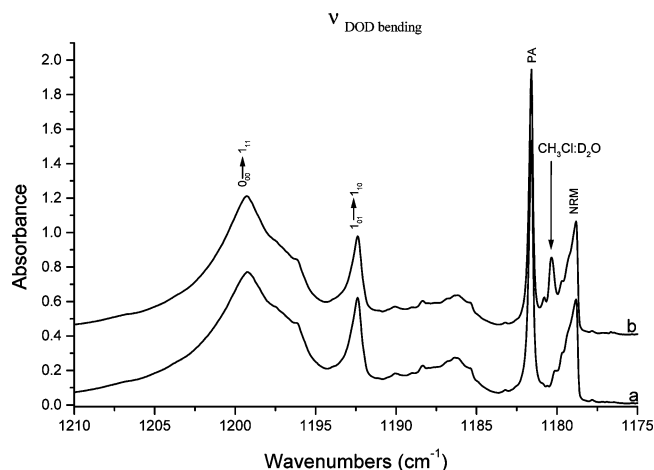


Figure 7. DOD bending (ν_2) region of D_2O and the $\text{CH}_3\text{Cl}:\text{D}_2\text{O}$ complex after deposition at 5 K: (a) $\text{D}_2\text{O}:\text{Ne} = 5:10\ 000$; (b) $\text{CH}_3\text{Cl}:\text{D}_2\text{O}:\text{Ne} = 5:5:10\ 000$.

TABLE 3: Frequencies (cm^{-1}) and Assignments of Absorption Lines of Monomeric D_2O

transition	gas ^{16–18}	solid argon ¹⁰	solid neon (this work)	solid neon ¹⁰
ν_2 Region				
NRM ^a		1174.6	1178.8	1178.7
000 → 111 ortho	1199.793	1196.0	1199.3	1199.3
101 → 212 para	1209.388	1206.0	1206.7	1206.7
ν_1 Region				
NRM ^a		2657.7	2676.7	2672.7
101 → 101 para	2681.894	2667.8	2686.6	2686.6
000 → 111 ortho	2691.606	2677.3	2695.4	2695.8
ν_3 Region				
NRM ^a		2771.1	2785.9	<i>b</i>
000 → 101 ortho	2799.759	2783.0	2801.6	2801.6
101 → 202 para	2811.214	2795.0	2811.6	2811.3

^a NRM: nonrotating molecule. ^b Not observed.

D_2O Region. D_2O spectral regions are similar to those of H_2O . However, they are spectrally more compact due to the smaller rotational constant of D_2O .¹⁰ Figure 7a shows the ν_2 D_2O spectral region. The most intense peaks of rotating D_2O molecules are situated at 1199.3 cm^{-1} ($1_{01} \rightarrow 1_{10}$ states) and 1206.7 cm^{-1} ($0_{00} \rightarrow 1_{11}$). The NRM peak is located at 1178.8 cm^{-1} . Another intense peak at 1181.2 cm^{-1} belongs to the proton acceptor (PA) of $(\text{D}_2\text{O})_2$.¹⁰ A summary of D_2O data and assignments is given in Table 3. When CH_3Cl and D_2O are co-deposited in a neon matrix, a new band due to the complex $\text{CH}_3\text{Cl}:\text{D}_2\text{O}$ appears at 1180.3 cm^{-1} in the ν_2 region (Figure 7). In the ν_1 and ν_3 mode regions, the NRM bands are located at 2676.7 and 2785.9 cm^{-1} , respectively, while bands belonging to the complex $\text{CH}_3\text{Cl}:\text{D}_2\text{O}$ are situated at 2649.8 and 2767.4 cm^{-1} , respectively. These results are summarized in Table 4.

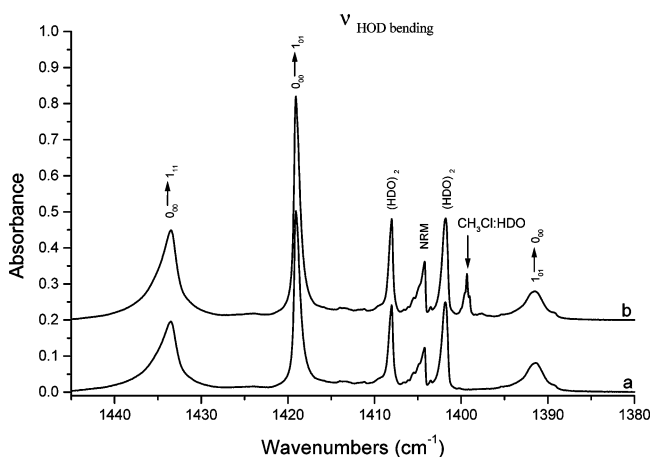
HDO Region. HOD spectral regions are similar to those of H_2O and D_2O . In the HDO molecule, the two O–D and O–H bonds are no longer equivalent. ν_1 corresponds to the O–D stretching mode, and ν_3 corresponds to the O–H stretching mode. The HOD bending mode (ν_2) is situated at 1404.2 cm^{-1} , the O–D stretching mode (ν_1), at 2727.4 cm^{-1} , and the O–H stretching mode (ν_3), at 3706.6 cm^{-1} . Rovibrational transitions have also been assigned and compared to data from the literature (see Table 5). Spectra of the DOH bending region are shown in Figure 8. A band belonging to the complex $\text{CH}_3\text{Cl}:\text{HDO}$ is situated at 1399.7 cm^{-1} . Finally, the O–D and O–H stretching modes of $\text{CH}_3\text{Cl}:\text{HDO}$ are observed at 2681.5 and 3704.8 cm^{-1} , respectively. These results are summarized in Table 4.

TABLE 4: Vibrational Mode Frequencies (in cm⁻¹) of the CH₃Cl:H₂O, CH₃Cl:HDO, and CH₃Cl:D₂O Complexes in a Neon Matrix

mode	CH ₃ Cl	water monomer	complex	shift
H ₂ O				
ν_3 CH ₃ Cl (³⁷ Cl)	726.9		CH ₃ Cl:H ₂ O	-12.1
ν_3 CH ₃ Cl (³⁵ Cl)	732.7			-12.2
ν_2 H ₂ O		1595.6	1600.5	4.9
ν_1 H ₂ O		3665.5	3625.9	-39.6
ν_3 H ₂ O		3761.1	3738.8	-22.3
HDO				
ν_3 CH ₃ Cl (³⁷ Cl)	726.9		CH ₃ Cl:HDO	-12.6
ν_3 CH ₃ Cl (³⁵ Cl)	732.7			-12.8
ν_2 HDO		1404.2	1399.7	-4.5
ν_1 HDO		2727.4	2681.5	-45.9
ν_3 HDO		3706.6	3704.8	-1.8
D ₂ O				
ν_3 CH ₃ Cl (³⁷ Cl)	726.9		CH ₃ Cl:D ₂ O	-12.6
ν_3 CH ₃ Cl (³⁵ Cl)	732.7			-12.8
ν_2 D ₂ O		1178.8	1180.3	1.5
ν_1 D ₂ O		2676.7	2649.8	-26.9
ν_3 D ₂ O		2785.9	2767.4	-18.5

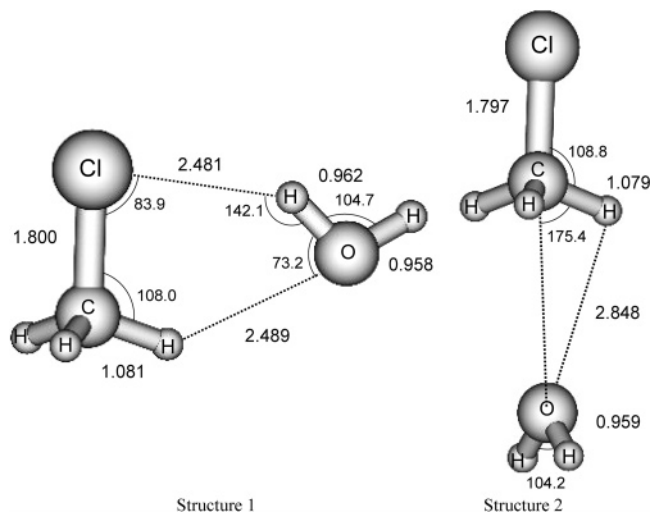
TABLE 5: Frequencies (cm⁻¹) and Assignments of Absorption Lines of Monomeric HDO

transition	gas ^{15,19}	solid argon ¹⁰	solid neon (this work)	solid neon ¹⁰
ν_2 Region				
NRM ^a		1398.8	1404.2	1404.2
000 → 101	1419.041	1414.0	1419.1	1419.0
000 → 111	1435.300	1428.0	1433.5	1433.2
ν_1 Region				
101 → 000	2708.172		2712.6	2712.7
NRM ^a		2710.0	2727.4	2722.9
000 → 101	2738.914	2724.7	2742.2	2742.3
ν_3 Region				
NRM ^a		3687.3	3706.6	3699.0
000 → 111	3736.160	3716.0	3728.7	3728.9
101 → 212	3748.720	-	3739.8	3739.3

^a NRM: nonrotating molecule.**Figure 8.** HOD bending (ν_2) region of HDO and the CH₃Cl:HDO complex after deposition at 5 K: (a) H₂O + HDO/Ne = 5:5:10 000; (b) CH₃Cl/H₂O + HDO/Ne = 5:5:10 000.

Discussion

The wavenumber shifts of the CH₃Cl:H₂O complex from H₂O monomer are measured to be -39.6 and -22.3 cm⁻¹ for OH symmetric and antisymmetric stretching modes, respectively, and +4.9 cm⁻¹ for the HOH bending mode. The OH symmetric and antisymmetric stretching modes are red shifted, with respect to H₂O monomer, by -1.1 and -0.6%, respectively, and the

**Figure 9.** Calculated geometries of the two stable structures of the CH₃Cl:H₂O complex.

HOH bending mode is blue shifted by +0.31%. D₂O and D₂O:CH₃Cl spectral observations give the same trends for OD symmetric (-1%) and antisymmetric stretching (-0.61%) modes, but the DOD bending mode is blue shifted by only +0.13% (less than half in comparison with the HOH bending shift). However, the partially deuterated CH₃Cl:HDO complex exhibits red shifts from HDO monomer, for all HDO vibrational modes. The OD stretching, OH stretching, and HOD bending modes are red shifted by -1.7, -0.05, and -0.32%, respectively.

From CH₃Cl monomer, the complex exhibits blue shifts for all vibrational modes with the exception of the C-Cl stretching mode which is red shifted by -12.2 and -12.8 cm⁻¹ for CH₃³⁵Cl:H₂O and CH₃³⁵Cl:D₂O, respectively. Since the bands of CH₃Cl:D₂O and CH₃Cl:HDO overlap with each other in all CH₃Cl spectral regions, the wavenumber shifts of CH₃Cl:D₂O and CH₃Cl:HDO, with respect to CH₃Cl monomer, are the same.

The C-Cl rocking mode, the C-H symmetric bending mode, and the C-H antisymmetric bending mode are blue shifted by +2.8, +2.5, and +3.7 cm⁻¹, respectively. For the C-H symmetric and antisymmetric stretching modes, larger blue shifts are measured: +4.7 and +7.5 cm⁻¹, respectively. The wavenumber shifts for all of these vibrational modes are not sensitive to the H₂O/D₂O isotopic substitutions.

Theoretical Calculations

All calculations have been performed with the Gaussian 03 quantum chemical package²⁰ using second-order Møller-Plesset perturbation theory (denoted as MP2). For all atoms, the 6-311++G(2d,2p) extended basis set of Pople et al.²¹⁻²³ was used. Theoretical study of the CH₃Cl:H₂O complexes has been previously reported by Kryachko et al.²⁴ using the MP2/6-31+G(d,p) approach. They showed that the global minimum corresponds to a cyclic structure (11.5 kJ/mol) with two hydrogen bonds: the first between the chlorine atom and one of the hydrogens of water and the second between the oxygen atom and one hydrogen of CH₃Cl.

In the present study, the optimization of the 1:1 compound without constraint results in two minima: a first one corresponding to the ground state of the complex characterized by two hydrogen bonds (structure 1) and a second structure as a local minimum with only one hydrogen bridge (structure 2). The most significant geometrical parameters of the studied complexes are displayed in Figure 9, and the corresponding

TABLE 6: Calculated and Experimental Shifts (cm^{-1}) of the Vibrational Frequencies of the Two Stable Structures (kJ/mol) of the $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ Complex (Structures 1 and 2)

		structure 1	structure 2	exptl
D_e^{BSSE}		12.7	6.6	
D_0^{BSSE}		7.3	4.2	
C–Cl stretching	$\nu_3 \text{ CH}_3\text{Cl}$	-14.7	-9.6	-12.2
C–Cl rocking	$\nu_6 \text{ CH}_3\text{Cl}$	2.9	-7.6	2.8
		15.1	-4.6	
C–H symmetric bending	$\nu_2 \text{ CH}_3\text{Cl}$	2.3	-12.8	2.5
C–H antisymmetric bending	$\nu_5 \text{ CH}_3\text{Cl}$	-2.6	-6.1	
		4.1	-3.0	3.7
C–H symmetric stretching	$\nu_1 \text{ CH}_3\text{Cl}$	2.1	12.0	4.7
C–H antisymmetric stretching	$\nu_4 \text{ CH}_3\text{Cl}$	5.7	11.8	7.5 ^a
		9.6	17.4	
O–H bending	$\nu_2 \text{ H}_2\text{O}$	4.1	2.0	4.9
O–H symmetric stretching	$\nu_1 \text{ H}_2\text{O}$	-44.1	-7.8	-39.6
O–H antisymmetric stretching	$\nu_3 \text{ H}_2\text{O}$	-28.1	-8.7	-22.3

^a 7.5 cm^{-1} has to be compared to either 5.7 or 9.6 cm^{-1} .

binding energies (corrected for the basis set error, D_e^{BSSE} , and for the zero-point energy, D_0^{BSSE}) are given in Table 6. The binding energy of structure 1 is found to be 12.7 kJ/mol (very close to that reported by Kryachko et al.²⁴), while that of structure 2 is 6.6 kJ/mol. The difference between the stability of the two structures could be due to the fact that, in structure 2, only O and H (CH_3Cl) interact, while, in structure 1, there is also an interaction between chlorine and a hydrogen atom of water.

The harmonic frequency shifts calculated with the MP2 method for the two optimized geometries (structures 1 and 2) of the $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ complex and the experimental shifts in neon matrix are listed in Table 6. The calculated vibrational wavenumber shifts for structure 1 are found to reproduce the observed wavenumber shifts more satisfactorily than those for structure 2. The calculated shifts for H_2O in structure 1 are -44.1, +4.1, and -28.1 cm^{-1} for the ν_1 , ν_2 , and ν_3 modes, respectively, and those for H_2O in structure 2 are -7.8, +2.0, and -8.7 cm^{-1} . The measured shifts for the ν_1 , ν_2 , and ν_3 modes, respectively, are close to those calculated for structure 1: -39.5, +4.9, and -22.3 cm^{-1} . The same observation can be made for the wavenumber shifts of the $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ complex from CH_3Cl monomer, calculated for structure 1, which agree essentially with the observed values. These results suggest that the $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ complex isolated in neon matrix corresponds to structure 1. Structure 2 has not been observed experimentally even after annealing the matrix or photoexciting the sample.

Since it can be assumed that the complex has structure 1 and belongs to the C_1 -symmetry group, the modes of symmetry E (in free CH_3Cl) are not degenerate anymore and two different frequencies are calculated for the C–Cl rocking, C–H antisymmetric bending, and C–H antisymmetric stretching modes. However, only one frequency was experimentally observed for each mode in the complex. Nevertheless, the absorption bands of CH_3Cl trapped in neon matrix corresponding to these modes are broad and could hide the other absorption bands of the complex.

Finally, we note that the experimental frequency shifts for the C–Cl rocking (+2.8 cm^{-1}), C–H symmetric (+2.5 cm^{-1}), and C–H antisymmetric (+3.7) bending modes are well reproduced by MP2 calculations for structure 1 (C–Cl rocking, +2.9 cm^{-1} ; C–H symmetric bending, +2.3 cm^{-1} ; C–H antisymmetric bending, +4.1 cm^{-1}).

The cyclic structure of the 1:1 complex is confirmed in turn by the experimental observations in the C–H and O–H spectral

TABLE 7: Calculated and Experimental Shifts (cm^{-1}) of the Vibrational Frequencies of the Most Stable Structure (kJ/mol) of the $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ Complex (Structure 1)^a

	structure 1	experimental
$\text{CH}_3\text{Cl}:\text{HOH}$		
D_0^{BSSE}	7.3	
ν_2 (OH bending)	4.1	4.9
ν_1 (symmetric OH stretching)	-44.1	-39.6
ν_3 (antisymmetric OH stretching)	-28.1	-22.3
$\text{CH}_3\text{Cl}:\text{HOD}$		
D_0^{BSSE}	7.6	
ν_2 (HOD bending)	15.5	-
ν_1 (OD stretching)	-0.8	-
ν_3 (OH stretching)	-70.7	-
$\text{CH}_3\text{Cl}:\text{DOH}$		
D_0^{BSSE}	8.0	
ν_2 (HOD bending)	-7.6	-4.5
ν_1 (OD stretching)	-50.9	-45.9
ν_3 (OH stretching)	-1.4	-1.8
$\text{CH}_3\text{Cl}:\text{DOD}$		
D_0^{BSSE}	8.3	
ν_2 (DOD bending)	1.3	1.5
ν_1 (symmetric OD stretching)	-29.1	-26.9
ν_3 (antisymmetric OD stretching)	-22.5	-18.5

^a H/D water isotopic substitution.

regions. The observed wavenumber shifts imply an intermolecular hydrogen bonding between CH_3Cl and H_2O . O–H modes are red shifted which suggests an intermolecular hydrogen bonding between the H atom of H_2O and the Cl atom of CH_3Cl . C–H modes are blue shifted which suggests an intermolecular hydrogen bonding between the H atom of CH_3Cl and the O atom of H_2O .²⁴

Vibrational wavenumbers for the four isotopic complexes $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$, $\text{CH}_3\text{Cl}:\text{HOD}$, $\text{CH}_3\text{Cl}:\text{DOH}$, and $\text{CH}_3\text{Cl}:\text{D}_2\text{O}$ were calculated for structure 1. The wavenumber shifts are compared with the observed values in Table 7. The calculated shifts agree with the observed values in the case of $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ and $\text{CH}_3\text{Cl}:\text{D}_2\text{O}$. However, for the partially deuterated complex, the calculated wavenumbers reproduce the observed wavenumbers only for the $\text{CH}_3\text{Cl}:\text{DOH}$ species, a complex with an intermolecular D bonding. Experimentally, the HOD bending mode in the complex is found to be red shifted by -4.5 cm^{-1} which agrees with $\text{CH}_3\text{Cl}:\text{DOH}$ (calculated shift -7.6 cm^{-1}) rather than with $\text{CH}_3\text{Cl}:\text{HOD}$ (calculated shift +15.5 cm^{-1}). No infrared bands of $\text{CH}_3\text{Cl}:\text{HOD}$ (complex with an intermolecular H bonding) were observed in our spectra. The absence of any signal from the $\text{CH}_3\text{Cl}:\text{HOD}$ complex in our spectra could be explained by the fact that the dissociation energy of $\text{CH}_3\text{Cl}:\text{DOH}$ is larger than that of $\text{CH}_3\text{Cl}:\text{HOD}$, since the zero-point vibrational energy of the species with D-atom bonding is lower (by 0.4 kJ/mol = 35 cm^{-1}) than that of the H-atom one. According to the Boltzmann distribution law, the population ratio at 5 K for this energy difference is found to be $[\text{CH}_3\text{Cl}:\text{HOD}]/[\text{CH}_3\text{Cl}:\text{DOH}] = 0.000\ 05$. This phenomenon was already observed by Nakata et al.²⁵ who reported the structure of $\text{CH}_3\text{F}:\text{H}_2\text{O}$ which is similar to structure 1 for $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$. The energy of dimerization of $\text{CH}_3\text{F}:\text{H}_2\text{O}$ was found to be 13.6 kJ/mol. Indeed, in the partially deuterated complexes $\text{CH}_3\text{F}:\text{DOH}$ and $\text{CH}_3\text{F}:\text{HOD}$, Nakata et al.²⁵ detected only the $\text{CH}_3\text{F}:\text{DOH}$ complex and no bands of $\text{CH}_3\text{F}:\text{HOD}$ were observed. This is also a consequence of the preference for HDO to form $\text{HO}\cdots\text{D}\cdots\text{A}$ (A: electronegative element) deuterium bonds rather than the $\text{DO}\cdots\text{H}\cdots\text{A}$ bonds already discussed in the literature.^{26–27}

Finally, we would like to compare the H bonding properties between two complexes: $\text{CH}_3\text{Cl}:\text{H}_2\text{O}$ and $\text{H}_2\text{O}:\text{H}_2\text{O}$ both

contain a water molecule. The H₂O molecule in CH₃Cl:H₂O is both the proton acceptor (PA, O interacting with H of CH₃Cl) and donor (PD, H interacting with Cl). These intermolecular hydrogen bonds could be compared to those of (H₂O)₂, where one water molecule is the PA and the other is the PD. The behavior of the H₂O molecule in CH₃Cl:H₂O is expected to range between the PA and PD of (H₂O)₂. The OH symmetric mode is red shifted, with respect to H₂O monomer, by -1.1 and -2.1% for CH₃Cl:H₂O and PD (H₂O)₂, respectively. The OH stretching mode detected at 3625.9 cm⁻¹ for CH₃Cl:H₂O is closer to the proton acceptor (PA, 3660.6 cm⁻¹ of (H₂O)₂) than to the proton donor (PD, 3590.5 cm⁻¹ of (H₂O)₂).¹⁴ The OH antisymmetric stretching detected at 3738.8 cm⁻¹ for CH₃Cl:H₂O is closer to the proton donor (PD, 3733.7 cm⁻¹ of (H₂O)₂) than to the proton acceptor (PA, 3750.0 cm⁻¹ of (H₂O)₂). Finally, the OH bending mode detected at 1600.5 cm⁻¹ for CH₃Cl:H₂O is closer to the proton acceptor (PA, 1599.2 cm⁻¹ of (H₂O)₂) than to the proton donor (PD, 1616.4 cm⁻¹ of (H₂O)₂). However, by comparing the wavenumber shifts, this "double" intermolecular hydrogen bonding is weaker than that observed in (H₂O)₂.

Conclusion

Formation and structure of the CH₃Cl:H₂O weakly bonded complex has been investigated by the neon matrix isolation technique combined with infrared absorption spectroscopy. Detailed vibrational assignments were made on the observed spectra of water and deuterated water engaged in the CH₃Cl:H₂O complex. With the use of MP2 calculations, the geometrical and vibrational properties of the complex have been estimated. The complex was found to have a cyclic structure, where the chlorine atom is weakly bonded to one of the hydrogen atoms of water, while the oxygen atom is weakly bonded to one of the hydrogen atoms of CH₃Cl. The binding energy of CH₃Cl:H₂O is 12.7 kJ/mol. The calculated and observed wavenumbers of the partially deuterated complex established that only the CH₃Cl:DOH species was formed with hydrogen bonding to D. No bands of CH₃Cl:HOD (complex with H bonding) were observed.

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