The proton-bound complex Cl⁻···H-CCl₃: A high-level theoretical study

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Abstract

Large-scale coupled cluster calculations within variant CCSD(T) have been employed to study major portions of the potential energy and electric dipole moment surfaces for the hydrogen-bonded anionic complex Cl⁻···H-CCl₃. The recommended dissociation energy D_0 is 6280 cm⁻¹ or 75.1 kJ mol⁻¹, with an estimated error of ca. 1%. Upon complex formation, the weak CH stretching vibration (ν_1) of free HCCl₃ experiences an intensity enhancement by four orders of magnitude, with anharmonicity effects playing an important role. The band origins of the ν_1 bands of ^{35}Cl⁻···H-C^{35}Cl₃ and ^{35}Cl⁻···H-D^{35}Cl₃ are calculated at 2553 and 1949 cm⁻¹, respectively.
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1. Introduction

During the past decade, the spectroscopic investigation of charged complexes in the gaseous phase has made great progress. In an increasingly larger number of cases, at least partial rotational resolution could be achieved such that some structural information was obtainable (see Refs. [1,2] for recent reviews). The majority of charged complexes, which have been spectroscopically studied so far, carries a positive charge. Comparable work on anion complexes is still scarce. Noteworthy exceptions are studies of the complexes formed between halide ions and water, ammonia, acetylene, methane and hydrogen molecules (see Ref. [2] and references therein). Likewise, only a limited number of high-quality theoretical investigations which include the effects of vibrational anharmonicity, have been published for such negatively changed species. Our previous work [3–5] concentrated on complexes of type Hal⁻···HCCH, where Hal denotes one of the halogen atoms F–I. Making use of the coupled cluster variant CCSD(T) [6] with large basis sets of at least aug-cc-pVQZ quality [7–9] and taking important anharmonicity effects into account in variational calculations of vibrational states and transition dipole moments among them, excellent agreement with experiment [10–13] could be achieved and var-

ious predictions could be made. The experimental work was restricted to complexes of the heavier halide ions (Cl⁻, Br⁻ and I⁻) with acetylene. According to our previous work [3], the complex formed between F⁻ and HCCH is too strongly bound to be directly accessible to infrared predissociation (IRPD) spectroscopy.

Already in the case of Cl⁻···HCCH, the predicted dissociation energy ($D_0 \approx 3600$ cm⁻¹) [5] is significantly larger than one quantum of either of the two CH stretching vibrations (ν_1 or ν_2) and only a broad, rotationally unresolved band could be observed by IRPD spectroscopy [11], not allowing for a precise determination of the wavenumber of the hydrogen-bonded CH stretching vibration (ν_2). However, making use of a technique introduced by Johnson and co-workers termed argon predissociation spectroscopy [14,15], Bieske was able to get an estimate for ν_2 (Cl⁻···HCCH) of 2876 ± 5 cm⁻¹ (E.J. Bieske, private communication), in complete agreement with our theoretical result [5].

A more strongly bound binary anionic complex than Cl⁻···HCCH is provided by the complex formed between a chloride ion and a chloroform molecule, i.e., Cl⁻···H-CCl₃. This species appears to be an interesting link between relatively weakly bound Cl⁻···HA complexes, such as Cl⁻···H-CH₃ [16–18] and very strongly bound ClHCl⁻ [19,20], in which the proton is shared by the two chloride ions. To the authors' knowledge, surprisingly little is known about Cl⁻···H-CCl₃. Indeed, we were able to find only one study which reports results of

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a mass-spectrometric investigation including $CHCl_4^-$ ions as products of gas-phase reactions of the CH_2S^- radical anion [21]. In that paper, thermochemical data compiled by Lias et al. [22] were employed to give an estimate of the dissociation energy of $CHCl_4^-$ of $\approx 65\,kJ\,mol^{-1}$ or $\approx 5400\,cm^{-1}$.

The present paper reports the results of a rather elaborate theoretical study of the anionic complex $Cl^- \cdots H\text{-}CCl_3$. Like in our last paper on $Cl^- \cdots HCCH$ [5], particular emphasis will be given to an accurate prediction of the dissociation energy D_0, which measures the energy difference between fragments $Cl^- + HCCl_3$ and the complex $Cl^- \cdots H\text{-}CCl_3$ in their vibrational ground states. Furthermore, the effects of vibrational anharmonicity on the totally symmetric vibrations of $^{35}Cl^- \cdots H\text{-}C^{35}Cl_3$ and $^{35}Cl^- \cdots D\text{-}C^{35}Cl_3$ will be investigated in considerable detail, with particular attention being given to the rarely studied field of anharmonicity contributions to absolute infrared intensities.

2. Details of calculations

Most of the electronic structure calculations of the present work make use of coupled cluster theory at the CCSD(T) level [6], which accounts for the effects of connected triple substitutions by means of perturbation theory. With this method, larger portions of the potential energy surfaces for $HCCl_3$ and $Cl^- \cdots H\text{-}CCl_3$ have been computed. In addition, results of single-point calculations will be reported for five further methods: Hartree–Fock Self Consistent Field (HF-SCF), second order perturbation theory according to Møller and Plesset (MP2) and its spin-component scaled variant (SCS-MP2) as introduced by Grimme [23], coupled cluster with single and double excitation operators (CCSD) and another variant including connected triples in a perturbative way termed CCSD-T [24]. Throughout, valence electrons were correlated in the post-Hartree–Fock calculations which were carried out with the MOLPRO suite of programs [24–26].

The majority of the CCSD(T) calculations of the present work employ the aug-cc-pVQZ basis of Dunning and co-workers [7–9]. For the chlorine atom, a modification is employed in which the four sets of d functions are replaced by five [27]. In the original paper, this chlorine basis is termed aug-cc-pV$(Q+d)$Z. For brevity, we will uniformly denote the basis set for the whole complex and its fragments by "avqz-mod". Single-point calculations were also carried out with the corresponding smaller and larger basis sets which are denoted as "avtz-mod" and "av5z-mod", some MP2 calculations also with the conventional aug-cc-pVTZ basis.

The familiar harmonic approximation for the treatment of molecular vibrations, which is currently still the method of choice in the majority of quantum chemical studies, quite frequently finds its limits in the investigation of spectroscopic properties of molecular complexes. On the other hand, the efforts in going beyond that approximation in order to arrive at very accurate results may be very high and so some sort of compromise may be appropriate. In the present work, we therefore make no attempt to arrive at a quantitative treatment of the 12-dimensional anharmonic vibrational problem. Instead, we

concentrate on an approximate treatment of those vibrations of the chloroform molecule which are expected to undergo most noticeable changes upon forming the complex $Cl^- \cdots H\text{-}CCl_3$, in particular as far as the change in absolute IR intensities is concerned. Since the chloroform molecule and the hydrogen-bonded complex have the same symmetry in their energetically most favourable nuclear configurations (C_{3v} symmetry), we are tempted to give most attention to the totally symmetric vibrations of a_1 symmetry.

Like in previous work of the corresponding author and his coworkers (see, e.g., Refs. [28,29]), effects of vibrational anharmonicity were taken variationally into account for the N totally symmetric (a_1) vibrational modes by means of the approximate vibrational Hamiltonian

$$\hat{H}_{vib} = \frac{-\hbar^2}{2} \sum_{i=1}^{N} \frac{\partial^2}{\partial Q_i^2} + V_{anh} \quad (Q_i : \text{normal coordinates}) \quad (1)$$

as incorporated in the program C3VVIB (author: P. Botschwina). This approach is comparable to our recent studies of hydrogen-bonded complexes of type rare gas-linear cation or $Hal^- \cdots HCCH$ [3–5]. The analytical anharmonic potential energy function V_{anh} employed for the anionic complex was obtained by least-squares fit to 282 CCSD(T) energy points (under the restriction of C_{3v} symmetry), making use of the avqz-mod basis. As checked by numerous tests, it gives a faithful representation up to energies of ca. $10{,}000\,cm^{-1}$ above equilibrium.

The calculation of absolute IR intensities for transitions among vibrational states involving only a_1 modes requires the knowledge of three- or four-dimensional electric dipole moment surfaces (EDMFs) for $CHCl_3$ and $Cl^- \cdots H\text{-}CCl_3$, respectively. These were also constructed from CCSD(T)/avqz-mod electric dipole moments, using 39 data for the neutral molecule and 119 data for the anionic complex. In the latter case, dipole moments were evaluated in the center-of-mass coordinate system. Since C_{3v} symmetry is maintained in all of the calculations, only the z component of the dipole moment has non-vanishing values. Making use of analytical EDMFs for μ_z, absolute IR intensities arising from the vibrational ground state are calculated according to the formula

$$A_{f0} = \left(\frac{\pi N_A}{3\hbar c \varepsilon_0} \right) \tilde{\nu}_{f0} |\langle \psi_f | \mu_z | \psi_0 \rangle|^2. \quad (2)$$

In Eq. (2), the vibrational wavefunctions of the ground state and the final state are denoted by ψ_0 and ψ_f, respectively, and $\tilde{\nu}_{f0}$ is the wavenumber of the transition between these states. Common symbols are used for the fundamental physical constants.

3. Results and discussion

3.1. Equilibrium structure, equilibrium dipole moment and equilibrium dissociation energy

After initial MP2 calculations with the aug-cc-pVTZ basis set, which established the expected C_{3v} equilibrium structure for hydrogen-bonded $Cl^- \cdots H\text{-}CCl_3$, the equilibrium geometri-
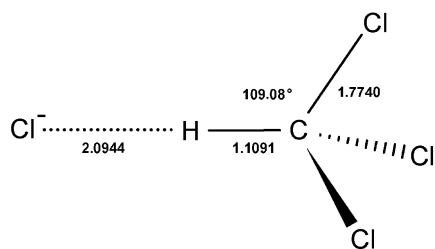
Fig. 1. Equilibrium structure of $Cl^-\cdots H\text{-}CCl_3$ (CCSD(T)/avqz-mod).

cal parameters of the complex and free $HCCl_3$ were determined by CCSD(T) with the larger basis termed "avqz-mod" (see Section 2). The results are displayed in Fig. 1. The intermolecular equilibrium distance $R_{Cl^-\cdots H}$ is obtained to be 2.0944 Å, to be compared with a value of 2.2526 Å as obtained for $Cl^-\cdots HCCH$ from CCSD(T) calculations with the aug-cc-pVQZ basis set [3]. Upon formation of the hydrogen bond, the intramolecular CH equilibrium distance experiences an elongation by 0.0267 Å, slightly shorter than the value of 0.0286 Å as obtained for $Cl^-\cdots HCCH$. The three equivalent CCl equilibrium bond lengths increase by 0.0095 Å when the complex is formed and the HCCl equilibrium angles change from $107.96°$ for free $HCCl_3$ to $109.08°$ in the hydrogen-bonded complex.

The equilibrium dipole moment of $^{35}Cl^-\cdots H\text{-}C^{35}Cl_3$, evaluated within the corresponding center-of-mass coordinate system, is μ_e(CCSD(T)/avqz-mod) = 9.453 D. The sign convention is such that the negative end of the dipole is located at the Cl^- site. Electron correlation makes only a minor contribution to μ_e, since the calculated Hartree–Fock value is 9.572 D and thus only 1.3% larger than the CCSD(T) value. The complex under discussion is a prolate symmetric top, with calculated equilibrium rotational constants of $A_e = 1713.7$ MHz and $B_e = 962.8$ MHz. The corresponding CCSD(T)/aug-mod values for free $HC^{35}Cl_3$, an oblate symmetric top, are $B_e = 3294.7$ MHz and $C_e = 1710.4$ MHz. Experimentally derived values for the ground-state rotational constants of $HC^{35}Cl_3$ are $B_0 = 3302.1$ MHz [30] and $C_0 = 1714.0$ MHz [31], the latter being an indirect value calculated by making use of experimental data for an asymmetrically substituted isotopomer.

CCSD(T) calculations with the avqz-mod basis set predict an equilibrium dissociation energy (D_e) for the process $Cl^-\cdots H\text{-}CCl_3 \rightarrow Cl^- + HCCl_3$ of 6325 cm^{-1} or 75.6 kJ mol^{-1}. This value is uncorrected for the so-called basis set superposi-
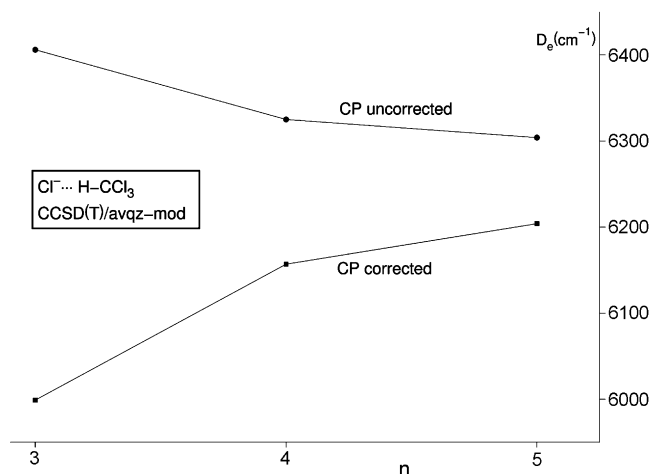

Fig. 2. Variation of the CCSD(T) equilibrium dissociation energy with the size of the basis set, denoted by cardinal number n.

tion error (BSSE) and, according to our experience with other anionic hydrogen-bonded systems [4,5], is considered to be an overestimate. Consideration of the BSSE is always an issue if one aims at high accuracy of intermolecular dissociation energies in the context of traditional quantum-chemical calculations operating with delocalized molecular orbitals and one-electron basis functions. In order to study the basis set dependence of D_e and the significance of BSSE in more detail, we have made a series of calculations with three different basis sets and six different methods, the results of which are collected in Table 1. In all of these calculations, which make use of the familiar counterpoise (CP) procedure of Boys and Bernardi [32], the optimized CCSD(T)/avqz-mod geometrical parameters of $Cl^-\cdots HCCl_3$ (see Fig. 1) and $HCCl_3$ (see the text) have been employed. Like in our previous work on $I^-\cdots HCCH$, $Br^-\cdots HCCH$ and $Cl^-\cdots HCCH$ [4,5], CP uncorrected and CP corrected CCSD(T) values for D_e are also plotted in Fig. 2 as a function of cardinal number n, this time for basis sets of type avnz-mod. Again the CP corrected data show smooth monotonic behaviour. Provided that a similar situation applies as for $Cl^-\cdots HCCH$ (see Fig. 1 of Ref. [5]), the CP uncorrected data should show a stronger decrease in D_e when going from $n = 5$ to 6 compared to $4 \rightarrow 5$. For $n \rightarrow \infty$, both CP uncorrected and CP corrected data have to arrive at the same limit and so a value of $D_e\,(\infty) \approx 6240$ cm^{-1} appears to be reasonable (see also below).

Table 1
Equilibrium dissociation energies D_e (in cm^{-1}) of $Cl^-\cdots H\text{-}CCl_3$

Method	avtz-mod		avqz-mod		av5z-mod	
	CP uncorrected	CP corrected	CP uncorrected	CP corrected	CP uncorrected	CP corrected
HF-SCF	4476	4453	4436	4431	4432	4431
MP2	6589	6189	6540	6317	6525	6371
SCS-MP2	6108	5662	6053	5799	6034	5857
CCSD	6025	5657	5943	5794	5920	5831
CCSD-T	6401	5994	6321	6153	6300	6200
CCSD(T)	6406	5999	6325	6157	6304	6204

All calculations are carried out at the CP uncorrected CCSD(T)/avqz-mod equilibrium structures: (1) $HCCl_3$: r_e(CH) = 1.0824 Å, β_e(HCCl) = 107.96° and R_e(CCl) = 1.7645 Å. (2) $Cl^-\cdots H\text{-}CCl_3$: see Fig. 1.

Upon inspection of the values given in Table 1, very similar results are obvious for the two coupled cluster variants CCSD(T) and CCSD-T. Compared to these two methods, the MP2 calculations provide overestimates of D_e by ca. 3%, whereas SCS-MP2 and CCSD lead to underestimates between 5 and 7%. At the HF-SCF level, convergence of the D_e value within 1 cm^{-1} appears to have been achieved with basis set av5z-mod. We therefore take the Hartree–Fock contribution to the equilibrium dissociation energy as $D_e^{\text{HF}} = 4432 \text{ cm}^{-1}$. From the data given in the first and the last columns of Table 1, we may get estimates of the basis set limit of the CCSD(T) valence correlation energy contribution to D_e, termed $\Delta D_e^{\text{corr}}(\infty)$. The individual contributions $\Delta D_e^{\text{corr}}(n)$ for $n = 3$–5 are 1546, 1726 and 1773 cm^{-1}. Unfortunately, the performance of common extrapolation schemes has not yet been tested in detail for anionic hydrogen-bonded complexes. A simple two-point formula assuming a n^{-3} dependence of $\Delta D_e^{\text{corr}}(n)$ as suggested by Halkier et al. [33] produces $\Delta D_e^{\text{corr}}(\infty) = 1822 \text{ cm}^{-1}$ and thus $D_e(\infty) = 6254 \text{ cm}^{-1}$, when the results for $n = 4$ and 5 are employed. A three-parameter extrapolation formula which makes use of a $(n + \gamma)^{-3}$ dependence was discussed by Huh and Lee [34]. Adjusting all three parameters to the $\Delta D_e^{\text{corr}}(n)$ values quoted above, one arrives at $\Delta D_e^{\text{corr}}(\infty) = 1809 \text{ cm}^{-1}$ and consequently $D_e(\infty) = 6241 \text{ cm}^{-1}$. Of course, other extrapolations are possible as well, but we think that $D_e(\infty) \approx 6240 \text{ cm}^{-1}$ should be reasonably accurate. Remaining errors in the calculations which arise from the use of an incomplete coupled cluster expansion, the neglect of core–valence and core–core correlation and relativistic effects should not exceed 15 cm^{-1}. In summary, we recommend $D_e (\text{Cl}^- \cdots \text{H-CCl}_3) = 6240 \pm 25 \text{ cm}^{-1}$.

3.2. Spectroscopic properties within the harmonic approximation

The totally symmetric vibrations of $\text{Cl}^- \cdots \text{H-CCl}_3$ and chloroform were first studied within the (double) harmonic (DH) approximation which requires the knowledge of the corresponding quadratic force constants and the first dipole moment derivatives, both taken at equilibrium. For this purpose, we make use of symmetry coordinates defined as follows:

$$S_1 = \Delta r \quad \text{CH stretch} \tag{3a}$$

$$S_2 = \frac{1}{\sqrt{3}}(\Delta R_1 + \Delta R_2 + \Delta R_3) \quad \text{symmetric CCl}_3 \text{ stretch} \tag{3b}$$

$$S_3 = \frac{1}{\sqrt{3}}(\Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3) \quad \text{symmetric HCCl bend} \tag{3c}$$

$$S_4 = \Delta \tilde{R} \quad \text{intermolecular stretch} \tag{3d}$$

The quadratic force constants are defined as

$$F_{ij} = \left(\frac{\partial^2 V}{\partial S_i \partial S_j} \right)_e \tag{4}$$

Their numerical values as obtained by CCSD(T) with the avqz-mod basis set are listed in Table 2 together with the first dipole

moment derivatives. Upon complex formation, the CH stretching force constant F_{11} experiences a reduction by 15.2%. The other two diagonal force constants F_{22} and F_{33} are also reduced, but by only 6.6 and 2.5%, respectively. For both species, the coupling force constants involving the CH stretching coordinate, F_{12} and F_{13}, are rather small. Since the diagonal G matrix element G_{11} of HCCl_3 is also much larger than the off-diagonal elements G_{12} and G_{13}, the totally symmetric normal vibration of chloroform with highest wavenumber may well be described as a local CH stretching vibration. Owing to the small value of -0.0490 e calculated for $(\partial \mu_z / \partial S_1)_e$, the DH approximation yields a small value of 1.1 km mol^{-1} for the absolute IR intensity of this vibration (see Table 3). Although the corresponding dipole moment derivative for the anionic complex is even smaller, the intensity is calculated to be as high as 1150 km mol^{-1}. In the complex, as common to hydrogen-bonded systems, we have strong kinematic coupling between CH stretching and intermolecular stretching and thereby the hydrogen-bonded CH stretching vibration aquires practically all of its intensity from the intermolecular stretching part of the electric dipole moment function which, in the DH approximation, is merely a linear one-dimensional function involving $(\partial \mu / \partial S_4)_e = 1.1374 \text{ e}$ (see Table 2). As will be seen in Section 3.3, "electrical anharmonicity" will have a very substantial effect on the intensity of the hydrogen-bonded CH stretching vibration.

3.3. Anharmonic treatment of the totally symmetric vibrations

Upon inspection of the underlying CCSD(T)/avqz-mod potential energy surface for $\text{Cl}^- \cdots \text{H-CCl}_3$, the largest degree of anharmonicity (i.e., deviations from the quadratic force field, Section 3.2) is apparent for a two-dimensional cut through the hypersurface which involves coordinates $\Delta \tilde{R}$ and Δr. The corresponding contour diagram, which covers the range -0.8 Å

Table 2

Quadratic force constants and first dipole moment derivatives for totally symmetric vibrations of HCCl_3 and $\text{Cl}^- \cdots \text{H-CCl}_3$ (CCSD(T)/avqz-mod)

	HCCl_3	$\text{Cl}^- \cdots \text{H-CCl}_3$[a]
F_{11}	0.354541	0.300575
F_{22}	0.273616	0.255500
F_{33}	0.511364	0.498407
F_{12}	0.008191	−0.000009
F_{13}	0.004649	−0.005973
F_{23}	−0.046218	−0.068999
F_{44}		0.021832
F_{14}		0.024449
F_{24}		0.004070
F_{34}		0.005764
$(\partial \mu_z / \partial S_1)_e$	−0.0490	0.0144
$(\partial \mu_z / \partial S_2)_e$	−0.1013	−0.1320
$(\partial \mu_z / \partial S_3)_e$	−0.3261	0.6609
$(\partial \mu_z / \partial S_4)_e$		1.1374

All values are given in atomic units.

[a] First dipole moment derivatives are calculated in the center-of-mass coordinate system for $^{35}\text{Cl}^- \cdots \text{H-C}^{35}\text{Cl}_3$.

Table 3
Harmonic wavenumbers (in cm^{-1}) and absolute IR intensities (in $km\,mol^{-1}$; in parentheses) for totally symmetric vibrations of $HCCl_3$, $Cl^- \cdots H\text{-}CCl_3$ and the corresponding deuterated species (CCSD(T)/avqz-mod)

Band	$HC^{35}Cl_3$	$^{35}Cl^- \cdots H\text{-}C^{35}Cl_3$	$DC^{35}Cl_3$	$^{35}Cl^- \cdots D\text{-}C^{35}Cl_3$
$\omega_1(\sim CH, CD)$	3175 (1.1)	2803 (1150)	2337 (0.1)	2075 (540)
$\omega_2(\sim CCl_3$ symmetric stretching)	683 (3.8)	657 (64)	664 (3.5)	634 (64)
$\omega_3(\sim CCl_3$ symmetric bend)	371 (0.3)	374 (6.9)	368 (0.3)	372 (7.6)
ω_s (intermolecular stretching)		140 (41)		140 (41)

$\Delta \tilde{R} \leq 4\,\text{Å}$ and $-0.3\,\text{Å} \leq \Delta r \leq 0.8\,\text{Å}$ and includes relative energies with respect to the energy minimum at $\Delta \tilde{R} = \Delta r = 0$ up to $10{,}000\,cm^{-1}$ (or $119.6\,kJ\,mol^{-1}$), is shown in Fig. 3. Already for the first contour line at $400\,cm^{-1}$, the deviation from an ellipse (which would correspond to the harmonic approximation of the potential) is clearly obvious. The highest almost closed contour line at $5600\,cm^{-1}$ extends to $(\Delta \tilde{R}, \Delta r)$ values of ca. $(4.0\,\text{Å}, 0.36\,\text{Å})$, far off from the corresponding situation for the harmonic limit.

While spectroscopists talk of "mechanical anharmonicity" when deviations of the potential from the quadratic (harmonic) shape are considered, non-linearity of the electric dipole moment function (EDMF) is denoted as "electrical anharmonicity". Like in the DH approximation dealt with in Section 3.2, the variation of the electric dipole moment ($\Delta \mu$) with the intermolecular stretching vibrational coordinate $\Delta \tilde{R}$ plays the major role. However, as is shown in Fig. 4, plots of $\Delta \mu (\Delta \tilde{R})$ for four different values of Δr show both a significant deviation from linearity and a significant dependence on Δr. Curves showing $\Delta \mu$ as a function of the CH stretching coordinate Δr, with all other coordinates kept fixed at their equilibrium values, are displayed in Fig. 5. Both are very flat around $\Delta r = 0$ and show highly non-linear character.

Results of the dimensionality-reduced variational calculations for $HCCl_3$, $Cl^- \cdots H\text{-}CCl_3$ and the corresponding deuterated species are given in Table 4. Good agreement with experimental gas-phase values is observed for the totally sym-
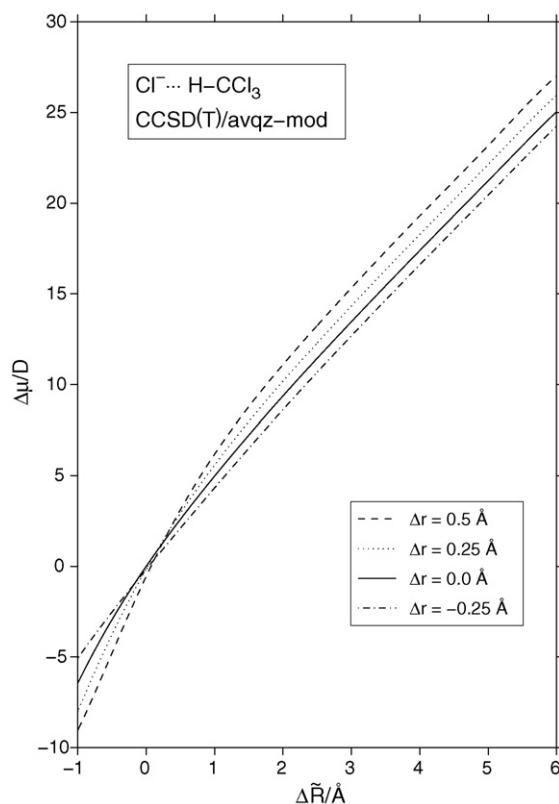

Fig. 4. Variation of the electric dipole moment of $^{35}Cl^- \cdots H\text{-}C^{35}Cl_3$, evaluated in the center-of-mass coordinate system, with the intermolecular stretching coordinate $\Delta \tilde{R}$ (for four different values of Δr, the CH stretching coordinate).

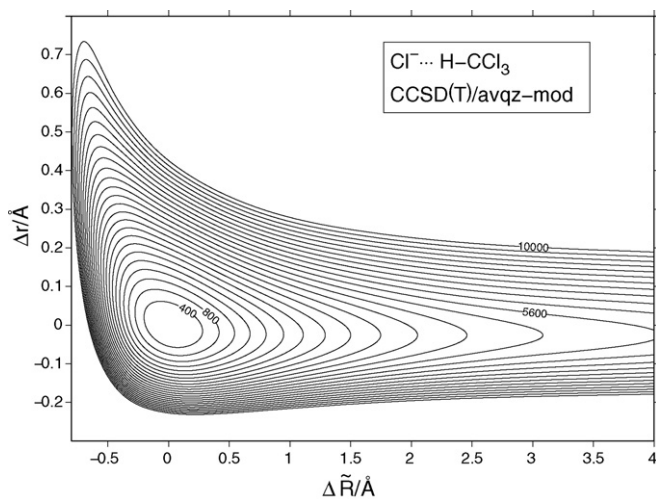
Fig. 3. Dependence of the CCSD(T)/avqz-mod potential energy surface of $Cl^- \cdots H\text{-}CCl_3$ on the intermolecular coordinate $\Delta \tilde{R}$ ($Cl^- \cdots H$) and the CH stretching coordinate Δr.
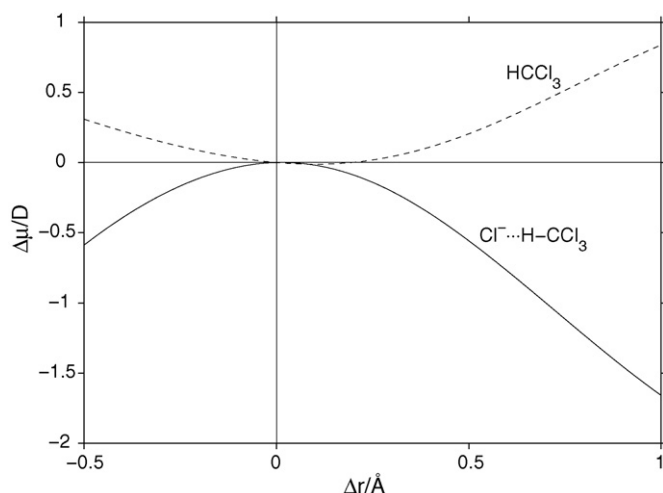

Fig. 5. Variation of the electric dipole moment with the CH stretching coordinate Δr for $HCCl_3$ (upper curve) and $^{35}Cl^- \cdots H\text{-}C^{35}Cl_3$ (lower curve).

Table 4
Anharmonic wavenumbers (in cm^{-1}) and absolute IR intensities (in km mol^{-1}; in parentheses) for totally symmetric vibrations of HCCl$_3$, Cl$^-$···H-CCl$_3$ and the corresponding deuterated species (CCSD(T)/avqz-mod)

Band	HC^{35}Cl$_3$[a]	^{35}Cl$^-$···H-C^{35}Cl$_3$	DC^{35}Cl$_3$[b]	^{35}Cl$^-$···D-C^{35}Cl$_3$
ν_1	3047 (0.3)	2553 (5745)	2268 (0.01)	1949 (2691)
ν_2	679 (3.9)	647 (290)	661 (3.6)	625 (276)
ν_3	370 (0.3)	375 (32)	367 (0.3)	372 (33)
ν_s		142 (71)		141 (69)
$\nu_1 + \nu_s$		2706 (104)		2096 (15)

[a] Experimental values: $\nu_1 = 3032.9$ cm^{-1} [35], $\nu_2 = 676.6$ cm^{-1} [36] and $\nu_3 = 367.3$ cm^{-1} [37].
[b] Experimental values: $\nu_1 = 2264.8$ cm^{-1} [38], $\nu_2 = 657.6$ cm^{-1} [38] and $\nu_3 = 364.2$ cm^{-1} [38].

metric fundamentals of HC^{35}Cl$_3$ and DC^{35}Cl$_3$. The largest error of the present calculations (14.6 cm^{-1}) occurs for ν_1 of HC^{35}Cl$_3$ and is mainly a result of the approximations made in the dimensionality-reduced calculation of vibrational states. For the ν_2 and ν_3 bands of both isotopomers, the deviations from experiment do not exceed 4 cm^{-1}. Calculated anharmonicity contributions for the wavenumbers of the symmetric bending vibrations of all species are only of the order of 1 cm^{-1}. Anharmonicity effects on the CCl$_3$ stretching vibrations of the normal and deuterated complex are larger, but do not exceed 10 cm^{-1}. Somewhat surprisingly, anharmonicity effects on the intensities of the ν_2 and ν_3 bands of ^{35}Cl$^-$···H-C^{35}Cl$_3$ and ^{35}Cl$^-$···H-C^{35}Cl$_3$ are quite large. In particular, the symmetric Cl$_3$ stretching vibrations are calculated to have intensities of 290 and 276 km mol^{-1} in the anharmonic treatment while the DH approximation yields only a common value of 64 km mol^{-1} for both isotopomers. As is expected for a complex with a rather strong hydrogen bond, anharmonicity effects have the largest influence on the hydrogen-bonded CH(D) stretching vibrations. Compared with the DH approximation, the ν_1 band of ^{35}Cl$^-$···H-C^{35}Cl$_3$ experiences an intensity enhancement by a factor of 5.0 and practically the same factor is obtained for ^{35}Cl$^-$···D-C^{35}Cl$_3$. In both cases, electrical anharmonicity plays the decisive role, since calculations including only the linear parts of the EDMFs (those for ^{35}Cl$^-$···H-C^{35}Cl$_3$ and ^{35}Cl$^-$···D-C^{35}Cl$_3$ are slightly different) yield 1041 and 507 km mol^{-1}, very close to the results of the DH approximation.

The combination tones between CH(CD) stretching and intermolecular stretching vibrations, termed $\nu_1 + \nu_s$, are predicted at 2706 cm^{-1} for ^{35}Cl$^-$···H-C^{35}Cl$_3$ and at 2096 cm^{-1} for ^{35}Cl$^-$···D-C^{35}Cl$_3$. Together with the values for the fundamentals ν_1 and ν_s, this allows for an approximate calculation of the anharmonicity constants X_{1s} according to

$$X_{1s} \approx (\nu_1 + \nu_s) - \nu_1 - \nu_s.$$

The results are 11.1 cm^{-1} (^{35}Cl$^-$···H-C^{35}Cl$_3$) and 6.5 cm^{-1} (^{35}Cl$^-$···D-C^{35}Cl$_3$). The former value is slightly smaller than the corresponding value for the Cl$^-$···HCCH (see Table 3 of Ref. [5]; X_{24} corresponds to X_{1s}). Positive values of this type of anharmonicity constants are quite characteristic for hydrogen-bonded complexes.

3.4. MP2 results for the asymmetric vibrations and prediction of D_0 value for Cl$^-$···H-CCl$_3$

In order to predict the ground-state dissociation energy D_0 of Cl$^-$···H-CCl$_3$ with a precision of ca. 1%, the zero-point vibrational (ZPV) contribution to D_0 has to be known with an accuracy of about 40 cm^{-1}. In an attempt to achieve this goal, we proceed as follows: the contribution arising from the totally symmetric (a_1) modes, which involve the CH stretching vibration with its significant change in anharmonicity occurring upon complex formation, is taken from the (dimensionality reduced) variational calculations. The result (in cm^{-1}) is $\Delta ZPV = (2099 - 1954) = 145$. The corresponding value as obtained within the harmonic approximation, using data collected in Table 3, is 128. For the contribution of the intramolecular asymmetric vibrations of e symmetry, MP2 calculations with the conventional aug-cc-pVTZ basis set and employing the harmonic approximation, are expected to provide a sufficiently accurate value according to the lines requested above. The result of such calculations is -51 cm^{-1}. The remaining doubly degenerate intermolecular bending vibration which, according to the rather large mass of the chloride ion, is of relatively low amplitude and should be described reasonably well within the harmonic approximation. The MP2/avtz calculations yield 53 cm^{-1} for its wavenumber and consequently a contribution of -53 cm^{-1} to D_0. Summing up the described contributions leads to the result that the zero-point vibrational energy of H-C^{35}Cl$_3$ is higher than the corresponding value for ^{35}Cl$^-$···HC^{35}Cl$_3$ by 41 cm^{-1}, which also corresponds to the difference D_0–D_e for the complex. According to the above discussion, the assumption of a maximum error of ca. 40 cm^{-1} in this quantity appears to be appropriate. Together with a recommended D_e value of ≈ 6240 cm^{-1} (see Section 3.1) we thus arrive at a D_0 prediction of ≈ 6280 cm^{-1} (75.1 kJ mol^{-1}), expected to be accurate to ca. 1%.

4. Conclusions

High-level ab initio calculations have been carried out in order to investigate important regions of the potential energy and dipole moment surfaces of the Cl$^-$ + HCCl$_3$ system. Various spectroscopic properties are predicted for the hydrogen-bonded complex ^{35}Cl$^-$···H-C^{35}Cl$_3$ and its deuterated species, which may be of help to experimentalists in forthcoming spectroscopic

investigations, e.g., by means of argon predissociation spectroscopy. The hydrogen-bonded CH stretching vibration with calculated band origin at 2553 cm^{-1} should be a good candidate since its intensity increases from 0.3 $km\,mol^{-1}$ in free $HCCl_3$ to 5745 $km\,mol^{-1}$ in the complex. This large value corresponds to a transition dipole moment of 0.947 D, substantially higher than previous calculated for $Cl^{-} \cdots HCCH$ (0.388 D, see Ref. [5]) and not too far from the value of 1.333 D obtained for strongly bound $ClHCl^{-}$ [19]. Interestingly, as much as 82% of the intensity of the ν_1 band of $^{35}Cl^{-} \cdots H\text{-}C^{35}Cl_3$ arises from electrical anharmonicity, i.e., the deviation of the electric dipole moment function from the linear approximation. So far, the effects of vibrational anharmonicity (mechanical and electrical) on the IR intensities of anionic complexes have been largely unexplored and the present paper is expected to provide an important investigation to this field.

A major topic of the present work concerns the prediction of an accurate dissociation energy D_0 for $Cl^{-} \cdots H\text{-}CCl_3$. A composite procedure, making use of basis set extrapolation and a thorough investigation of the zero-point vibrational contribution, is employed. The result is $D_0 = 6280\ cm^{-1}$ which is expected to have an uncertainty of ca. 1%. For comparison, the D_0 value for $Cl^{-} \cdots HCCH$ was predicted to be 3600 cm^{-1} [5].

Acknowledgements

References

[1] E.J. Bieske, O. Dopfer, Chem. Rev. 100 (2000) 3963.
[2] D.A. Wild, E.J. Bieske, Int. Rev. Phys. Chem. 22 (2003) 129.
[3] P. Botschwina, T. Dutoi, M. Mladenović, R. Oswald, S. Schmatz, H. Stoll, Faraday Discuss. 118 (2001) 433.
[4] P. Botschwina, H. Stoll, Phys. Chem. Chem. Phys. 3 (2001) 1965.
[5] P. Botschwina, R. Oswald, J. Chem. Phys. 117 (2002) 4800.
[6] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, Chem. Phys. Lett. 157 (1989) 479.
[7] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.
[8] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, J. Chem. Phys. 96 (1992) 6796.
[9] D.E. Woon, T.H. Dunning Jr., J. Chem. Phys. 98 (1993) 1358.
[10] P.S. Weiser, D.A. Wild, E.J. Bieske, Chem. Phys. Lett. 299 (1999) 303.
[11] P.S. Weiser, D.A. Wild, E.J. Bieske, J. Chem. Phys. 110 (1999) 9443.
[12] D.A. Wild, P.J. Milley, Z.M. Loh, P.S. Weiser, E.J. Bieske, Chem. Phys. Lett. 323 (2000) 49.
[13] D.A. Wild, P.J. Milley, Z.M. Loh, P.P. Wolynec, P.S. Weiser, E.J. Bieske, J. Chem. Phys. 113 (2000) 1075.
[14] P. Ayotte, G.H. Weddle, J. Kim, M.A. Johnson, J. Am. Chem. Soc. 120 (1998) 12361.
[15] W.H. Robertson, M.A. Johnson, Annu. Rev. Phys. Chem. 54 (2003) 173, and references therein.
[16] D.A. Wild, Z.M. Loh, P.P. Wolynec, P.S. Weiser, E.J. Bieske, Chem. Phys. Lett. 332 (2000) 531.
[17] Z.M. Loh, R.L. Wilson, D.A. Wild, E.J. Bieske, M.S. Gordon, Aust. J. Chem. 57 (2004) 1157.
[18] Z.M. Loh, R.L. Wilson, D.A. Wild, E.J. Bieske, M.S. Gordon, J. Chem. Phys. A 109 (2005) 8481.
[19] P. Botschwina, P. Sebald, R. Burmeister, J. Chem. Phys. 88 (1988) 5246.
[20] K. Kawaguchi, J. Chem. Phys. 88 (1988) 4186.
[21] P.O. Staneke, G. Groothuis, S. Ingemann, N.M.M. Nibbering, Int. J. Mass Spectrom. Ion Process. 142 (1995) 83.
[22] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.F. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (Suppl. 1) (1988).
[23] S. Grimme, J. Chem. Phys. 118 (2003) 9095.
[24] M.J. Deegan, P.J. Knowles, Chem. Phys. Lett. 227 (1994) 321.
[25] C. Hampel, K. Peterson, H.-J. Werner, Chem. Phys. Lett. 190 (1992) 1.
[26] H.-J. Werner, P.J. Knowles, R. Lindh, F.R. Manby, M. Schütz, P. Celani, T. Korona, G. Rauhut, R.D. Amos, A. Bernhardsson, A. Berning, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, A.W. Lloyd, S.J. McNicholas, W. Meyer, M.E. Mura, A. Nicklaß, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A.J. Stone, R. Tarroni, T. Thorsteinsson., MOLPRO (Versions 2002.6 and 2006.1), a package of ab initio programs, see http://www.molpro.net.
[27] T.H. Dunning Jr., K.A. Peterson, A.K. Wilson, J. Chem. Phys. 114 (2001) 9244.
[28] Y. Liu, M.A. Suhm, P. Botschwina, Phys. Chem. Chem. Phys. 6 (2004) 4642.
[29] P. Botschwina, R. Oswald, Z. Phys. Chem. 219 (2005) 399.
[30] G. Cazzoli, G. Cotti, L. Dore, Chem. Phys. Lett. 203 (1993) 227.
[31] J.-M. Colmont, D. Priem, P. Drean, J. Demaison, J.E. Boggs, J. Mol. Spectrosc. 191 (1998) 158.
[32] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553.
[33] A. Halkier, W. Klopper, T. Helgaker, P. Jørgensen, P.R. Taylor, J. Chem. Phys. 111 (1999) 9157.
[34] S.B. Huh, J.S. Lee, J. Chem. Phys. 118 (2003) 3035.
[35] J. Pietilä, S. Alanko, V.-M. Horneman, R. Anttila, J. Mol. Spectrosc. 216 (2002) 271.
[36] R. Paso, V.-M. Horneman, J. Pietilä, R. Anttila, Chem. Phys. Lett. 247 (1995) 277.
[37] J. Pietilä, V.-M. Horneman, R. Anttila, Mol. Phys. 96 (1999) 1449.
[38] A. Ruoff, H. Bürger, Spectrochim. Acta 26A (1970) 989.