

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/223470812>

A cryosolution infrared and DFT study of the complexes formed between vinylacetylene and hydrogen chloride

ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE · DECEMBER 2002

Impact Factor: 1.6 · DOI: 10.1016/S0022-2860(02)00399-X

CITATIONS

9

READS

36

2 AUTHORS:



W. A. Herrebout

University of Antwerp

185 PUBLICATIONS 3,352 CITATIONS

SEE PROFILE



Benjamin Van der Veken

University of Antwerp

226 PUBLICATIONS 3,860 CITATIONS

SEE PROFILE

A cryosolution infrared and DFT study of the complexes formed between vinylacetylene and hydrogen chloride

W.A. Herrebout, B.J. van der Veken*

Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, B2020 Antwerp, Belgium

Abstract

The formation of weak molecular complexes between vinylacetylene (1-buten-3-yne, $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$) and HCl or DCl dissolved in liquid argon has been investigated using infrared spectroscopy. In all spectra, evidence was found for the formation of a 1:1 van der Waals complex. At higher concentrations of hydrogen chloride, weak absorption bands due to 1:2 species were also observed. Using spectra recorded at different temperatures between 102 and 125 K, the complexation enthalpies for the 1:1 and the 1:2 complex were determined to be $-10.2(9)$ and $-16.9(15)$ kJ mol^{-1} . A density function theory study of the structures and the vibrational frequencies of the complexes is performed at the B3LYP/6-311++G(d,p) level. These calculations show that HCl can form a complex with either the triple or the double carbon–carbon bond, with the former giving stable *endo* and *exo* conformers. Comparison of the experimental frequencies with the calculated ones shows that all observed complex bands are due to the *endo* conformer of the triple bond complex, while those of the 1:2 complex are due to a chain-type complex in which the second HCl is attached to the first one. Using free energy perturbation Monte Carlo simulations to calculate the solvent influences, and statistical thermodynamics to account for zero-point vibrational and thermal contributions the complexation energies for the $\text{C}_4\text{H}_4\cdot\text{HCl}$ and $\text{C}_4\text{H}_4\cdot(\text{HCl})_2$ are estimated from the experimental complexation enthalpies to be $-17.3(20)$ and $-34.6(32)$ kJ mol^{-1} . These numbers are compared with the theoretical values obtained at the B3LYP/6-311++G(d,p) level and with single-point energies calculated at the MP2/aug-cc-PVTZ level. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cryosolution; Vibrational spectra; Vinylacetylene; Hydrogen chloride

1. Introduction

Vinylacetylene is the simplest hydrocarbon in which a double and a triple carbon–carbon bond are simultaneously present. In such a system, two isomers of the complex with hydrogen chloride can be formed, one in which the HCl interacts with the double bond,

and another in which the interaction takes place with the triple bond. This problem has been investigated experimentally, using Fourier Transform microwave spectroscopy [1], and theoretically, using both electrostatic models [1] and ab initio calculations [2]. Both types of calculations confirm the possibility of the double bond/triple bond isomerism and also show that for the complexation via the triple bond two conformers are possible, one in which the HCl approaches from the *endo* side, the other with the HCl approaching from the *exo* side [1,2].

Optimized ab initio geometries of monomers and complexes were obtained by Tang et al. [2] at the RHF/6-31G level. Using these geometries, single-point

* This paper is dedicated to Professor Paolo G. Favero and Professor Helmut Dreizler in appreciation of their significant contributions to the field of microwave spectroscopy; Refer to PII: S0022-2860(02)00076-5

* Corresponding author. Tel.: +32-3-2180-372; fax: +32-3-2180-233.

E-mail address: bvdveken@ruca.ua.ac.be (B.J. van der Veken).

correlation energy corrected calculations were made at the MP2 = full/6-311++G(d,p)//6-31G(d,p) level that resulted in an energy difference of 3.8 kJ mol^{-1} between the global minimum, the *endo* complex, and the one in which the complexation occurs via the double bond. Treating this value as a Gibbs energy allows to predict that at 100 K, a temperature characteristic for our study, the relative population of the latter should be just over 1% of that of the *endo* complex. This is quite small, and, given that the ab initio energy difference is a correct measure of the Gibbs energy difference between the isomers, it suggests that the complex with the double bond will be difficult to observe. Although the vibrational temperature in a molecular beam is difficult to estimate, this energy difference presumably also explains why the double bond isomer has not been detected in the microwave study [1].

Potentially of more importance is the fact that the energy of the *exo* complex is predicted to be 1.2 kJ mol^{-1} above that of the *endo* complex: treating this number in the same way as the one above, the relative population of the *exo* complex is found to be 25% of that of the *endo* complex. In contrast with this, in the microwave spectra only the *endo* complex has been detected [1]. It can, however, not be excluded that with this technique a second isomer is being overlooked [3]. In an attempt to shed light on the possible presence of the *exo* conformer, and on the formation of the complex with the double bond, we have set out to investigate the complexes of vinylacetylene with hydrogen chloride in liquid argon, using infrared spectroscopy to detect the species. In this environment, the interaction between the monomers is studied under equilibrium conditions, at temperatures sufficiently low to allow a significant fraction of the monomers to be engaged in the more stable complexes. The advantage of this technique may be illustrated by the recent results on the complexes of HCl and BF_3 with methylcyclopropane: both in matrix isolation infrared and in Fourier transform microwave studies only one isomer of the 1:1 complex had been detected [4–6], while the infrared spectra of liquid argon solutions clearly proof the presence of two isomers [7].

In the following paragraphs, we hope to demonstrate that using predicted vibrational spectra to assign experimentally observed complex bands, the evidence

is that in liquid argon only the *endo* complex is sufficiently stable to be present in measurable quantities. For this complex, the complexation enthalpy has been derived, and Monte Carlo simulation of the liquid argon solutions have been used to derive a value for the complexation energy of the complex in the vapor phase.

2. Experimental

Vinylacetylene was obtained from Praxair, and was used as obtained. The HCl was prepared by hydrolyzing small amounts of PCl_3 . The gas was pumped through a cold slush, and further purified by low temperature vacuum fractionation. The solvent gas, Ar, obtained from L'Air Liquide, had a stated purity of 99.9999%.

The infrared spectra were recorded on a Bruker IFS 66v interferometer, equipped with a Globar source, a Ge/KBr beam splitter and a broad band MCT detector. For each spectrum, 250 interferograms were averaged, phase corrected, Happ Genzel apodized and Fourier transformed using a zero filling factor of 8, to yield spectra at a resolution of 0.5 cm^{-1} . The solutions were studied in a 4 cm cell, equipped with wedged Si windows, as described before [8].

In cryosolutions, infrared bandwidths in general are a few wavenumbers; for such sharp bands, maxima can be read with a reproducibility of a few tenths of a wavenumber. Therefore, band maxima are believed to be accurate to 0.1 cm^{-1} and will be specified to that precision. Because of the significant temperature shift of the band maxima in cryosolutions [9], the frequencies specified below were taken from spectra recorded at 107 K.

Density functional theory (DFT) calculations were performed using GAUSSIAN98 [10]. For all calculations, Becke's three-parameter exchange functional [11] was used in combination with the LYP correlation functional [12], while the 6-311++G(d,p) basis set was used throughout. To reduce errors arising from the numerical integration for all calculations the finegrid option, corresponding to roughly 7000 grid points per atom was used.

The complexation energies were calculated by subtracting the energies of the monomers from those of the complexes, and these energies were corrected

for basis set superposition error using the counterpoise method of Boys and Bernardi [13]. For all equilibrium geometries, the vibrational frequencies and infrared intensities were calculated using standard harmonic force fields.

Solvation Gibbs energies of monomers and complexes were obtained from Monte Carlo perturbation calculations, using a modified version of BOSS 4.1 [14]. All simulations were run in the NPT ensemble, using standard procedures including a cubic box and periodic boundary conditions. The systems consisted of one solute molecule surrounded by 256 solvent atoms. Preferential Metropolis sampling was used as described before [7]. An attempt to move the solute molecule was made on every 50th configuration and a change in volume was tried on every 600th configuration. The ranges for the attempted moves were the same in each calculation, and provided a $\sim 40\%$ acceptance probability for new configurations.

The path from $\lambda = 0$ (pure argon) to $\lambda = 1$ (a solution with one solute molecule) was completed in 32 equidistant steps. Double-wide sampling was applied [15]. Each step consisted of an equilibration phase for 10.0×10^6 configurations, followed by a production phase of 30.0×10^6 configurations. The Gibbs energy changes between perturbed and reference systems were always small enough ($\approx kT$) to guarantee reliable results by the statistical perturbation theory.

To extract the enthalpy of solvation $\Delta_{\text{sol}}H$ and the entropy of solvation $\Delta_{\text{sol}}H$ in LAr, the Gibbs energy of solvation $\Delta_{\text{sol}}G$ was calculated at 11 different temperatures between 88 and 138 K, at a pressure of 28.2 bar, i.e. the vapor pressure of LAr at 138 K [16].

3. Results

3.1. DFT calculations

Complexation shifts of vibrational modes calculated obtained from DFT calculations on single molecules show a high degree of correlation with the shifts observed in liquid argon [7,17,18]. For the present purpose, therefore, we have predicted the vibrational frequencies of monomers and complexes using this method, at the B3LYP/6-311++G(d,p) level.

The first step in the calculation of the force fields is the full structural optimization of the structures. In agreement with the ab initio calculations of Tang et al. [2], the DFT calculations result in three stable minima, which are shown in Fig. 1, and which correspond to the *endo* (**I_a**) and *exo* (**I_b**) forms of the triple bond complex and to the double bond complex (**II**). Relevant structural parameters, and energies, have been collected in Table 1. Comparison of these data with those of Tang et al. [2] shows that upon complexation the structures of the monomers are perturbed in a similar way. For instance, with both methods of calculation, for the *endo* and *exo* complexes the triple bond length increases by 0.13–0.14%, and the double bond length decreases by 0.03%, while the changes for the double bond complex occur in the opposite sense,

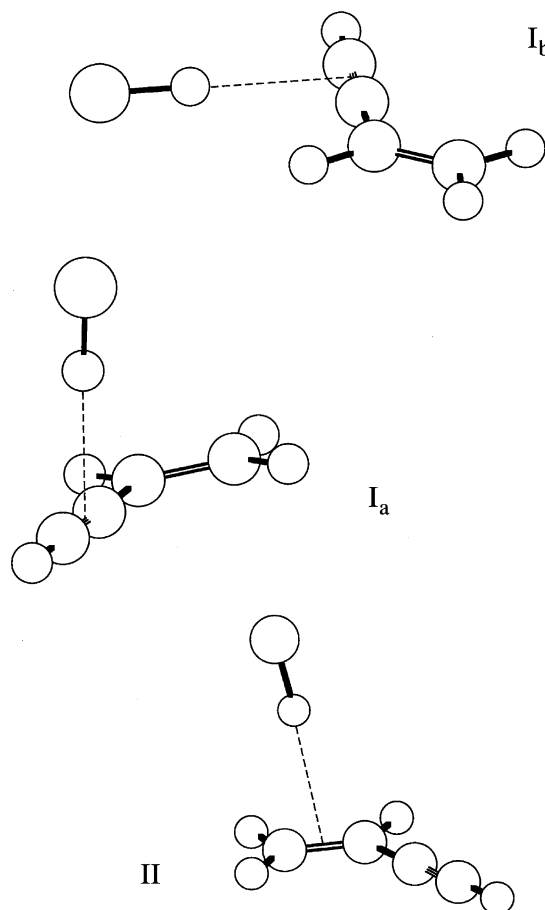


Fig. 1. B3LYP/6-311++G(d,p) equilibrium geometries for the different 1:1 complexes formed between HCl and vinylacetylene.

Table 1

Relevant structural parameters and complexation energies for the different 1:1 complexes between vinylacetylene and HCl

| | Monomer | I _a | I _b | II | III |
|---|---------|----------------|----------------|--------|---------------|
| $r_{C\equiv C}$ (Å) | 1.2055 | 1.2070 | 1.2072 | 1.2050 | 1.2076 |
| $r_{C=C}$ (Å) | 1.3381 | 1.3377 | 1.3377 | 1.3410 | 1.3380 |
| r_{C-C} (Å) | 1.4224 | 1.4234 | 1.4232 | 1.4218 | 1.4277 |
| r_{vdW} (Å) | | 2.360 | 2.345 | 2.360 | 2.257 |
| r_{HCl} (Å) | 1.2869 | 1.2978 | 1.2982 | 1.2946 | 1.3047/1.2956 |
| ΔE (kJ mol ⁻¹) | | -11.33 | -11.01 | -7.96 | -23.22 |
| E_{BSSE} (kJ mol ⁻¹) | | -2.03 | -2.09 | -1.67 | -4.81 |
| ΔE_{corr} (kJ mol ⁻¹) | | -9.30 | -8.92 | -6.29 | -18.41 |

Obtained at the B3LYP/6-311++G(d,p) level.

the double bond length increasing by some 0.2%, and the triple bond length decreasing by 0.04%. Important structural differences between the two methods are found in the van der Waals bond lengths, which in the ab initio calculations are systematically longer, by 8–9% for the triple bond complexes, and by 16% for the double bond complex. These differences presumably must be attributed to the neglect of electron correlation in the ab initio calculations: the evidence for this is that the separation between the chlorine atom and the center of the triple bond calculated by Tang et al. [2] for the *endo* complex is about 0.2 Å higher than the experimental value of 3.629 Å [1]. It has been suggested that in the DFT/B3LYP method at least intramolecular electron correlation is incompletely accounted for [19–21]. It is reasonable to expect that this is also the case for the intermolecular correlation, and it is of interest to see if this affects the van der Waals bond length. Comparison shows, however, that this is not the case, as our DFT/B3LYP value for the chlorine to triple bond distance was calculated to be 3.6476 Å, in excellent agreement with experiment.

A significant difference is also found in the value of the out-of-plane bending angle ϕ of the HCl molecule: the experimental value equals 33.6° [1], the RHF value is 62.7° [2], while the DFT value is 80.4°. The non-planarity of the *endo* complex has been discussed in terms of the steric repulsion between the HCl molecule and the *endo* hydrogen atom of the ethylenic moiety, which was thought to be due to the large amplitude motion of the HCl molecule away from the hydrogen-bond axis [1]. The latter is clearly not considered in the ab initio nor in the DFT calculations, and yet the out-of-plane angle is calculated to be much higher

than the experimental value: this appears to point at a rather poor representation of non-bonded interactions by the basis sets used in both types of calculations.

The vibrational frequencies, infrared intensities and complexation shifts, defined as $\Delta\nu = \nu_{\text{complex}} - \nu_{\text{monomer}}$, calculated for the three complexes, have been collected in Table 2. It can be seen that the intermolecular van der Waals modes are predicted in the far-infrared, which was not investigated in this study. Therefore, only modes localized in the constituent molecules can be used to identify the complex(es) formed in solution. In order to be able to associate an observed complex band with one of the complexes, the shifts predicted for that mode must be sufficiently large, and, if possible, in different directions in the different complexes. Inspection of Table 2 suggests that a distinction between the double and the triple bond complexes may be possible on the basis of ν_{HCl} , and of ν_1 , ν_4 through ν_6 , and ν_{14} of vinylacetylene. Given that triple bond complex bands are observed, distinction between the *endo* and the *exo* complex should be particularly clear from ν_{17} .

3.2. Vibrational spectra

The vibrational spectra of monomer HCl and monomer DCl in liquefied rare gases are well documented [8,22,23] and need not be commented upon here. In contrast, no infrared data of vinylacetylene in cryosolutions have been reported. Therefore, the characteristic frequencies for vinylacetylene observed for a solution in LAr at 107 K, have been summarized in Table 3. The assignments given are

Table 2

B3LYP/6-311++G(d,p) vibrational frequencies, in cm^{-1} , infrared intensities, in km mol^{-1} , and complexation shifts, in cm^{-1} , for the different isomers of the vinylacetylene–HCl complex

| Assignment | Monomer | | Complex I _a | | | Complex I _b | | | Complex II | | | |
|-----------------------|---------|--------|------------------------|--------|-------------|------------------------|--------|-------------|------------|--------|-------------|--------|
| | ν | Int. | ν | Int. | $\Delta\nu$ | ν | Int. | $\Delta\nu$ | ν | Int. | $\Delta\nu$ | |
| Vinylacetylene moiety | | | | | | | | | | | | |
| ν_1 | A' | 3477.0 | 75.3 | 3468.5 | 91.9 | −8.5 | 3468.4 | 87.7 | −8.4 | 3475.1 | 76.6 | −1.9 |
| ν_2 | A' | 3236.3 | 6.3 | 3239.5 | 4.0 | +3.2 | 3240.2 | 3.4 | +4.4 | 3236.3 | 2.9 | 0.0 |
| ν_3 | A' | 3147.1 | 3.3 | 3150.0 | 2.5 | +2.9 | 3150.2 | 2.4 | +3.1 | 3145.1 | 1.2 | −2.0 |
| ν_4 | A' | 3136.7 | 4.9 | 3142.9 | 2.3 | +6.2 | 3142.2 | 1.2 | +5.5 | 3136.0 | 3.4 | −0.7 |
| ν_5 | A' | 2199.0 | 0.6 | 2190.7 | 8.7 | −8.3 | 2189.5 | 9.4 | −9.5 | 2202.1 | 17.4 | +3.1 |
| ν_6 | A' | 1662.7 | 11.7 | 1663.1 | 5.3 | +0.4 | 1663.5 | 7.8 | +0.8 | 1654.6 | 20.9 | −8.1 |
| ν_7 | A' | 1442.9 | 2.9 | 1443.8 | 5.0 | +0.9 | 1443.7 | 2.9 | +0.8 | 1442.2 | 3.0 | −0.7 |
| ν_8 | A' | 1320.2 | 0.4 | 1320.3 | 0.9 | +0.1 | 1322.6 | 0.3 | +2.4 | 1320.1 | 0.5 | −0.1 |
| ν_9 | A' | 1110.9 | 4.7 | 1110.7 | 3.6 | −0.2 | 1110.9 | 4.7 | 0.0 | 1112.1 | 5.8 | +1.2 |
| ν_{10} | A' | 891.8 | 2.2 | 891.0 | 1.3 | −0.8 | 890.1 | 1.7 | −1.7 | 893.0 | 3.0 | +1.2 |
| ν_{11} | A' | 686.6 | 51.4 | 691.5 | 52.0 | +4.9 | 701.3 | 0.9 | +14.7 | 691.7 | 48.9 | +5.1 |
| ν_{12} | A' | 558.9 | 5.3 | 559.5 | 5.7 | +0.6 | 565.9 | 7.6 | +6.4 | 558.5 | 5.8 | −0.4 |
| ν_{13} | A' | 225.9 | 3.3 | 225.8 | 1.9 | −0.1 | 231.2 | 2.5 | +5.9 | 225.2 | 3.5 | −0.7 |
| ν_{14} | A'' | 1007.1 | 17.2 | 1005.9 | 14.9 | −1.2 | 1005.2 | 13.9 | −1.8 | 1014.4 | 21.0 | +7.3 |
| ν_{15} | A'' | 956.3 | 48.0 | 969.6 | 47.8 | +13.3 | 964.9 | 49.2 | +8.3 | 962.4 | 62.2 | +6.1 |
| ν_{16} | A'' | 703.0 | 1.7 | 704.1 | 0.6 | +1.1 | 709.5 | 68.0 | +6.5 | 711.8 | 2.9 | +8.8 |
| ν_{17} | A'' | 653.3 | 53.9 | 672.7 | 66.2 | +18.9 | 649.4 | 52.6 | −3.9 | 666.2 | 52.5 | +12.9 |
| ν_{18} | A'' | 321.6 | 10.9 | 327.2 | 19.5 | +5.6 | 328.7 | 19.4 | +6.7 | 341.2 | 10.2 | +19.6 |
| ν_{HCl} | | 2935.6 | 31.7 | 2788.3 | 462.1 | −147.3 | 2765.5 | 507.6 | −170.1 | 2830.2 | 362.9 | −105.4 |
| van der Waals modes | | | | | | | | | | | | |
| | | | | 351.9 | 6.8 | | 372.6 | 18.5 | | 287.9 | 17.0 | |
| | | | | 288.4 | 25.2 | | 263.2 | 16.7 | | 261.3 | 27.6 | |
| | | | | 91.7 | 3.0 | | 92.9 | 3.9 | | 74.5 | 1.4 | |
| | | | | 43.7 | 0.4 | | 31.5 | 1.1 | | 70.8 | 1.1 | |
| | | | | 21.7 | 0.3 | | 2.6 | 0.0 | | 26.9 | 0.4 | |

based on those reported for the vapor phase [24], and on the calculated frequencies summarized in Table 2.

Comparison of the spectra of the monomers with those of the mixed solution shows that in the latter several new bands are observed. Their presence signals the formation of complexes between vinylacetylene and HCl. The observed frequencies, with their proposed assignment, are summarized in Table 4.

The HCl stretching region of spectra recorded, at different temperatures, from a solution in LAr that contains mole fractions of approximately 2.0×10^{-4} of HCl and 0.1×10^{-4} of vinylacetylene are compared with those of solutions containing only vinylacetylene or HCl in Fig. 2. For the mixed solutions, apart from the monomer bands and the bands at 2828 and 2797 cm^{-1} , which are assigned to $(\text{HCl})_2$ and $(\text{HCl})_3$, respectively [8], an intense band is

observed at 2750.6 cm^{-1} . This band is shifted by -119.1 cm^{-1} from the monomer frequency, and can straightforwardly be assigned to a 1:1 complex between vinylacetylene and HCl. At lower temperatures other complex bands become more clearly visible, at 2689.4 and 2813.3 cm^{-1} . Such weaker secondary bands, one on each side of the dominant 1:1 band, have been observed for other HCl complexes dissolved in LAr studied. It has been shown [7,17, 25–29] that they belong to species in which two molecules of HCl are complexed with an electron donor. Therefore, here also we assign them to a 1:2 species. This stoichiometry is confirmed by the concentration studies discussed below.

It is the general experience that with ab initio and DFT calculations the complexation shift for the HCl stretching is larger than the observed value: the experimental/DFT value ratio, averaged over 7π and

Table 3

Characteristic vibrational frequencies, in cm^{-1} , and assignments for vinylacetylene dissolved in liquid argon, at 107 K

| ν_i | Approximate description | | Vapor phase ^a | Rel. int. ^{a,b} | Liquid argon |
|------------|-------------------------|---|--------------------------|--------------------------|---------------------|
| ν_1 | A' | $\equiv\text{C}-\text{H}$ stretch | 3330 | vs | 3330.7 |
| ν_2 | A' | $=\text{CH}_2$ asymm. stretch | 3114 | m | 3112.4 |
| ν_3 | A' | $=\text{C}-\text{H}$ stretch | 3060 | m | 3057.2 |
| ν_4 | A' | $=\text{CH}_2$ symm. stretch | 3029 | w | 3330.7 |
| ν_5 | A' | $\text{C}\equiv\text{C}$ stretch | 2117 | vw | (2115) ^c |
| ν_6 | A' | $\text{C}=\text{C}$ stretch | 1599 | vs | 1596.4 |
| ν_7 | A' | $=\text{CH}_2$ deformation | 1410 | w | 1408.1 |
| ν_8 | A' | $\text{C}=\text{C}-\text{H}$ in plane deformation | 1320 | vw | 1314.0 |
| ν_9 | A' | $=\text{CH}_2$ rocking | 1096 | m | 1094.1 |
| ν_{10} | A' | $\text{C}-\text{C}$ stretch | 874 | vs | 877.0 |
| ν_{11} | A' | $\text{C}\equiv\text{C}-\text{H}$ bending | 630 | vs | 634.1 |
| ν_{12} | A' | $\text{C}=\text{C}-\text{C}$ bending | 538 | vs | 539.5 |
| ν_{13} | A' | $\text{C}-\text{C}\equiv\text{C}$ bending | 217 | s | No |
| ν_{14} | A'' | $\text{C}=\text{C}-\text{H}$ out-of-plane | 974 | vs | 972.0 |
| ν_{15} | A'' | $=\text{CH}_2$ wagging | 927 | vs | 924.8 |
| ν_{16} | A | $=\text{CH}_2$ twist | 676 | w | 679.0 |
| ν_{17} | A'' | $\text{C}\equiv\text{C}-\text{H}$ bending | 618 | vs | 620.5 |
| ν_{18} | A'' | $\text{C}-\text{C}\equiv\text{C}$ bending | 305 | m | No |

^a Taken from Ref. [24].^b Abbreviations: vs, very strong; s, strong; w, weak; vw, very weak; no, not observed.^c See text.

pseudo- π complexes equals 0.8 [7,17,25–29]. Correcting the present DFT shifts with this factor results in values of -84 cm^{-1} for the double bond complex, -118 cm^{-1} for the *endo* complex, and -136 cm^{-1} for the *exo* complex. The observed shift for the dominant complex band, -119.1 cm^{-1} is in excellent agreement with the value predicted for the *endo* complex, and we may safely conclude that this proves that the *endo* complex is formed in the LAr solutions. The above shifts for the other complexes indicate that

when formed, must give rise to well separated bands. It is obvious from Fig. 2, however, that in the predicted regions only bands due to a 1:2 complex are detected. Hence, the HCl region strongly suggest that in our solutions the concentrations of the *exo* and double bond complexes were below the detection limit.

The complexes have also been studied using DCI as the Lewis acid. The DCI stretching region of spectra of a typical vinylacetylene/DCI mixture and of monomer vinylacetylene is given in Fig. 3. Apart from

Table 4

Observed vibrational frequencies and experimental and calculated complexation shifts, in cm^{-1} , for the 1:1 complexes formed between vinylacetylene, HCl and DCI

| | Experiment in LAr | | | B3LYP/6-311++G(d,p) | | |
|--------------------|-----------------------|---------|-------------|-------------------------|-------------------------|------------------------|
| | Monomer | Complex | $\Delta\nu$ | $\Delta\nu(\text{I}_a)$ | $\Delta\nu(\text{I}_b)$ | $\Delta\nu(\text{II})$ |
| ν_1 | 3330.7 | 3316.2 | -14.5 | -8.5 | -8.4 | -1.9 |
| ν_5 | (2115.0) ^a | 2108.7 | $(-6.3)^a$ | -8.3 | -9.5 | $+3.1$ |
| $2\nu_{15}$ | 1852.8 | 1868.5 | $+15.7$ | $+26.6$ | $+16.6$ | $+12.2$ |
| ν_6 | 1596.4 | 1600.5 | $+4.1$ | $+0.4$ | $+0.8$ | -8.1 |
| ν_{15} | 924.8 | 933.4 | $+8.6$ | $+13.3$ | $+8.3$ | $+6.1$ |
| ν_{HCl} | 2869.7 | 2750.6 | -119.1 | -147.5 | -170.3 | -105.6 |
| ν_{DCI} | 2083.4 | 1997.2 | -86.2 | -107.1 | -123.5 | -76.5 |

^a See text.

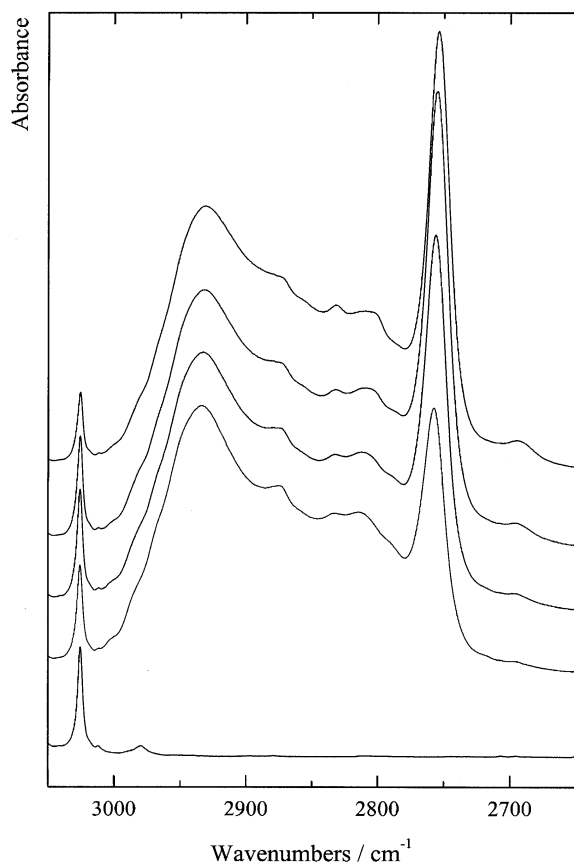


Fig. 2. The HCl stretching region for a solution in liquid argon containing vinylacetylene and HCl. From top to bottom, the temperature of the solution increases from 117 to 130 K. The bottom trace is the spectrum a solution containing only vinylacetylene.

the bands at 2049.2 and 2030.1 cm^{-1} due to $(\text{DCI})_2$ and $(\text{DCI})_3$ [23], in the spectra of the mixed solution new bands assignable to complexes between vinylacetylene and DCI are observed at 2039.8 , 1997.2 and 1958.8 cm^{-1} , with an intensity pattern similar to that observed for the HCl complexes. Consequently, it is straightforward to assign the more intense 1997.2 cm^{-1} band to the *endo* complex, and the 2039.8 and 1958.5 cm^{-1} bands to the 1:2 complex. Also in this region of the spectra no indication was found for the presence of a second 1:1 complex.

Figs. 4 and 5 illustrate that also for modes localized in vinylacetylene complex bands have been observed. In Fig. 4, the complex can be seen to give rise to new bands at 1868.5 and 1600.5 cm^{-1} , which we attribute

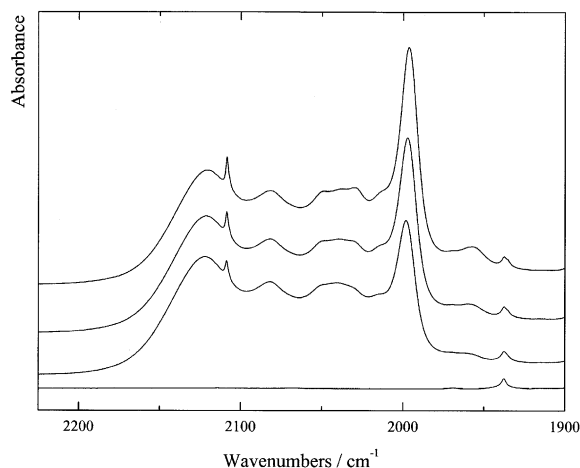


Fig. 3. The DCI stretching region for a solution in liquid argon containing vinylacetylene and DCI. From top to bottom, the temperature of the solution increases from 116 to 128 K. The bottom trace shows the spectrum of a solution containing only vinylacetylene.

to the monomer bands at 1852.8 and 1596.4 cm^{-1} , respectively. The latter is assigned as ν_6 , the C=C stretching. Table 2 shows that for the double bond complex the complexation shift of this mode should be negative, but that it is positive for the triple bond complexes. The complex band is observed on the high frequency side of ν_6 , while no indication is found for a complex band on the low frequency side. The latter observation confirms that the double bond complex cannot be detected in our solutions. Although

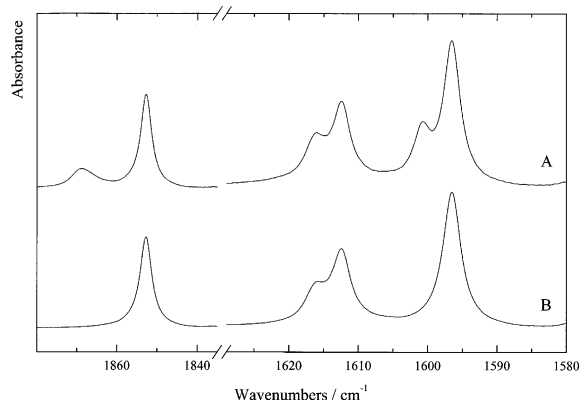


Fig. 4. The $1880\text{--}1835$ and $1630\text{--}1580\text{ cm}^{-1}$ spectral regions of a solution containing both vinylacetylene and HCl (A) and of a solution containing only vinylacetylene (B), at 121 K.

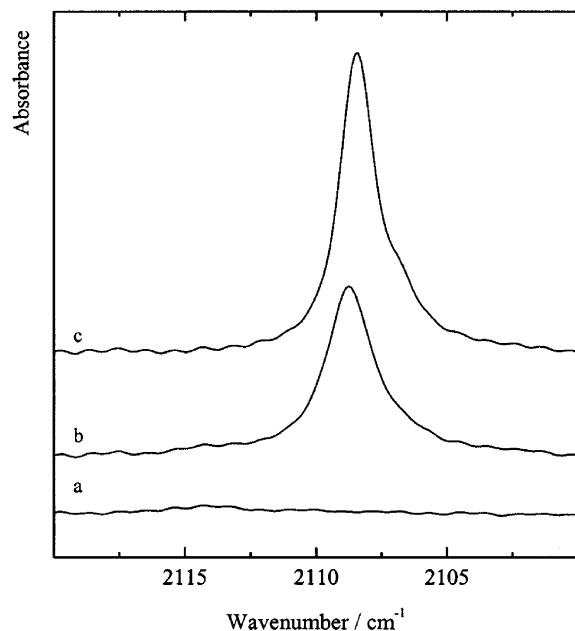


Fig. 5. The C≡C stretching region of a solution in liquid argon containing both vinylacetylene and HCl. Traces *a* and *b* refer to a mixed solution, at 126 and 113 K, respectively. Trace *c* shows the spectrum a solution containing only vinylacetylene.

the agreement is far from quantitative, the direction of the shift of the observed complex band supports the conclusion that the band must be associated with a triple bond complex, the lack of quantitative agreement preventing a more detailed assignment.

Fig. 5 gives the region of ν_5 , the C≡C stretch, of the spectra. The lower trace, recorded from a solution containing only vinylacetylene, shows that the monomer ν_5 is too weak to be detected, in agreement with its low predicted intensity, given in Table 2. The table also suggests that in the complexes a significantly more intense ν_5 should be present, the intensification ranging from a factor 14.5 for the *endo* complex to 29 for the double bond complex. Fig. 5 shows that at higher temperatures, when the concentration of the 1:2 complex is low, a single complex band is observed at 2108.7 cm^{-1} . We assign this band to ν_5 in a 1:1 complex. At lower temperatures a low frequency shoulder emerges near 2107 cm^{-1} . The temperature dependence of the intensity of that shoulder follows the pattern of the 1:2 HCl and DCl stretches and, consequently, we assign this shoulder to a 1:2 complex.

The ν_5 mode is predicted, Table 2, to shift downward by more than 8 cm^{-1} in the triple bond complexes, and upward by 3.1 cm^{-1} in the double bond complex. The absence of monomer ν_5 from the solution spectra makes it difficult to experimentally determine the complexation shift, but a good estimate can be made in the following way. In the vapor phase infrared spectrum of monomer vinylacetylene two very weak features, at 2117 and 2105 cm^{-1} , have been attributed to ν_5 [24]. We have re-investigated this spectrum and were able to detect a single Q branch only, at 2117 cm^{-1} , which we assign to ν_5 . Inspection of Table 2 shows that in liquid argon most fundamentals are shifted downward by a mere $2\text{--}3\text{ cm}^{-1}$ from their vapor phase value, and in methylacetylene the C≡C stretch is shifted by -1.5 cm^{-1} [30]. Adopting a shift of 2 cm^{-1} for ν_5 in the present compound puts the monomer frequency at 2115 cm^{-1} in LAr. The observed complex band at 2108.7 cm^{-1} falls 6.3 cm^{-1} below that monomer frequency, in reasonable agreement with the predictions for the triple bond complex, while assignment of the experimental band to the double bond complex requires an unreasonably high solvent shift of the monomer frequency in order for the complexation shift to be compatible with the prediction in Table 2. Therefore, we propose to assign the 2108.7 cm^{-1} band to a triple bond complex. Evidently, the similarity of the complexation shifts predicted for the *endo* and *exo* complexes renders impossible a more detailed analysis.

Table 4 reveals that for ν_1 , the $(\equiv)\text{C-H}$ stretch, a complex band shifted by -14.5 cm^{-1} has been identified in the spectra of the mixtures. This shift is closer to the values predicted for the triple bond complexes, -8.5 and -8.4 cm^{-1} , than for the double bond complex, -1.9 cm^{-1} , and may be taken to support the conclusion that in our solutions a triple bond complex is formed. No other complex bands due to C-H stretching modes have been identified, and also for ν_{14} , of potential interest to distinguish between double and triple bond complexes, no complex bands have been found.

Above we have suggested ν_{17} as a possible clue for the distinction between *endo* and *exo* complexes. For monomer vinylacetylene this mode has been assigned to a very strong infrared band at 620.5 cm^{-1} . No corresponding complex bands have been observed.

The absence of an observable complex band on the high frequency side is easily explained by the presence of the equally very strong ν_{11} monomer band at 634.1 cm^{-1} , which may well overshadow a much weaker complex band, while the absence of a complex band on the low frequency side does not support the presence of the *exo* complex.

3.3. Stoichiometry of the observed complexes

The stoichiometry of the complexes has been determined as before, by investigating the linearity of the relationship between the band area of a band due to a complex and the product of the m th power of the band area of a band of monomer vinylacetylene and the n th power of the band area of the HCl monomer band [8]. Band areas were determined at 107 K for spectra of solutions in which the mole fraction of vinylacetylene was varied between 0.1×10^{-4} and 1.0×10^{-4} , and the mole fraction of HCl between 0.1×10^{-4} and 3.0×10^{-4} . For monomer vinylacetylene, the band area of the 1852.8 cm^{-1} band was obtained from least-squares band fitting, using Gauss–Lorentz sum functions. Band areas for monomer HCl and for the complexes were obtained from the HCl stretching region as follows. A spectrum of HCl in LAr, recorded at the same temperature as the mixtures, was rescaled and subtracted from the spectra of the mixtures. For each solution, the rescaling factor was adjusted so that in the difference spectrum the monomer HCl contribution was completely removed. The difference spectra were used to quantify the more intense complex band at 2750.6 cm^{-1} and the low frequency band at 2689.4 cm^{-1} ; because of its severe overlap with HCl oligomer bands, obvious from Fig. 2, no attempts were made to involve the high frequency complex band at 2813.3 cm^{-1} in the analysis. The band areas of the bands were derived from least-squares fittings using Gauss–Lorentz sum functions. Due to the pronounced asymmetry of the HCl stretches of the complexes [25], an optimal fit required a sum of three functions for the 2689.4 cm^{-1} band and a sum of two functions for the 2750.6 cm^{-1} band. The sum of the areas of the functions used to simulate each of these multiplets was then used as band area for the corresponding complex. Finally, for each solution the HCl monomer band area was determined by numerical integration of the HCl

Table 5

χ^2 values from the stoichiometry analysis of the complexes formed between vinylacetylene and HCl

| Proposed stoichiometry | 2750.6 cm^{-1} band | 2689.4 cm^{-1} band |
|---|------------------------------|------------------------------|
| $\text{C}_4\text{H}_4\cdot\text{HCl}$ | 0.012 | 0.176 |
| $(\text{C}_4\text{H}_4)_2\cdot\text{HCl}$ | 0.456 | 0.279 |
| $\text{C}_4\text{H}_4\cdot(\text{HCl})_2$ | 0.187 | 0.027 |

absorption band in the rescaled spectrum used in the subtraction.

Linear regressions were performed between the set of band areas of each complex band and different products of monomer intensities. The χ^2 values of these regressions are given in Table 5. It can be seen that for the 2750.6 cm^{-1} band the highest degree of linearity is obtained for the product $I_{\text{C}_4\text{H}_4} \times I_{\text{HCl}}$, from which follows that this band is due to a 1:1 complex $\text{C}_4\text{H}_4\cdot\text{HCl}$. For the band at 2689.4 cm^{-1} the smallest χ^2 value is found for the product $I_{\text{C}_4\text{H}_4} \times (I_{\text{HCl}})^2$, so that this band must be due to a complex with 1:2 stoichiometry.

3.4. Complexation enthalpy of the observed species

The relative stability of the 1:1 and 1:2 complexes in LAr was established from a temperature study, in which infrared spectra of solutions containing vinylacetylene and HCl, with mole fractions of 0.1×10^{-4} and 1.6×10^{-4} , respectively, were recorded between 102 and 125 K. From these, the complexation enthalpy ΔH^0 was determined using the van't Hoff isochore [31]. In this method, ΔH^0 is obtained from the slope of the graph obtained by plotting the logarithm of the equilibrium constant, expressed in terms of band areas of infrared bands of the species involved, against the inverse temperature [31]. Band areas for monomer and complex bands were derived for the same bands, using the same procedures, as in the concentration study discussed above. The van't Hoff plots derived from these are shown in Fig. 6. From the slope of the linear regressions through the experimental points, corrected for the density variation of the solution [31], the complexation enthalpies for the 1:1 complex and the 1:2 complex were calculated to be $-10.2(9)$ and $-16.9(15)\text{ kJ mol}^{-1}$, respectively.

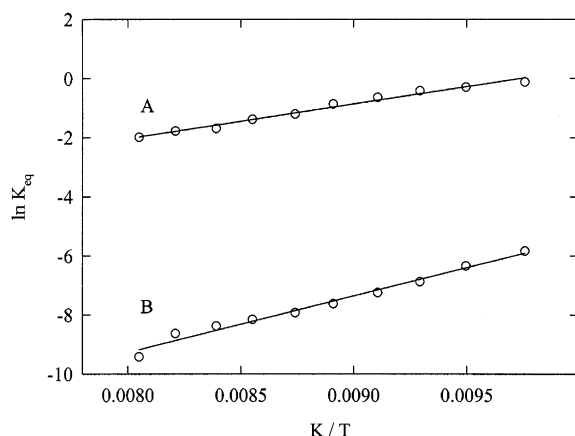


Fig. 6. van't Hoff plots for the $C_4H_4 \cdot HCl$ complex (a) and the $C_4H_4 \cdot (HCl)_2$ complex observed in liquid argon.

4. Discussion

The observed 1:1 complex bands have frequencies compatible with the DFT predictions for the triple bond complexes, from which we conclude that in our cryosolutions a triple bond complex is formed. The analysis of the observed frequencies further shows that the complex has the *endo* conformation, in which the HCl molecule approaches the triple bond from the side of the vinyl substituent. This is in agreement with relative stabilities obtained from *ab initio* [2] and DFT predictions, and is the same conformer as found in the microwave analysis [1].

Careful inspection of the regions in which diagnostic bands of the *exo* conformer and of the double bond complex were predicted gave no evidence for the presence of even the weakest absorption. From this, it must be concluded that the concentration of these species is below the detection limit. For the *exo* complex this implies that the prediction of the relative concentration made above is incorrect. This suggests that either the energy of the second conformer is seriously underestimated, or that the second minimum in the internal rotation potential of HCl around the triple bond is an artifact of the calculations.

In addition to the bands due to the 1:1 complex, in the spectra of the mixed solutions weaker bands were observed, which were assigned to 1:2 complexes involving one vinylacetylene and two HCl molecules.

On the basis of comparison with the spectra of other 1:2 complexes [7,17,25–29], this complex is proposed to have a chain structure $B \cdots HCl \cdots HCl$, with the second HCl molecule hydrogen bonded to the chlorine atom of the first. The plausibility of this structure was investigated using DFT calculations at the same level as that used for the 1:1 complexes. The resulting equilibrium geometry is shown in Fig. 7. The observed frequencies for this complex and the corresponding DFT values are compared with each other in Table 6. It can be seen that in agreement with the predictions, one of the HCl stretches in the 1:2 complex appears on the high frequency side of the 1:1 band, the other on the low frequency side. Also, the experimental 1:2 $C \equiv C$ stretch appears on the low frequency side of the 1:1 band, in agreement with the predictions. These observations support the proposed structure.

By correcting the solution value of ΔH^0 for solvation and for thermal and zero-point vibrational contributions, the complexation energy of the isolated complex can be obtained. We have derived the solvation enthalpies $\Delta_{sol}H^0$ of monomers and complexes from the temperature evolution of their Gibbs energy of solvation $\Delta_{sol}G^0$. The latter were obtained

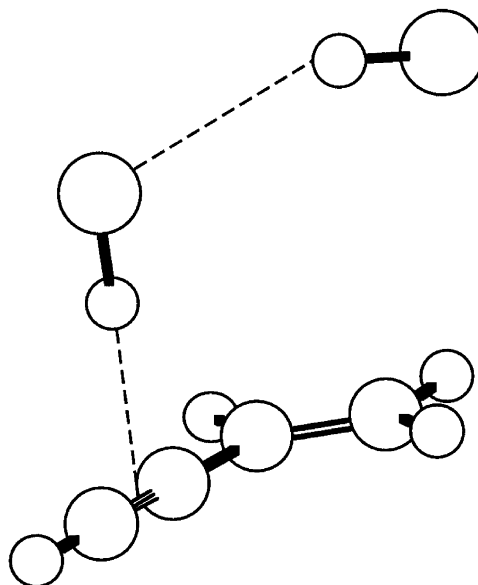


Fig. 7. B3LYP/6-311++G(d,p) equilibrium geometry for the 1:2 complex formed between vinylacetylene and HCl.

Table 6

Observed and calculated vibrational frequencies, in cm^{-1} , for $\text{C}_4\text{H}_4\cdot(\text{HCl})_2$

| Mode | Experimental | | | B3LYP/6-311++G(d,p) | | |
|--------------------------------|---------------------|---------------------------------------|---|---------------------|---------------------------------------|---|
| | Monomer | $\text{C}_4\text{H}_4\cdot\text{HCl}$ | $\text{C}_4\text{H}_4\cdot(\text{HCl})_2$ | Monomer | $\text{C}_4\text{H}_4\cdot\text{HCl}$ | $\text{C}_4\text{H}_4\cdot(\text{HCl})_2$ |
| ν_{HCl} | 2869.7 | 2750.6 | 2813.3; 2689.4 | 2935.6 | 2788.3 | 2810.0; 2682.9 |
| ν_{DCl} | 2083.4 | 1997.2 | 2039.8; 1958.8 | 2131.3 | 2024.3 | 2040.1; 1947.8 |
| $\nu_{\text{C}\equiv\text{C}}$ | (2115) ^a | 2108.7 | 2106.9 | 2199.0 | 2190.7 | 2186.9 |

^a See text.

from free energy perturbation Monte Carlo calculations on the solutions, using BOSS 4.1. The $\Delta_{\text{sol}}G$ were obtained at 11 temperatures centered around 113 K, using a finite difference method similar to the one described by Levy et al. [32,33].

The intermolecular interactions in these calculations were modeled by a combination of Lennard–Jones and polarization terms. A Lennard–Jones function was used for each pair of atoms. The parameters of these functions were taken from the OPLS all-atom potential functions [34]. The standard BOSS 4.1 program does not allow to take into account polarization contributions. Therefore, the program was expanded to include the interaction energy E_{pol} due to the polarization of the solvent atoms by the solute, as calculated by the non-iterative first-order approximation:

$$E_{\text{pol}} = -\frac{1}{2} \vec{\mu}_{\text{ind}} \cdot \vec{E} = -\frac{1}{2} \alpha_{\text{solvent}} (\vec{E} \cdot \vec{E})$$

In this expression α_{solvent} refers to the polarizability of the rare gas studied [35], and \vec{E} is the electric field generated at a solvent atom by the solute. This field was calculated from a charge model of the molecule. The partial charges located on the nuclei were calculated using the POP = (CHELPG, DIPOLE) keyword in GAUSSIAN98, at the B3LYP/6-311++G(d,p) level. The resulting solvation enthalpies and entropies are given in Table 7.

By combining the experimental ΔH^0 s with the data in Table 7, a vapor phase complexation enthalpy $\Delta H_{\text{vapor}}^0$ of $-14.0(10) \text{ kJ mol}^{-1}$ for $\text{C}_4\text{H}_4\cdot\text{HCl}$ and of $-28.0(16) \text{ kJ mol}^{-1}$ for $\text{C}_4\text{H}_4\cdot(\text{HCl})_2$ result. Subsequently, from these enthalpies, the complexation energies were derived by applying statistical thermodynamical corrections. The zero-point vibrational energies of the species were calculated using the

B3LYP/6-311++G(d,p) frequencies. The thermal contributions were calculated at 113 K; translational and rotational contributions were obtained in the classical limit and vibrational thermal contributions were calculated in the harmonic approximation using the DFT frequencies. In this way, corrections of -3.3 kJ mol^{-1} for $\text{C}_4\text{H}_4\cdot\text{HCl}$ and of -6.6 kJ mol^{-1} for $\text{C}_4\text{H}_4\cdot(\text{HCl})_2$ are obtained, which lead to ‘experimental’ complexation energies ΔE_{exp} of $-17.3(20) \text{ kJ mol}^{-1}$ for $\text{C}_4\text{H}_4\cdot\text{HCl}$ and of $-34.6(32) \text{ kJ mol}^{-1}$ for $\text{C}_4\text{H}_4\cdot(\text{HCl})_2$. The uncertainties on these are twice the values for the ΔH^0 s to account for the approximations made.

In view of earlier findings [7], it is not surprising that both uncorrected and BSSE corrected B3LYP/6-311++G(d,p) complexation energies are smaller than the experimental values. In general, the DFT structures obtained at this level are in good agreement with experiment [7,17,19,20]. It has been discussed above that this indeed is the case for the 1:1 complex, for which experimental data are available. Better values for the complexation energies can then be obtained from single-point calculations at these structures, using an expanded basis set and accounting for electron correlation [17]. We have made such

Table 7

Solvation enthalpies, in kJ mol^{-1} , and solvation entropies, in $\text{J K}^{-1} \text{ mol}^{-1}$ calculated using free energy perturbation theory

| Species | $\Delta_{\text{sol}}H$ | $\Delta_{\text{sol}}S$ |
|---|------------------------|------------------------|
| HCl | $-11.48(06)$ | $-44.7(5)$ |
| C_4H_4 | $-19.39(14)$ | $-70.5(12)$ |
| $\text{C}_4\text{H}_4\cdot\text{HCl}$ | $-27.05(15)$ | $-99.5(13)$ |
| $\text{C}_4\text{H}_4\cdot(\text{HCl})_2$ | $-31.19(21)$ | $-115.9(18)$ |

calculations at the MP2 = full/aug-cc-PVTZ level, resulting in BSSE corrected values of $-15.7 \text{ kJ mol}^{-1}$ for the 1:1 complex and $-31.4 \text{ kJ mol}^{-1}$ for the 1:2 complex. These energies are in good agreement with the above experimental values.

It is well known that the stability of chain-type HCl complexes is influenced by the cooperative effect. That this is also the case for the present complexes follows from the fact that the difference between the complexation energies of the 1:1 and 1:2 complexes, $-17.3(38) \text{ kJ mol}^{-1}$, is much more important than the complexation energy of the HCl dimer. The latter has been estimated at $-7.3(10) \text{ kJ mol}^{-1}$ using the same extrapolation from the complexation enthalpy as used here [17]. Thus, the present cooperative effect equals $17.3(38) - 7.3(10) = 10.0(40) \text{ kJ mol}^{-1}$. This is a relatively high value, but the scarcity of data on similar complexes makes it difficult to put this in perspective. For the complexes of ethene and allene with HCl the cooperative effect has been derived to be 6.9 kJ mol^{-1} in both cases [25,27], but in those studies the solvation enthalpies were calculated using the SCIPCM method [10], which may not be very reliable, because it does not properly account for all solvation effects [36]. Only for the 1:1 and 1:2 complexes of methylenecyclopropane has the cooperative effect been obtained by the same method as used here [17], resulting in a value of 4.5 kJ mol^{-1} . The higher value obtained for the vinylacetylene complexes most likely is due to the different nature of the nucleophilic center involved, i.e. a triple versus a double carbon–carbon bond. In order for this conclusion to be substantiated, it is clear that experimental evidence on other HCl complexes with π or pseudo- π bonds will have to become available.

Acknowledgments

W.A.H. thanks the Fund for Scientific Research (FWO—Vlaanderen, Belgium) for an appointment as Postdoctoral Fellow. The FWO is also thanked for financial help toward the spectroscopic equipment used in this study. Support by the Flemish Community, through the Special Research Fund (BOF) is gratefully acknowledged.

References

- [1] Z. Kisiel, P.W. Fowler, A.C. Legon, D. Devanne, P. Dixneuf, *J. Chem. Phys.* 93 (1990) 6249.
- [2] T.-H. Tang, Y.-P. Cui, *Can. J. Chem.* 74 (1996) 1162.
- [3] A.C. Legon, *Angew. Chem. Int. Ed.* 38 (1999) 2686.
- [4] C.E. Truscott, B.S. Ault, *J. Phys. Chem.* 89 (1985) 1741.
- [5] B.S. Ault, *J. Phys. Chem.* 90 (1986) 2825.
- [6] S.E. Forest, A.M. Andrews, R.L. Kuczkowski, *J. Phys. Chem.* 98 (1994) 2050.
- [7] G.P. Everaert, W.A. Herrebout, B.J. van der Veken, 105 (2001) 9058.
- [8] B.J. Van der Veken, F.R. De Munck, *J. Chem. Phys.* 97 (1992) 3060.
- [9] E.J. Sluyts, B.J. Van der Veken, *J. Am. Chem. Soc.* 118 (1996) 440.
- [10] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A.J. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN98 Gaussian Inc., Pittsburgh, PA, 1998.
- [11] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [12] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1998) 785.
- [13] S.F. Boys, F. Bernardi, *Mol. Phys.* 19 (1970) 553.
- [14] W.L. Jorgensen, BOSS version 4.1, Yale University, New Haven, CT, 1999.
- [15] M.P. Allen, D.J. Tildesley, *Computer Simulation of Liquids—Double Wide Sampling*, Clarendon, Oxford, 1987, p. 220.
- [16] N.B. Vargaftik, Y.K. Vinogradov, V.S. Yargin, *Handbook of Physical Properties of Liquids and Gases. Pure Substances and Mixtures*, Begell House Inc, New York, 1996, Third augmented and revised version.
- [17] R. Szostak, W.A. Herrebout, B.J. Van der Veken, *Phys. Chem. Chem. Phys.* 2 (2000) 3983.
- [18] W.A. Herrebout, R. Szostak, B.J. Van der Veken, *J. Phys. Chem. A* 104 (2000) 8480.
- [19] J. Lundell, Z. Latajka, *Chem. Phys.* 263 (2001) 221.
- [20] M. Hartmann, S.D. Wetmore, L. Radom, *J. Phys. Chem. A* 105 (2001) 4470.
- [21] S. Tsuzuki, H.P. Luthi, *J. Chem. Phys.* 114 (2001) 3949.
- [22] M.O. Bulanin, S. Velasco, A.C. Hernandez, *J. Mol. Liquids* 70 (1996) 107.
- [23] W.A. Herrebout, J. Van Gils, B.J. Van der Veken, *J. Mol. Struct.* 563-564 (2001) 249.
- [24] E. Torneng, C.J. Nielsen, P. Klaeboe, H. Hopf, H. Priebe, *Spectrochim. Acta A* 36 (1980) 975.
- [25] W.A. Herrebout, G.P. Everaert, M.O. Bulanin, B.J. Van der Veken, *J. Chem. Phys.* 107 (1997) 8886.

- [26] W.A. Herrebout, B.J. Van der Veken, *J. Mol. Struct.* 449 (1998) 231.
- [27] G.P. Everaert, W.A. Herrebout, B.J. Van der Veken, *Phys. Chem. Chem. Phys.* 1 (1999) 231.
- [28] G.P. Everaert, W.A. Herrebout, B.J. Van der Veken, *J. Mol. Struct.* 550–551 (2000) 399.
- [29] W.A. Herrebout, T. Van den Kerkhof, B.J. Van der Veken, *Phys. Chem. Chem. Phys.* 2 (2000) 4925.
- [30] W.A. Herrebout, J. Lundell, B.J. Van der Veken, *J. Mol. Struct.* 480–481 (1999) 489.
- [31] B.J. Van der Veken, *J. Phys. Chem.* 100 (1996) 17436.
- [32] M.M. Kubo, E. Gallicchio, R.M. Levy, *J. Phys. Chem. B* 101 (1997) 10527.
- [33] R.M. Levy, E. Gallicchio, *Ann. Rev. Phys. Chem.* 49 (1998) 531.
- [34] W.L. Jorgensen, in: P. von Ragué Schleyer (Ed.), *Encyclopedia of Computational Chemistry*, Wiley, West Sussex, 1998, p. 1986.
- [35] D.A. McQuarrie, J.D. Simon, *Physical Chemistry. A Molecular Approach*, University Science Books, Sausalito, CA, 1997.
- [36] M. Orocz, F.J. Luque, *Chem. Rev.* 100 (2000) 4187.