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Journal of Molecular Structure 706 (2004) 107-113



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On the formation of a van der Waals complex between ethene and carbon dioxide in liquid argon. An FTIR and ab initio study

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Available online 23 April 2004

Abstract

The mid-infrared spectra of mixtures of ethene and carbon dioxide dissolved in liquid argon have been investigated between 88 and 123 K. At higher concentrations of ethene, evidence was found for the formation of a 1:1 complex in which the carbon atom of the CO₂ moiety binds to the C=C double bond. By recording spectra at different temperatures, the complexation enthalpy for the 1:1 complex was determined to be -4.9(1) kJ mol⁻¹. Using Free Energy Perturbation Monte Carlo simulations to correct for solvent influences and statistical thermodynamics to account for zero-point vibrational and thermal influences, the complexation enthalpy was transformed into a vapor phase complexation energy. The resulting value, -6.8(8) kJ mol⁻¹, is compared with theoretical data obtained from ab initio calculations in which the equilibrium geometry of the complex is calculated using BSSE-corrected gradient techniques. © 2004 Published by Elsevier B.V.

Keywords: Cryospectroscopy; Van der Waals complexes; Ethene; Carbon dioxide

1. Introduction

Although carbon dioxide has no permanent dipole moment, there is considerable charge separation in the C=O bonds. This leads to a significant quadrupole moment, and results in a positive partial charge on the carbon atom and in negative ones on the oxygen atoms. This characteristic allows CO₂ to act both as a Lewis acid [1–16] and as a Lewis base [17–28], a property which is recognized [29–37] as being important in the solvation of molecules in liquid and supercritical CO₂.

In this study we focus on the Lewis acid properties of CO_2 . Although there is extensive literature on interactions of CO_2 with Lewis bases, very little is known about its interaction with π -type electron donors, for which ethene, C_2H_4 , is the obvious model compound. The structure of the van der Waals complex between CO_2 and ethene has been determined from a molecular beam rotationally resolved infrared study to be of the stacked parallel type, in which the CO_2 molecule sits above the ethene plane, with the CO_2 axis parallel to the C=C bond [38]. Detailed analysis of the fine structure using a two dimensional internal rotation model

allowed the barrier towards internal rotation around the axis connecting the centers of mass of the two monomers to be determined at the very low value of 6.6 cm^{-1} . In the same study ab initio results at the MP2/6-31G + (2p,2d) level are reported. The full structure optimization of the complex resulted in a stacked structure, however with an angle of approximately 40 degrees between the axis of the CO₂ molecule and the C=C bond. The internal rotation barrier was calculated at 15 cm⁻¹. Fragmentary ab initio results have also been reported by Jamroz et al. [11], at the relatively low HF/3-21G* level, and, more recently by Fedotov et al. [39], who discuss the nature of the interaction between the monomers, but who do not report on the optimized structure of the complex.

It is clear from the above that no experimental data regarding the stability of the ethene/ CO_2 complex are known, and we aim at filling this gap by studying the formation of the complex in liquid argon, using infrared spectroscopy. We will show in the following paragraphs that from the spectra the standard complexation enthalpy for the reaction in solution has been obtained, which was subsequently converted into a vapor phase complexation energy by correcting for solvation and for thermal effects. In addition, ab initio calculations, to support the vibrational

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analysis and to evaluate the experimental complexation energy, are discussed.

2. Experimental

 C_2H_4 was obtained from Aldrich with a stated purity of 99.9 + % and was used without further purification. ¹²CO₂ and ¹³CO₂ were prepared by mixing a small amount of the corresponding sodium carbonate with sulfuric acid. The gases were purified using a low-temperature, low-pressure fractionation column. The argon used was supplied by L' Air Liquide and had a stated purity of 99.9999%.

The infrared spectra were recorded using a Bruker IFS 66 v Fourier transform spectrometer, equipped with a Globar source, a Ge/KBr beamsplitter and a LN_2 -cooled broad band MCT detector. All interferograms were averaged over 250 scans, Blackman–Harris 3-Term apodized and Fourier transformed with a zero filling factor of 4, to yield spectra at a resolution of 0.5 cm⁻¹. 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 has a path length of 10 mm and is equipped with wedged Si windows.

The geometry of the 1:1 complex and its harmonic vibrational frequencies were calculated using the CP-corrected gradient techniques originally developed by Simon et al. [40], and included in GAUSSIAN 98-Rev. A11 [41]. Unless stated otherwise, all calculations were performed at the MP2 = FULL/6-311++G(2d,2p) level.

Solvation Gibbs energies of monomers and complexes were obtained from Monte Carlo perturbation calculations, using a modified version of BOSS 4.1 [42]. All simulations were run in the NPT ensemble, using periodic boundary conditions. The system consisted of one solute molecule surrounded by 256 solvent atoms. Preferential Metropolis sampling was used as described before [43,44]. 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 quantity calculated is the Gibbs energy $\Delta_{sol}G$ for the process of introducing one solute into the box with solvent atoms via a coupling parameter λ . The path for $\lambda = 0$ (pure argon) to $\lambda = 1$ (a solution with one solute molecule) was completed in 40 equidistant steps. Each step consisted of an equilibrium phase for 20.0×10^6 configurations, followed by a production phase of 50.0×10^6 configurations. The Gibbs energy changes between the perturbed and reference systems were always small enough ($\approx kT$) to guarantee reliable results by the statistical pertubation theory.

The enthalpy of solvation $\Delta_{sol}H$ and the entropy of solvation $\Delta_{sol}S$ in LAr were extracted from the Gibbs energies of solvation $\Delta_{sol}G$, using a method similar to that described by Levy et al. [45]. To this end, for each species,

the Gibbs energies of solvation were calculated at 10 different temperatures between 93 and 138 K, at a pressure of 28.2 bar, i.e. the vapor pressure of LAr at 138 K.

3. Results and discussion

3.1. Ab initio calculations

Our calculations using the BSSE-corrected PES result in a packed parallel structure for the complex [38], in agreement with the experimental one, and in agreement with the prediction based on the quadrupole moments of CO_2 and ethene, which are of opposite signs [38]. This result contrasts with the ab initio structure derived by Bemish et al. [38], where an angle of some 40° between the CO₂ axis and the C=C bond resulted. As in both calculations rather similar basis sets were used, this difference must be due to the use of the BSSE-corrected PES in our calculations. In view of the very low barrier towards internal rotation, 31 cm⁻¹ in the present calculations, the difference most likely is not as dramatic as the strongly different relative orientations of the monomers suggest. Fig. 1 shows the structure, together with the more relevant calculated structural parameters. The intermolecular distance, defined as the distance between the centers of mass of the two monomers, equals 3.38 Å, in good agreement with the experimental value of 3.43 Å [38].

The complexation energy calculated at this level equals $-5.81 \text{ kJ mol}^{-1}$, which puts the compound in the realm of



Fig. 1. MP2/6-311++G(2d,2p) equilibrium geometry for the complex of C_2H_4 with CO₂. The structural parameters obtained for the monomers are given between brackets.

weak complexes. In line with this, comparison of the structural data of the complex with those of the monomers, given in brackets in Fig. 1, shows that the complexation hardly influences the internal structures of the monomers.

It is clear from the above that the complex should preferably be discussed in terms of the symmetry group of the freely internally rotating structure. This is not a straightforward exercise, the more so because the energetic feasibility of other internal rotations, like the one of the ethene moiety around the C=C axis, is unknown. Therefore, and in view of the very limited number of complex modes observed (vide infra), we have chosen to take the low road and not to touch upon symmetry aspects of the complex. The very weak coupling between vibrational modes localized in different moieties of the complex allows, with the exception of the van der Waals modes, an unambiguous correlation of monomer and complex modes. Therefore, vibrational modes of the complex that are localized in one of the monomers will be identified with the Herzberg number and symmetry of the corresponding monomer mode.

The harmonic vibrational frequencies and infrared intensities calculated for the monomers and for the complex have been collected in Table 1. In agreement with the weakness of the complex, only minor shifts of the monomer frequencies upon complexation are predicted. For example, the predicted shift for $\nu_{9}^{C_2H_4}$ equals 0.1 cm⁻¹, which must be

Table 1

MP2/6-311++G(2d,2p) vibrational frequencies (cm^{-1}) and infrared intensities $(km mol^{-1})$ for C_2H_4 ·CO₂, C_2H_4 and CO₂

		Monomer		Complex		
		ν	Int.	ν	Int.	$\Delta \nu$
C_2H_4 s	ubmolect	ule				
Ag	ν_1	3198.4	0.0	3197.9	0.0	-0.5
Ag	ν_2	1681.2	0.0	1678.1	0.0	-3.1
Åg	ν_3	1384.5	0.0	1383.4	0.0	-1.1
Au	ν_4	1070.8	0.0	1071.8	0.0	1.0
B_{1g}	ν_5	3270.2	0.0	3270.3	0.0	0.1
B_{1g}	ν_6	1245.7	0.0	1244.9	0.0	-0.8
B _{1u}	ν_7	974.3	99.0	977.2	105.7	2.9
B_{2g}	ν_8	913.0	0.0	910.0	0.2	- 3.0
B _{2u}	ν_9	3296.8	14.8	3296.9	11.4	0.1
B_{2u}	ν_{10}	834.8	0.1	833.7	0.1	- 1.1
B_{3u}	ν_{11}	3179.6	10.4	3179.5	7.0	-0.1
B_{3u}	ν_{12}	1493.1	8.8	1492.9	8.3	-0.2
$^{12}CO_{2}$	submoled	cule				
$\sigma_{\rm u}$	ν_1	2403.0	286.5	2403.7	483.3	0.7
σ_{g}	ν_2	1320.5	0.0	1321.6	0.0	1.1
π_{u}°	ν_{3a}	665.6	21.9	666.1	19.0	0.5
π_{u}	ν_{3b}	665.6	21.9	657.0	33.0	- 8.6
van de	r Waals r	nodes				
				74.1	0.0	
				71.4	0.3	
				63.7	0.0	
				55.0	0.0	
				7.2	0.0	

compared with the shift of 0.843 cm^{-1} derived from the high resolution infrared study [38]. A more significant influence is calculated for the bending mode of the CO₂ moiety: upon complexation, the degeneracy of this mode is lifted, one component giving rise to a small blue shift of 0.5 cm^{-1} , the other red-shifting by 8.6 cm^{-1} . At this stage the possibility must be considered that the predicted splitting of the bending mode is an artefact of the semi-rigid structure assumed in the ab initio force field calculations. Simple arguments, however, show that this is not the case. Thus, in view of the very low internal rotation barrier, the bending mode localized in the plane perpendicular to the internal rotation axis will be hardly influenced by the presence of the ethene molecule, while the opposite is true for the other bending mode, in which the atoms of the CO₂ molecule move back and forth the ethene molecule. Hence, also in the freely internally rotating complex the two CO₂ bending modes must have different frequencies. Refering to the symmetry plane of the global minimum structure of the complex, the former can be described as the out-of-plane bending, and the latter as the inplane bending. A similar splitting of the bending mode has been observed for other complexes of CO_2 [14–16], and also for solutions of CO₂ in certain strong Lewis bases such as tertiary amines and dimethyl sulfoxide [4,11]. For the complex of CO₂ with dimethyl ether [14], the corresponding shifts are 4.9 and -12.1 cm⁻¹, and the ab initio complexation energy, at the same level, equals $-13.06 \text{ kJ mol}^{-1}$, which makes clear that the complexation shifts of these modes are related to the strength of the complex.

3.2. Vibrational spectra

Due to the limited solubility of CO₂ at lower temperatures, measurable fractions of complexes can be obtained only by using a large excess of C₂H₄. Therefore, in all experiments, the mole fraction of C₂H₄ was chosen to be much higher than that of CO₂, typical values being in the order of 10^{-2} for C₂H₄ and 10^{-4} for CO₂. In Fig. 2, the $\nu_3^{CO_2}$ region recorded for a mixed solution

In Fig. 2, the $\nu_3^{CO_2}$ region recorded for a mixed solution with mole fractions $x_{CO_2} = 2.0 \times 10^{-4}$ and $x_{C_2H_4} = 1.8 \times 10^{-2}$, studied at temperatures between 88 and 98 K, and that of a solution containing only ¹²CO₂ are compared. Apart from the 664.3 cm⁻¹ monomer band, in the spectra of the mixed solution a new band appears at 659.8 cm⁻¹. This band is not observed in the spectra containing only ¹²CO₂ or C₂H₄, and we assign it to the in-plane CO₂ bending of 1:1 complex C₂H₄.¹²CO₂. A similar band is observed for solutions containing C₂H₄ and ¹³CO₂: on the low frequency side of the 645.5 cm⁻¹ monomer band, the new band is being observed at 640.9 cm⁻¹.

It must be stressed that even at the lowest temperatures studied, no evidence was found for the occurence of a complex band on the high frequency side of the $\nu_3^{CO_2}$ monomer band. It must, therefore, be concluded that the out-of-plane bending vibration of the complex occurs accidentally degenerate with the monomer mode.



Fig. 2. The CO_2 bending region for a solution in liquid argon contaning both C_2H_4 and CO_2 . From top to bottom, the temperature of the solution decreases, from 97 to 88 K. The bottom trace is the spectrum obtained for a solution containing only CO_2 . The tick mark interval on the vertical axis equals 0.5 absorbance units.

Close scrutiny of the regions of the spectra in which transitions due to ethene occur has yielded no bands due to the complex. This is explained by the large excess of ethene used in the experiments. It is clear from Fig. 2 that only a small fraction of the CO₂ used was converted into complex. Thus, with an excess by two orders of magnitude in ethene, the fraction of ethene converted into complex is very small. Compounded by the fact that complexation shifts for these modes likely are very small, as suggested by the ab initio calculations, this makes that complex bands due to transitions localized in the ethene moiety of the complex are completely overshadowed by the corresponding monomer bands. One way out is to look for complex bands due to modes that are symmetry-forbidden in the monomers, of which there are several in the present case. Some of these modes can acquire small but non-negligible induced intensities, and have been experimentally observed for other complexes [14,46]. In most of those cases, the intensity for a mode localized in the one moiety was induced by the dipole moment of the other moiety. In the present complex, however, both moieties lack a permanent dipole moment, so that infrared intensity must be quadrupole-induced. Combined with the weakness of the complex, and the ensuing larger distance between the monomers in the complex, this suggests that the induced modes will be very weak. This anticipation is supported by the ab initio data in Table 1, which show that a very small induced intensity is predicted for $\nu_{10}^{C_3H_4}$ only. Inspection of the spectra

recorded in this study corroborate this, as no induced bands could be detected.

3.3. Relative stability

The stability of the complex in LAr was established from temperature studies in which spectra were recorded at temperatures between 88 and 128 K. From these, the complexation enthalpy was determined using the Van't Hoff isochore. In this method, the complexation enthalpy $\Delta_{\text{LAr}}H^0$ is determined form the slope of the plot obtained by plotting the logarithm of the equilibrium constant, expressed in terms of band areas *I* of infrared bands assigned to the different species involved, against the inverse temperature *T*:

$$\ln\left(\frac{I_{\text{complex}}}{I_{\text{C}_{2}\text{H}_{4}} \times I_{\text{CO}_{2}}}\right) = -\frac{\Delta_{\text{LAr}}H^{0}}{T} + c^{\text{st}}$$
(1)

Because all observed C_2H_4 transitions overlap with the corresponding modes in the complex, the determination of the monomer band area $I_{C_2H_4}$ is not straightforward. Moreover, the 664.3 cm⁻¹ band is assigned to the bending vibration in monomer CO₂ as well as to the out-of-plane bending mode in the complex, and its band area cannot be used directly as a measure of the monomer intensity I_{CO_2} .

In was observed above that due to experimental circumstances, the large majority of the C₂H₄ molecules were not involved in complexe. Thus, the intensity contributions of the complex to bands due to transitions localized in the ethene moiety can be neglected without problem. Therefore, the areas of the $\nu_3^{C_2H_4} + \nu_{10}^{C_2H_4}$ and the $\nu_6^{C_2H_4} + \nu_{10}^{C_2H_4}$ combination bands at 2167.3 and 2042.8 cm⁻¹, respectively, determined by numerical integration, were used as $I_{C_2H_4}$.

In order to be used as a measure for I_{CO_2} , the area of the 664.3 cm⁻¹ band must be corrected for the presence of the out-of-plane bending mode of the complex. This was accomplished by relating the band areas of the in- and out-of-plane modes via Beer's law as:

$$I_{\rm oop} = \frac{\varepsilon_{\rm oop}}{\varepsilon_{\rm ip}} I_{\rm ip} \tag{2}$$

in which ε_{oop} and ε_{ip} are the infrared intensities of the outof-plane and the in-plane mode, respectively. Then, I_{CO_2} can be expressed as:

$$I_{\rm CO_2} = I_{664.3} - I_{\rm oop} = I_{664.3} - \frac{\varepsilon_{\rm oop}}{\varepsilon_{\rm ip}} I_{658.9}$$
(3)

in which $I_{664.3}$ and $I_{658.9}$ are the band areas of the experimental 664.3 and 658.9 cm⁻¹ bands, respectively. Unfortunately, no experimental value for the ratio $\varepsilon_{oop}/\varepsilon_{ip}$ is available, because the out-of-plane band was not observed in a separable manner.

Insight into the effect of this correction was gained by calculating $\Delta_{\text{LAr}} H^0$ as function of the value of $\varepsilon_{\text{oop}}/\varepsilon_{\text{ip}}$.

For this, $I_{\rm CO_2}$ was determined at each temperature via Eq. (3), with $I_{664.3}$ and $I_{658.9}$ determined from least squares band fitting, and with $I_{658.9}$ taken as $I_{\rm complex}$. The resulting complexation enthalpies are shown in Fig. 3. It can be seen that $\Delta_{\rm LAr}H^0$ changes from -4.2(2) kJ mol⁻¹ for $\varepsilon_{\rm oop}/\varepsilon_{\rm ip} = 0.0$ to -6.0(2)kJ mol⁻¹ for $\varepsilon_{\rm oop}/\varepsilon_{\rm ip} = 1.5$. It is clear that the influence of the out-of-plane bending mode is too big to allow the determination of a reliable enthalpy without information on the intensity ratio $\varepsilon_{\rm oop}/\varepsilon_{\rm ip}$. Here, the ab initio calculations come to the rescue, and we have used the predicted value for $\varepsilon_{\rm oop}/\varepsilon_{\rm ip}$, calculated from the data in Table 1. This choice can be justified as follows.

For the complex of CO_2 with dimethyl ether [14], the components of the bending doublet are observed well separated from the monomer mode and can be reliably integrated using least squares band fitting. This was preformed for a series of 20 spectra recorded at various temperatures and concentrations, and from the linear regression of $I_{\rm oop}$ against $I_{\rm ip}$, the ratio $\varepsilon_{\rm oop}/\varepsilon_{\rm ip}$ was found to be 0.48(2). Ab intio calculations on that complex [14] lead to infrared intensities of 22.6 and 49.7 km mol⁻¹ for the oop and ip bending modes, respectively. Their ratio, 0.46, is in excellent agreement with experiment. For weaker complexes the ratio must approach its value in the monomer, equal to 1.0. In line with this, for the present complex, the data in Table 1 result in $\varepsilon_{oop}/\varepsilon_{ip} = 0.57$. Thus, there is no reason why the ab intio ratio for the ethene complex should be less good than that for the dimethyl ether complex. Consequently, it may be assumed that a reliable value for the complexation enthalpy can be derived using the ab initio ratio.

In Fig. 4, Van 't Hoff plots obtained by using the ab initio ratio $\varepsilon_{oop}/\varepsilon_{ip} = 0.57$ are shown for two different temperature studies. The value for the complexation enthalpy, derived from linear regressions, averaged over the two experiments, and corrected for density variations of the solvent [47,48], is -4.9(1) kJ mol⁻¹.



Fig. 3. Complexation enthalpies for the complex of C_2H_4 with CO_2 as function of the intensity ratio $\varepsilon_{oop}/\varepsilon_{ip}$.



Fig. 4. Van 't Hoff plots for the complex of C_2H_4 with CO_2 observed in liquid argon. The monomer intensity I_{CO_2} required for the analysis was obtained by assuming an intensity ratio $\varepsilon_{oop}/\varepsilon_{ip}$ equal to 0.574. The plots were obtained using temperature studies of two different solutions, and using the band areas of the $\nu_3^{C_2H_4} + \nu_{10}^{C_2H_4}$ (top) and the $\nu_6^{C_2H_4} + \nu_{10}^{C_2H_4}$ (bottom) combination bands as a measure of the C_2H_4 monomer intensity.

The vapor phase complexation enthalpy, $\Delta_{vap}H^0$, can be obtained by correcting the solution value for solvation effects. This has been accomplished by Monte Carlo Free Energy Perturbation calculations, at different temperatures, using a procedure similar to that used before [14]. In short, the Monte Carlo calculations yield the solvation Gibbs energies $\Delta_{sol}G$, as function of the temperature. From these, the solvation entropies are calculated as $\Delta_{sol}S = -\partial(\Delta_{sol}G)/\partial A_{sol}G$ ∂T , while the solvation enthalpies are obtained as $\Delta_{sol}H =$ $\Delta_{\rm sol}G + T\Delta_{\rm sol}S$. The resulting enthalpies $\Delta_{\rm sol}H$ for a solution in LAr are -13.1(2) kJ mol⁻¹ for C₂H₄, -16.8(3) kJ mol⁻¹ for CO₂ and -29.8(2) kJ mol⁻¹ for C₂H₄·CO₂. Combining these values with the experimental $\Delta_{\text{LAr}}H^0$ yields a vapor phase complexation enthalpy $\Delta_{\text{vap}}H^0$ equal to -5.1(4) kJ mol⁻¹. Comparison with the value in LAr shows that there is hardly a solvation influence on the complexation enthalpy. This is surprising, because for sterical reasons the monomers must give up an important fraction of their solvation in order to form a complex. It follows that the interaction of the complex with solvent atoms from the solvation sphere must be stronger than in the monomers. A possible explanation for this is offered by induced dipole moment in the complex. For the global minimum, the ab initio calculations predict a dipole moment of 0.17 D, while for the structure in which the CO_2 axis is at right angle to the C=C bond the calculated value is 0.16 D. In both cases the dipole moment is oriented along the axis connecting the monomer centers of mass, and the similarity of the two values suggest that also for free internal

Table 2 BSSE-corrected complexation energies for C_2H_4 ·CO₂

MP2 = FULL/6-311 + +G(2d,2p)	175 bf	- 5.81 kJ mol ⁻¹
MP2 = FULL/aug-cc-PVDZ	151 bf	$-6.54 \text{ kJ mol}^{-1}$
MP2 = FULL/aug-cc-PVTZ	322 bf	$-7.38 \text{ kJ mol}^{-1}$
MP2 = FULL/aug-cc-PVQZ	584 bf	$-7.72 \text{ kJ mol}^{-1}$
<i>.</i>		



Fig. 5. Extrapolation of the calculated complexation energies obtained for the complex of C_2H_4 with CO_2 . The complexation energies obtained by using the different basis sets, and the number of basis functions in each calculations were taken from Table 2.

rotation states of the complex a similar dipole moment will be present. This relatively small but not insignificant dipole moment, and the absence of a permanent dipole moment in the monomers, will certainly contribute to the increased solute/solvent interaction for the complex. Then, the Monte carlo calculations show that this very nearly compensates the sterical loss of solvation.

In a next step $\Delta_{vap}H^0$ was converted into an 'experimental' complexation energy $\Delta_{exp}E$ by correcting for thermal effects, using statistical thermodynamics. Zero-point vibrational energies and thermal vibrational contributions for the different species were calculated using the ab initio frequencies. Thermal contributions were calculated at 96 K, i.e. at the midpoint of the temperature intervals used to determine $\Delta_{LAr}H^0$. Translational and rotational contributions were obtained in the classical limit. These calculations yielded a correction of 1.6 kJ mol⁻¹, and result in a complexation energy $\Delta_{exp}E$ equal to -6.8(8) kJ mol⁻¹. As before [14], the uncertainty on this number was taken to be twice the experimental value, to account for the approximations made while transforming the liquid phase complexation enthalpy into a vapor phase complexation energy.

It is of interest to compare $\Delta_{exp}E$ with theoretical data obtained from ab initio calculations. $\Delta_{exp}E$ is somewhat larger than the MP2 = FULL/6-311++G(2d,2p) value of -5.8 kJ mol⁻¹. This is in line with previous results showing that at the level used, the CP-corrected complexation energies tend to be underestimated, most likely due to a basis set incompletness error.

The effect of the size of the basis set on the complexation energy was investigated by performing single point calculations at the MP2/aug-cc-PVXZ (with X = D, T and Q) level, using the MP2/6-311++G(2d,2p) geometries. The resulting energies are collected in Table 2. It can be seen that enlarging the basis set from aug-cc-PVDZ to augcc-PVQZ increases the complexation energy by 18%. The influence of a further increase of the basis set was obtained by extrapolation of the plot of the complexation energies for the aug-cc-PVXZ (X = D, T and Q) levels as a function of 1/n, in which *n* is the number of basis functions. The plot and the linear regression line are shown in Fig. 5. The abscissa of the linear regression line, -8.1(2) kJ mol⁻¹, gives the energy for an infinite basis set and can be considered as the basis set limit. This value is in acceptable agreement with the experimental value of of -6.8(8) kJ mol⁻¹.

Acknowledgements

S.N.D. thanks the FWO-Vlaanderen for an appointment as a research assistant. Gratitude is expressed to the FWO-Vlaanderen for their assistance toward the purchase of spectroscopic equipment used in this study. The authors thank the Flemish Community for financial support through the Special Research Fund (BOF).

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