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NOTES

Infrared spectra of isotopic (HCl)₃ clusters in solid neon

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Binary and ternary complexes are currently receiving wide attention in matrix-isolation and nozzle-beam experiments.¹⁻¹⁷ One of the intriguing questions is structure for these complexes, and in particular the possibility of a cyclic structure for ternary complexes.^{7,8,12-14,17} The identification and vibrational assignments for (HF)₃ have finally settled on a cyclic structure.⁹⁻¹⁴ Trimers of CO₂ and C₂H₂ are characterized by cyclic structures.^{7,8} The analogous (HCl)₃ species has only been studied to date in matrices,¹⁵⁻¹⁸ and the cyclic structure has been convincingly demonstrated by stepwise deuterium substitution and vibrational analysis.¹⁷ In the course of neon matrix studies with HCl, we have observed the (HCl)₃ species¹⁸ with sufficiently sharp bandwidths to resolve natural chlorine isotopic splittings, which provide an independent confirmation of the stoichiometry of

the (HCl)_x(DCl)_y trimer species and a guide for future gas phase studies.

The cryogenic apparatus and gas handling systems have been described earlier.^{3,18} Briefly, Ne/HCl and stepwise deuterated samples were condensed at 5 K using rates of 1-2 mmol/h for 1-2 h and FTIR spectra were recorded on a Nicolet 7199 system with 0.24 cm⁻¹ resolution giving a frequency accuracy of ± 0.1 cm⁻¹ for these sharp bands.

Figure 1 illustrates composite high resolution spectra in the H-Cl and D-Cl stretching regions for a Ne/(HCl + DCl) = 100/1 mixture with 70% DCl enrichment. Not shown are the *R*(0) bands of HCl and DCl at 2899.6 and 2097.8 cm⁻¹, respectively, (HCl)₂ at 2839.7 cm⁻¹, and tetramer at 2765 and 2002 cm⁻¹; the latter are unfortunately too broad to resolve chlorine isotopic splittings. The first

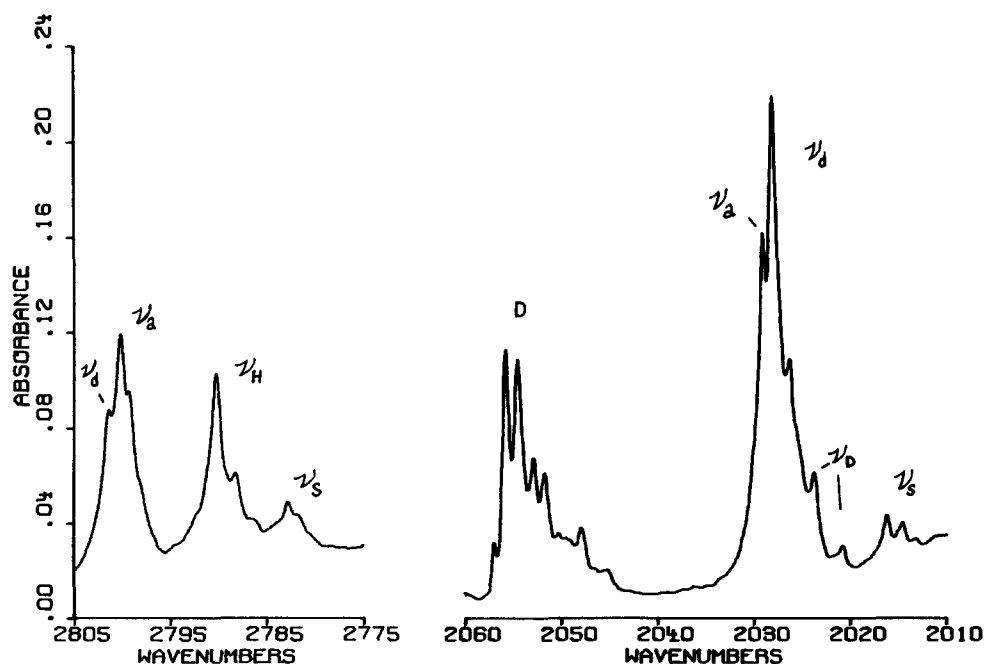


FIG. 1. Infrared spectra in the 2805-2775 and 2060-2010 cm⁻¹ regions for 2 mmol of Ne/(HCl + DCl) = 100/1 sample (70% DCl) deposited at 5 K for 1 h.

band at 2801.5 cm^{-1} (labeled ν_d following Ref. 17) is the major product band in the Ne/HCl studies, where it is sharp (full-width at half-maximum = 0.9 cm^{-1}) and it exhibits shoulders at 2800.2 and 2799.4 cm^{-1} with one-third and one-ninth of the intensity of the main band. The second band (labeled ν_a for antisymmetric stretch) is split into a 9:6:1 relative intensity chlorine isotopic triplet at 2800.2 , 2799.2 , and 2798.0 cm^{-1} , showing the involvement of two equivalent chlorine atoms. The third band (labeled ν_H) is split into a 3:1 relative intensity chlorine isotopic doublet at 2790.3 and 2788.2 cm^{-1} for a motion of one chlorine atom, and the fourth band (labeled ν_s for symmetric stretch) is split into a 9:6:1 chlorine isotopic triplet at 2782.7 , 2781.7 , and 2780.4 cm^{-1} , again involving two equivalent chlorine atoms. The isotopic absorptions are listed in Table I.

The overlapping pair of 3:1 doublet bands (labeled D) at 2055.9 , 2052.9 and 2054.6 , 2051.8 cm^{-1} are due to the dimers $(\text{HCl})(\text{DCl})$ and $(\text{DCl})_2$ where the vibration is due to the bonded submolecule.^{17,18} The final absorptions include a sharp ν_a band at 2029.0 cm^{-1} , ν_d bands at 2028.1 and 2026.3 cm^{-1} , a ν_D doublet at 2023.7 and 2020.7 cm^{-1} , and a ν_s triplet at 2016.1 , 2014.6 , and 2013.1 cm^{-1} .

The present neon matrix bands support the argon matrix observations and characterization of $(\text{HCl})_3$ as a C_{3h} cyclic species based on the vibrational analysis.¹⁷ Table I also includes (in parentheses) the argon matrix bands for the H^{35}Cl and D^{35}Cl trimer species; the former are $14.7 \pm 0.2\text{ cm}^{-1}$ below and the latter are $10.6 \pm 0.1\text{ cm}^{-1}$ below the neon matrix values.

The chlorine isotopic splittings and intensities confirm the stoichiometries of the two mixed $(\text{HCl})_x(\text{DCl})_y$ trimer species. First, for a H–Cl stretching mode at 2800.0 cm^{-1} , the calculated ^{35}Cl – ^{37}Cl shift for a harmonic oscillator is 2.1 cm^{-1} , and for a D–Cl stretching mode at 2028.0 cm^{-1} , the

calculated ^{35}Cl – ^{37}Cl shift is 3.0 cm^{-1} . The asymmetric cyclic $(\text{HCl})_3$ species involving head-to-tail hydrogen bonding has C_{3h} symmetry. The antisymmetric H–Cl fundamental of three equivalent H^{35}Cl species at 2801.5 cm^{-1} is doubly degenerate. The vibrational pattern for natural chlorine isotopes has been analyzed for BCl_3 and found to be a 9:1:3:1 quartet.^{19,20} In solid neon we observe the two stronger bands separated by 1.3 cm^{-1} , and a weak shoulder separated by 0.8 cm^{-1} for $(\text{H}^{37}\text{Cl})_3$. The ν_a and ν_s bands are the antisymmetric and symmetric stretching fundamentals for two H–Cl submolecules in *equivalent bonding positions* in the cyclic $(\text{HCl})_2(\text{DCl})$ species. As such each mode exhibits a 9:6:1 chlorine isotopic triplet for two equivalent chlorine atoms with the full chlorine isotopic shift (observed 2.2 cm^{-1} , calculated 2.1 cm^{-1}). The ν_H band is the H–Cl stretching fundamental in the $(\text{HCl})(\text{DCl})_2$ species, which is not coupled with DCl submolecules. As such it is intermediate between the ν_a and ν_s modes for $(\text{HCl})_2(\text{DCl})$ and it exhibits a 3:1 doublet for one chlorine with the full chlorine isotopic shift (observed 2.1 cm^{-1}). Analogous behavior is found for the corresponding D–Cl vibrations in the trimer species. One difference is the increased ^{35}Cl – ^{37}Cl shift for chlorine vibrating with deuterium. Another difference is appearance of the ν_D band for $(\text{HCl})_2(\text{DCl})$ 1.1 cm^{-1} above the median of ν_a and ν_s , whereas the ν_H band is 1.2 cm^{-1} below the median of ν_a and ν_s ; this points to a slightly different vibrational potential function for HCl and DCl in hydrogen and deuterium bonding roles.

Accordingly, the chlorine isotopic splittings definitively identify three stretching modes for $(\text{HCl})_2(\text{DCl})$ and three for $(\text{HCl})(\text{DCl})_2$, involving two HCl and two DCl submolecules, respectively, in *equivalent hydrogen bonding positions*, which requires the asymmetric cyclic C_{3h} structure.

Finally, the neon (2801 cm^{-1}) and argon (2787 cm^{-1}) matrix values for $(\text{HCl})_3$ allow a $2816 \pm 3\text{ cm}^{-1}$ prediction for the gaseous species based on a similar relationship for $(\text{HF})_3$ in the gas phase (3709 cm^{-1}), in solid neon (3706 cm^{-1}) and in solid argon (3702 cm^{-1}).^{10,11,13}

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TABLE I. Isotopic fundamentals (cm^{-1}) for hydrogen chloride trimer clusters in solid neon.

Assign ^a	$(\text{HCl})_3$	$(\text{HCl})_2(\text{DCl})$	$(\text{HCl})(\text{DCl})_2$	$(\text{DCl})_3$
ν_d, ν_a, ν_H	(2787.0) ^b 2801.5 ^c 2800.2 2799.4	(2785.5) 2800.2 2799.2 2798.0	(2775.5) 2790.3 2788.2	
ν_s, ν_a, ν_d		(2767.8) 2782.7 2781.7 2780.4	(2018.5) 2029.0 d 2026.3	(2017.5) 2028.1
ν_D, ν_s		(2013.0) 2023.7 2020.7	(2005.5) 2016.1 2014.6 2013.1	

^a Assignment symbols from Ref. 17; ν_d is degenerate mode of $(\text{HCl})_3$ and $(\text{DCl})_3$, ν_a and ν_s are antisymmetric and symmetric stretching modes of $(\text{HCl})_2$ and $(\text{DCl})_2$ subgroups in mixed trimers, and ν_H and ν_D are stretching modes of HCl and DCl submolecules, respectively, in mixed trimers.

^b Argon matrix ^{35}Cl values in parentheses from Ref. 17 for comparison.

^c From Ne/HCl experiments.

^d Splittings obscured by stronger $(\text{DCl})_3$ band.

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Type I isotherms for N₂ adsorption on vapor deposited amorphous solid water

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Vapor deposited amorphous solid water, H₂O(as), is being discussed as a major component of comets, of satellites of the outer planets, and of interstellar dust.¹⁻¹⁰ Its adsorption behavior is one of the properties important for discussions of astrophysical implications, and apparent surface areas of between ~ 12 and ~ 420 m² g⁻¹ have been reported.¹¹⁻¹⁵ We had recently investigated adsorption of N₂ on H₂O(as) and had observed that H₂O(as) when prepared carefully at ~ 77 K contains a large fraction of micropores (i.e., pores of < 2.0 nm diameter), the evidence being composite isotherms of type II which contained contributions from both micropores (type I) and external surface (type II).¹⁴ This was subsequently confirmed by Schmitt *et al.*¹⁵ In this Note we report pure type I isotherms for N₂ adsorption of H₂O(as) which was prepared under "optimized" conditions, and on their dependence on experimental details of H₂O(as) preparation. The advantages over the former work^{14,15} are that we do not need assumptions for determining micropore volumes such as the selection of a proper "standard" isotherm,^{16,17} and that we obtain a better understanding of the factors controlling formation of micropores, respectively, external surface.

H₂O(as) was prepared as described before¹⁴ in a sublimation apparatus made of glass, with H₂O vapor entering through a fine metering valve and nozzle of 4 mm diameter at the bottom of the apparatus. For H₂O(as) formation only the cold finger was cooled to 77 K, so that the flat bottom part with 10 cm² area acted as a cryoplate. For isotherm measurements, the whole apparatus was immersed in liquid N₂ and adsorption and desorption were measured *in situ*. It is important to add gaseous N₂ (99.9995%) very slowly at each adsorption step to avoid local heating and annealing of the sample.

Figure 1(A) shows N₂ adsorption isotherms on three different H₂O(as) samples prepared by varying only the distance between nozzle and cryoplate from 3.6 cm (curve 1) to 6.5 cm (curve 2) and 8.2 cm (curve 3). Curves 1 and 2 are type I isotherms (i.e., concave to p/p^0 axis with a horizontal plateau).^{16,17} For this type of isotherm the uptake n_{ads} at a point close to saturation is a measure of the micropore volume^{16,17} and is indicated by broken lines; from these values micropore volumes of 0.13 and 0.18 cm³ g⁻¹ are obtained for curves 1 and 2, using 0.808 g cm⁻³ as the density of liquid

N₂ at 77 K. Curve 3 is similar to the isotherms described previously¹⁴ and is a composite isotherm of type II containing contributions from micropores and external surface. We surmise that the additional contribution from external surface in curve 3 is due to increasing deposition of water vapor in the upper, warmer part of the cold finger at $T > 77$ K with increasing nozzle-cryoplate distance.

Figure 1(B) shows N₂ adsorption isotherms on two different H₂O(as) samples prepared by varying only the water vapor deposition time from 1 h (curve 4) to 6 h (curve 5).

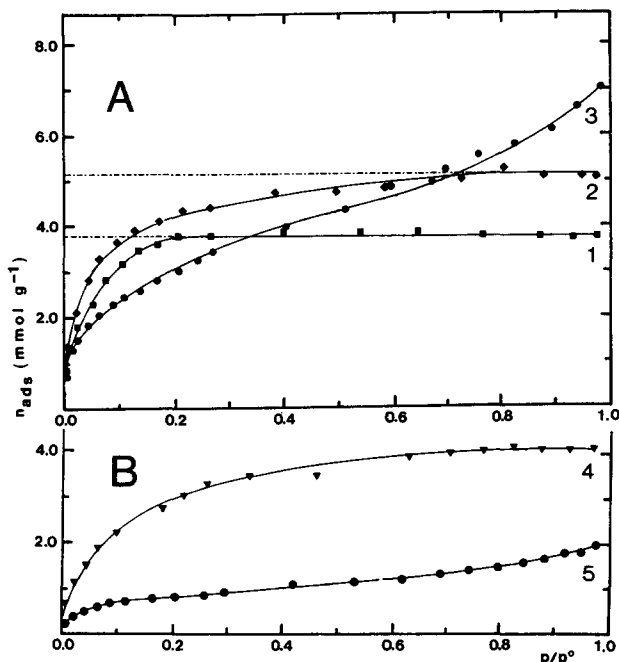


FIG. 1. N₂ adsorption isotherms (static volumetric at 77 K) on several samples of H₂O (as) prepared by vapor deposition, (A) varying thereby nozzle-cryoplate distance from 3.6 cm (for curve 1) to 6.5 cm (curve 2) and 8.2 cm (curve 3), and (B) varying deposition time from 1 h (curve 4) to 6 h (curve 5). For all H₂O (as) preparations the cryoplate was held at 77 K and H₂O vapor pressure before the nozzle was 0.030 mbar. Sample mass for curves 1 to 4 (1 h deposition time) was between 0.19 and 0.27 g, for curve 5 (6 h) 1.12 g, corresponding to deposition rates of between ~ 58 and ~ 75 nm s⁻¹. BET values [with $a_m(\text{N}_2) = 1.6$ nm²] for apparent surface areas and c values are 321/43 for curve 1, 356/70 for curve 2, 252/41 for curve 3, 258/28 for curve 4, and 55/47 for curve 5. For further experimental details see Ref. 14.