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A cryospectroscopic study of the oligomers of deuterium chloride in liquid argon, liquid krypton and in liquid nitrogen

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Abstract

The infrared spectra of HCl and DCl dissolved in liquid argon (94–148 K) in liquid krypton (117–167 K) and in liquid nitrogen (94–148 K) with mole fractions varying between 0.5×10^{-4} and 2.5×10^{-3} are discussed. In all solutions, bands proving the existence of oligomeric species $(DCl)_x$ were observed. Analysis of the spectra shows that these bands must be assigned to dimeric, trimeric and tetrameric species. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vibrational specroscopy; Van der Waals molecules; Cryosolutions; HCl; DCl

1. Introduction

The behavior of hydrogen chloride as a dilute species in an environment of inert noble gas atoms has been the subject of vibrational spectroscopic research for many years [1–11]. Depending on the phase of the environment, different aspects of this behavior were investigated. In 1992, Van der Veken and De Munck [12] reported a systematic study of HCl dissolved in liquid argon (LAr), in liquid krypton (LKr), and in liquid xenon (LXe). At sufficiently low concentrations, only the spectrum due to monomeric species was observed in each solvent. At higher concentrations in LAr and in LKr, however, new bands proving the existence due to a variety of oligomeric species $(HCl)_x$ were observed on the low frequency side of the monomer band. By comparing the spectra recorded at several concentrations, the authors were able to separate the contributions due to monomer and oligomeric species. Concentration studies in which the spectra of the oligomeric species were fitted using Gauss–Lorentz sum functions, allowed the assignment of the observed complex bands to a dimer, a trimer and a tetramer, while an analysis of the temperature dependence of the oligomeric band areas yielded the enthalpy of complexation, the values in LAr being −4.2(3), −13.5(19) and −20.1(32) kJ mol^{-1}, respectively [12,13].

In a continuing series of concerted experimental and ab initio studies of Van der Waals complexes formed between HCl and a variety of Lewis bases, we have investigated the formation of weakly bound complexes in solution, using LAr, LKr and liquid nitrogen (LN$_2$) as solvents. The solutions have the advantage over molecular beams and solid matrices of being in thermodynamic equilibrium, so that information on the stability of the complexes can easily be obtained. In those cases where the bands of the Lewis bases strongly overlap with the HCl monomer band, we have also investigated the spectra of solutions

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containing the appropriate Lewis base and DCl [14,15]. In addition to the bands assigned to the complexes under study, in some of the spectra weak features were observed which could not be assigned to the complexes with the Lewis bases under study. In agreement with the reported behavior of HCl solutions [12] for the solutions containing only HCl, these bands were tentatively assigned to DCl dimer and trimer species. To our knowledge, however, no detailed description of the behavior of monomer DCl dissolved in liquid noble gases has yet been reported. Therefore, we have undertaken a systematic study of solutions of DCl dissolved in LAr, in LKr, and in LN_2. In addition, for reasons of comparison, some spectra of HCl in the different solvents were re-investigated. The results of this study are presented below and it will be shown that oligomer spectra were obtained that are very similar to those of the HCl oligomers.

2. Experimental

The spectra were recorded on a Bruker IFS 66v Fourier Transform spectrometer, equipped with a Globar source, a Ge/KBr beamsplitter and a broadband MCT detector. For all spectra, 200 scans recorded at $0.5\ \mathrm{cm}^{-1}$ resolution were averaged, Happ–Genzel apodized and Fourier transformed using a zero filling factor of 4.

The experimental setup consists of a pressure manifold needed for filling and evacuating the cell and for monitoring the amount of gas used in a particular experiment, and the actual cell. The cell, with a path length of 70 mm, is equipped with slightly wedged, 5 mm thick Si windows, using a high pressure window seal [16].

The samples of HCl and DCl were synthesized in small amounts by hydrolyzing PCl_3 with H_2O and D_2O, respectively, and were purified by pumping the reaction mixture through a 180 K slush, followed by fractionation. The solvent gases Ar, N_2, and Kr, were supplied by l'Air Liquide and had stated purities of 99.9999, 99.9999, and 99.998%, respectively.

3. Results and discussion

Even after repeated deuteration of the experimental setup with D_2O vapor, bands, with non-negligible relative intensities, that are due to monomeric and oligomeric HCl species persisted in the spectra. Taking into account the lower infrared intensity of DCl compared to HCl [17], this signals loss of a small fraction of deuterium on the walls of the filling manifold and the cell during the preparation of the solutions. In the DCl solutions, therefore, also mixed complexes $(DCl)_x(HCl)_y$ must have been present, and it is useful to realize that the DCl stretching region must contain contributions due these mixed species (Fig. 1).

Previously, the bands due to HCl oligomers were isolated by subtracting out the monomeric HCl contribution, using spectra recorded at higher dilution [12]. The same procedure was applied in this study, both for the νHCl region of solutions containing HCl, and for the νDCl region of solutions containing DCl. As an example the results obtained at 104 K are given in Fig. 2A for the νHCl region, and in Fig. 2B for the νDCl region. In all attempts a dip in the baseline of the oligomer spectrum occurs near the maximum of the monomer band. Its persistence making it unlikely that the dip is due to small temperature differences between the spectrum of the more concentrated and the more dilute solution, it is believed that it must be due to an as yet not understood influence of the concentration of the monomer contour.

The quality of the subtracted spectra in the neighborhood of the oligomer bands is such that a least squares band fitting, using Gauss–Lorentz sum bands, could be used to isolate the different components of the multiplets. Such an analysis for the νHCl region has been made before [12], and was repeated here. Band fitting was also applied to the νDCl region. Results of such fittings are shown in Fig. 3 for the spectra recorded at 104 K. The frequencies of the component bands are given in Table 1, together with the corresponding band widths, expressed as Full Width at Half Height (FWHH).

Apart from minor differences in band positions and relative intensities, which are due to the difference in temperature and concentration, respectively, between the two studies, the present results for νHCl neatly reproduce previous ones [12]. In the latter study, a problem was encountered with the assignments for the dimer. For this species only two HCl stretches are expected, while the concentration study [12] showed that not only the more intense $2828\ \mathrm{cm}^{-1}$

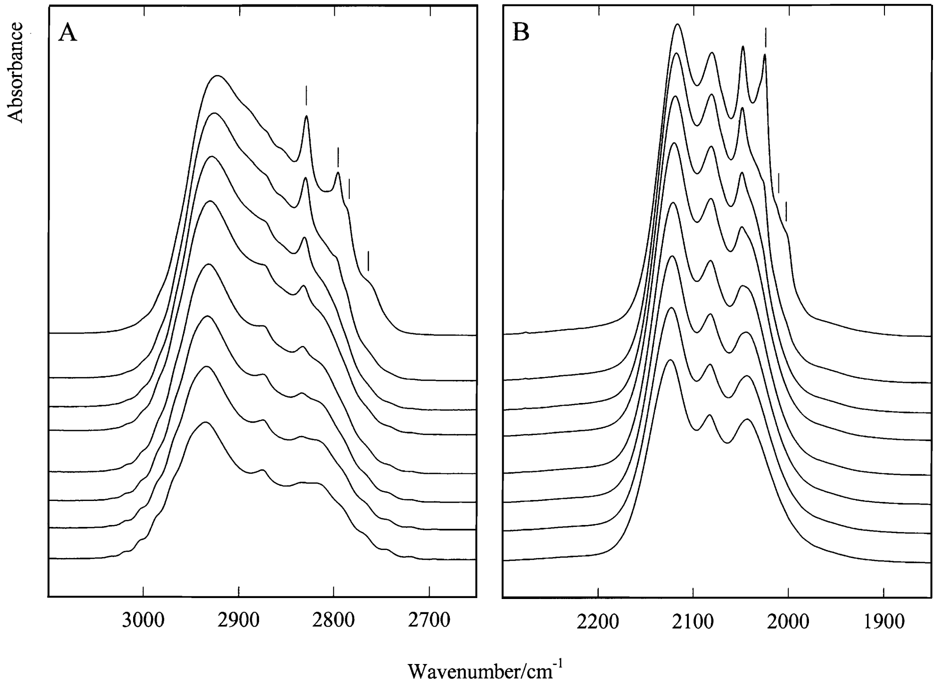

Fig. 1. The νHCl (A) and νDCl (B) regions for solutions of HCl (A, mole fraction = 1.0×10^{-3}) and DCl (B, mole fraction = 1.3×10^{-3}) in liquid argon. From top to bottom, the temperature of the solutions increases, from 101 to 149 K.

band but also the weaker components at 2854 and 2846 cm^{-1} had to be assigned to the dimer. Further research on HCl complexes has shown that the νHCl mode tails towards higher frequencies, which was interpreted to be due to the presence of excited state transitions [13]. The thermally excited states involved are the low frequency van der Waals modes and, therefore, their influence is felt only for the stretching mode of HCl molecules of which the H atom is part of the hydrogen bond. Evidently then, the weak, broad 2846 cm^{-1} band represents such thermal structure on the 2828 cm^{-1} fundamental, while the 2854 cm^{-1} band must be assigned to the free H–Cl bond of the L-shaped dimer. From Table 1 can be seen that the largest difference, 4.8 cm^{-1}, between present and previous [12] HCl oligomer band positions is found for the thermal structure band of the dimer, found here at 2841.2 cm^{-1}. The reason is that the temperature shifts of the fundamentals is mostly due to the changes in solvent density with temperature, whereas for the thermal structure band it is supplementary influenced by the (temperature-dependant) relative populations of the excited states.

Similarly, the 2797 cm^{-1} trimer band and the 2763 cm^{-1} tetramer band should tail towards higher frequencies. Due to the presence of other fundamentals of these oligomers at 2806 and 2774 cm^{-1}, respectively, no separate bands representing the thermal structure of the 2797 and 2763 cm^{-1} bands were detected in the least squares procedure. It is believed, however, that the high widths of the 2806 and 2774 cm^{-1} bands reflect the presence of some intensity due to the excited states.

Despite differences in relative intensities and relative widths, the analogy in the number of bands, and in their relative positions, of the νDCl and νHCl regions is striking. This strongly suggests that the bands in the νDCl region must be assigned in the same way as those of the νHCl region. These assignments have been included in Table 1. Inspection of the FWHH in Table 1 shows that the νDCl bands are systematically narrower than the corresponding νHCl bands.

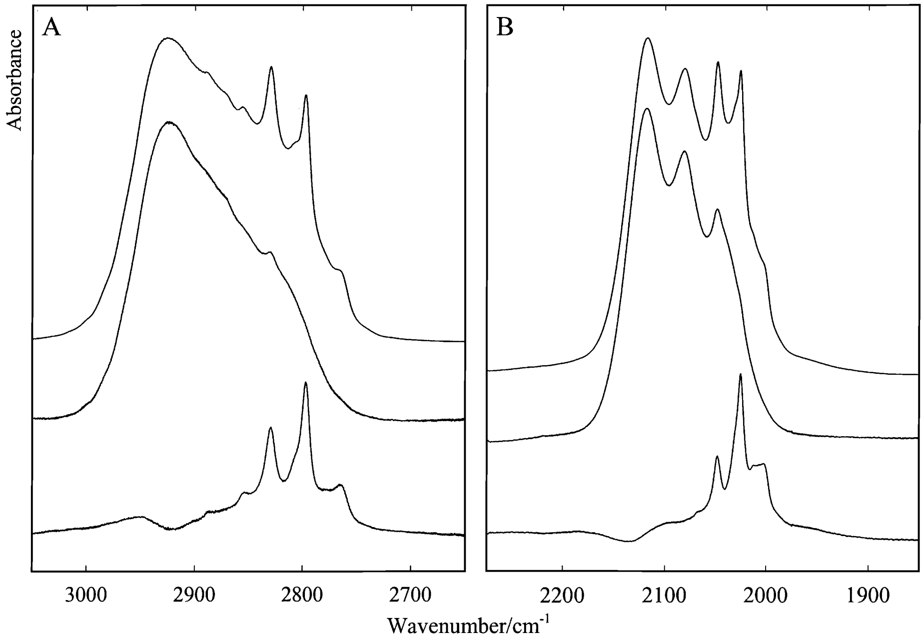

Fig. 2. The νHCl (A) and νDCl (B) regions of solutions of HCl (A) and DCl (B) in liquid argon at 104 K. In both panels the top trace was recorded from a concentrated solution (mole fraction = 1.3×10^{-3}), whereas the middle trace gives the (rescaled) spectrum recorded from a dilute solution (mole fraction = 2.0×10^{-4}). The lower trace in A and B was obtained by subtracting the middle from the top trace.

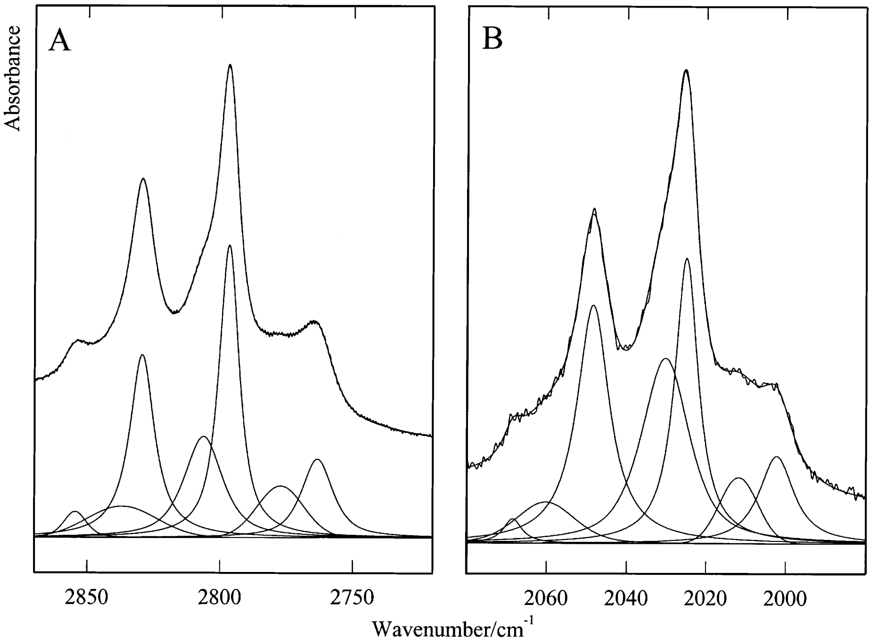

Fig. 3. Results of the least squares band fitting of the oligomer bands of HCl (A) and DCl (B). In each panel the top curves are the superposition of the experimental with the calculated spectrum, while the component bands are shown below.

Table 1
Vibrational frequencies for the oligomer species $(HCl)_x$ and $(DCl)_x$ observed in liquid argon, at 104 K

	$(HCl)_x$		$(DCl)_x$	
	ν (cm^{-1})	FWHH (cm^{-1})	ν (cm^{-1})	FWHH (cm^{-1})
$(H/D–Cl)_2$	2854.7	10.1	2068.5	4.8
$(H/D–Cl)_2$[a]	2841.2	25.5	2060.5	17.9
$(H/D–Cl)_2$	2829.5	11.6	2048.5	9.7
$(H/D–Cl)_3$	2805.9	18.7	2030.3	14.5
$(H/D–Cl)_3$	2796.8	8.5	2025.1	7.0
$(H/D–Cl)_4$	2774.4	30.0	2011.7	11.6
$(H/D–Cl)_4$	2763.1	11.1	2002.2	10.4

[a] See text.

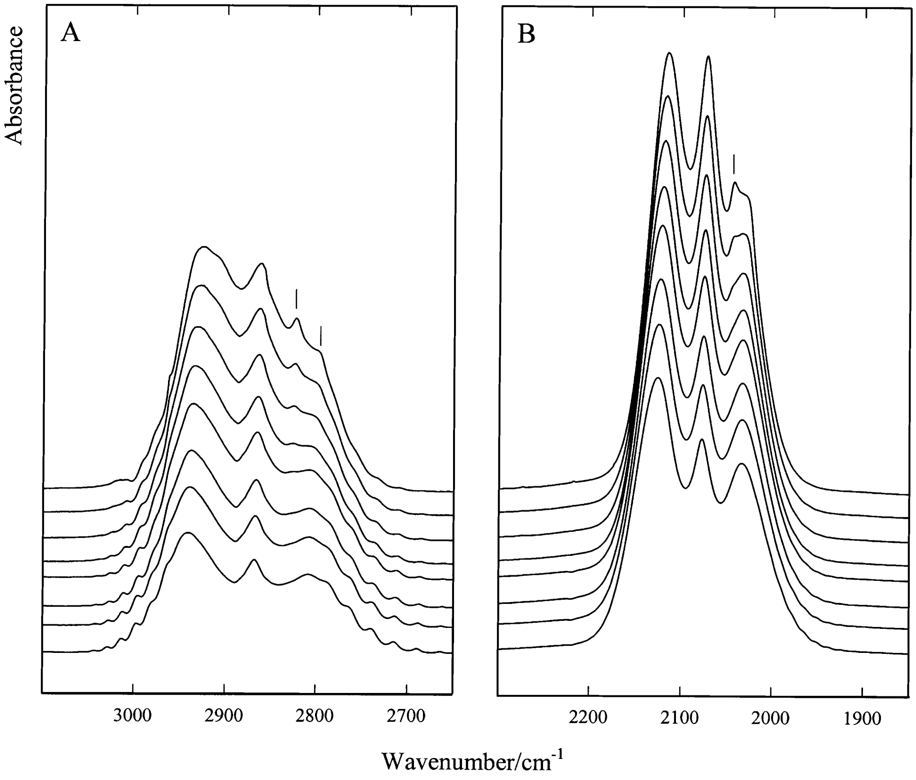

Fig. 4. The νHCl (A) and νDCl (B) regions for solutions of HCl (A, mole fraction = 1.3×10^{-3}) and DCl (B, mole fraction = 1.8×10^{-3}) in liquid krypton. From top to bottom, the temperature of the solution increases, from 126 to 194 K.

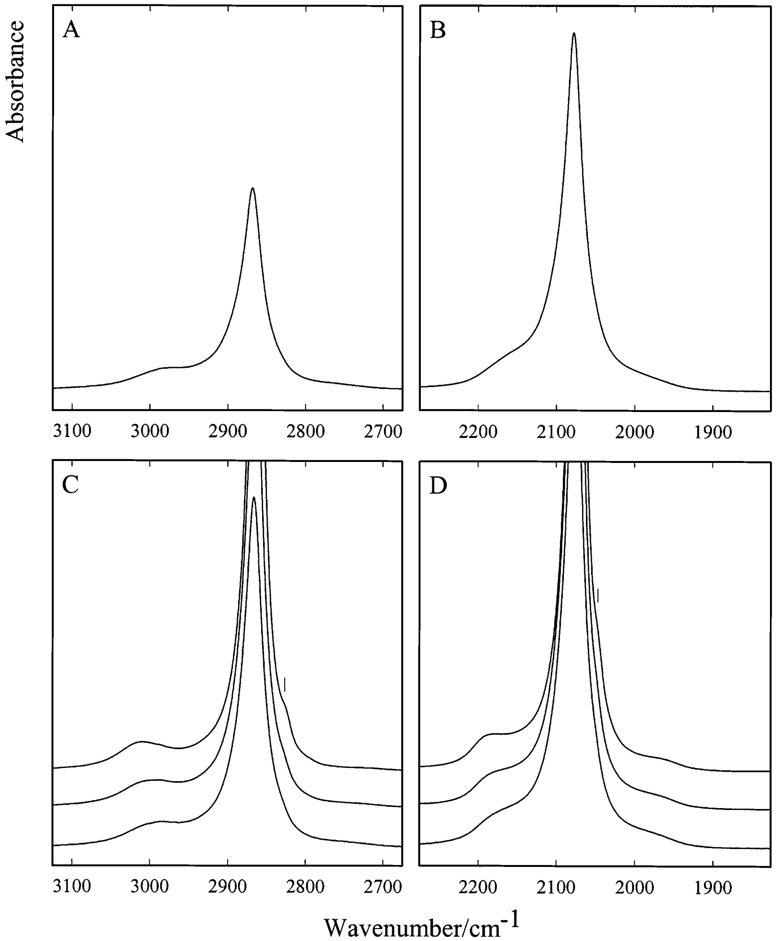

Fig. 5. The νHCl (A,C) and νDCl (B,D) regions for solution of HCl (A,C) and DCl (B,D) in liquid nitrogen. The spectra in (A) and (B) were recorded from a dilute solution (mole fraction = 0.4×10^{-3}) at 130 K. No oligomer bands can be observed in these spectra. The spectra in (C) and (D) were recorded from a more concentrated solution (mole fraction = 1.8×10^{-3}), in which measurable concentrations of the dimers are present. For plots C and D, the temperature for the top, middle and lower traces are 98, 110 and 118 K, respectively.

This characteristic has been observed before for other complexes involving HCl or DCl [14,15].

The above analysis of the νDCl region shows that no indications for bands due to mixed HCl/DCl oligomers have been found. While it is clear from what was said above that such mixed oligomers must be present, it follows that their DCl stretches must be very nearly accidentally degenerate with the corresponding stretches in the homogenous DCl oligomers. This must be a consequence of the absence of significant νDCl/νDCl and νHCl/νHCl couplings in the oligomers. This can be readily rationalized when the weakness of the interactions between the monomers in these complexes, and the relatively high mass of the interposed chlorine atoms, are considered.

Further analysis of the spectra, including the determination of the stoichiometry of the oligomers, and their complexation enthalpy, requires accurate band areas of the oligomer bands. In view of the presence of the contributions due to incompletely deuterated species, it was judged that the band areas derived from the band fitting are not sufficiently representative for the $(DCl)_x$ oligomers, and, therefore, no further analysis was attempted.

The study was completed by investigating solutions of DCl and HCl in LKr and in LN_2. In Fig. 4A some results for HCl in LKr are given, in Fig. 4B the corresponding results for DCl are given. In the spectra recorded at the lowest temperatures new bands can be seen to emerge on the low frequency side of the monomer bands. A weak band at 2824 cm^{-1} has previously been assigned [12] to $(HCl)_2$; its DCl-counterpart can be seen in Fig. 4B at 2043 cm^{-1}. For the HCl bands a second, weaker oligomer band is found at 2800 cm^{-1}. This band has not been reported before [12]. Its frequency is very close to the 2797 cm^{-1} band assigned to $(HCl)_3$ in LAr [12], and we assign the 2800 cm^{-1} to the same species.

For HCl in LN_2, the νHCl region, at 130 K, is shown in Fig. 5A. The more intense band at 2866 cm^{-1} is due to N_2·HCl, the weaker feature at 2987 cm^{-1} is assigned to HCl monomers [18]. Upon cooling the solution, a weak, new band becomes visible on the low frequency side of the N_2·HCl band, at 2827 cm^{-1}. Its frequency is very close to that of the more intense $(HCl)_2$ band in LAr, and we have assigned the 2827 cm^{-1} band accordingly [13]. Analogous behavior is observed for DCl, as can be seen in Fig. 5B and D: the dimer band is found at 2048 cm^{-1}.

The second dimer band is expected [12] some 20–25 cm^{-1} above the more intense one, with considerably less intensity [12]. The presence of the intense band due to the N_2-complex in LN_2 prevents this second band to be observed for $(HCl)_2$ as well as for $(DCl)_2$. In LN_2, also no bands due to trimers or tetramers have been identified.

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References

[1] H. Vu, B. Vodar, in: A. Mangini (Ed.), Advances in Molecular Spectroscopy, Pergamon Press, Oxford, 1962, p. 1058.

[2] H. Vu, M.-R. Atwood, M. Jean-Louis, C. R. Acad. Sci. Paris 262 (1966) 311.

[3] J. Kwok, G.W. Robinson, J. Chem. Phys. 36 (1962) 3137.

[4] H. Goldring, J. Kwok, G.W. Robinson, J. Chem. Phys. 43 (1965) 3220.

[5] R.M. Van Aalst, J. van der Elsken, Chem. Phys. Lett. 13 (1972) 631.

[6] R.M. Van Aalst, J. van der Elsken, Chem. Phys. Lett. 23 (1973) 198.

[7] M.A. Bernikov, M.O. Bulanin, K.G. Tokhadze, J. Mol. Liquids 32 (1986) 25.

[8] M.O. Bulanin, S. Velasco, A.C. Hernández, J. Mol. Liquids 70 (1996) 107 (and references therein).

[9] A. Padilla, J. Pérez, A.C. Hernández, J. Chem. Phys. 111 (1999) 11 015.

[10] A. Padilla, J. Pérez, A.C. Hernández, J. Chem. Phys. 111 (1999) 11 026.

[11] A. Padilla, J. Pérez, A.C. Hernández, J. Chem. Phys. 113 (2000) 4290.

[12] B.J. van der Veken, F.R. de Munck, J. Chem. Phys. 97 (1992) 3060.

[13] W.A. Herrebout, G.P. Everaert, B.J. van der Veken, M.O. Bulanin, J. Chem. Phys. 107 (1997) 8886.

[14] R. Szostak, W.A. Herrebout, B.J. van der Veken, Phys. Chem. Chem. Phys. 2 (2000) 3983.

[15] W.A. Herrebout, T. van den Kerkhof, B.J. van der Veken, Phys. Chem. Chem. Phys. 2 (2000) 4925.

[16] V.V. Bertsev, Experimental technique, in: R.J.H. Clark, R.E. Hester (Eds.), Molecular Cryospectroscopy, Wiley, Chichester, 1995, pp. 1–19.

[17] L.A. Pugh, K. Narahari Rao, Intensities from infrared spectra, in: K. Naharani Rao (Ed.), Molecular Spectroscopy: Modern Research, vol. 2, Academic Press, New York, 1976, pp. 165–228.

[18] K.G. Tokhadze, Spectra of molecular complexes, in: R.J.H. Clark, R.E. Hester (Eds.), Molecular Cryospectroscopy, Wiley, Chichester, 1995, pp. 133–174.