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# Accurate *ab initio* determination of spectroscopic and thermochemical properties of mono- and dichlorocarbenes†

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The best technically feasible values for the triplet–singlet energy gap and the enthalpies of formation of the HCCl and $CCl_2$ radicals have been determined through the focal-point approach. The electronic structure computations were based on high-level coupled cluster (CC) methods, up to quadruple excitations (CCSDTQ), and large-size correlation-consistent basis sets, ranging from aug-cc-pVDZ to aug-cc-pV6Z, followed by extrapolation to the complete basis set limit. Small corrections due to core correlation, relativistic effects, diagonal Born–Oppenheimer correction, as well as harmonic and anharmonic zero-point vibrational energy corrections have been taken into account. The final estimates for the triplet–singlet energy gap, $T_0(\tilde{a})$, are 2170 ± 40 $cm^{-1}$ for HCCl and 7045 ± 60 $cm^{-1}$ for $CCl_2$, favoring the singlet states in both cases. Complete quartic force fields in internal coordinates have been computed for both the $\tilde{X}$ and $\tilde{a}$ states of both radicals at the frozen-core CCSD(T)/aug-cc-pVQZ level. Using these force fields vibrational energy levels of {HCCl, DCCl, $CCl_2$} up to {6000, 5000, 7000} $cm^{-1}$ were calculated both by second-order vibrational perturbation theory (VPT2) and variationally. These results, especially the variational ones, show excellent agreement with the experimentally determined energy levels. The enthalpies of formation of HCCl ($\tilde{X}^1A'$) and $CCl_2(\tilde{X}^1A_1)$, at 0 K, are 76.28 ± 0.20 and 54.54 ± 0.20 kcal $mol^{-1}$, respectively.

## I. Introduction

Carbenes are among the most important of reactive chemical intermediates. Moreover their chemistry is particularly fascinating because their lowest singlet and triplet states are expected to be closely spaced in energy but have quite different chemistries.[1–5] Therefore a precise determination of the singlet/triplet gap, $\Delta E_{TS}$, is important for understanding reaction mechanisms. For this reason, the determination of these energy gaps has attracted intense interest from quantum chemists and experimentalists alike.

This paper will focus upon the study of the singlet/triplet gap of mono- and dichlorocarbene, HCCl and $CCl_2$, respectively, by state-of-the-art quantum chemistry techniques. It will also report related thermodynamic and spectroscopic properties of these molecules.

There has been a history of both experimental[6–55] and theoretical[56–83] studies of chlorocarbenes. Nonetheless as the brief discussion below shows, there are still major discrepancies and unanswered questions. In this work, we strive to produce calculations of $\Delta E_{TS}$ for both HCCl and $CCl_2$ of "near-spectroscopic" accuracy. Moreover, we give reasonable estimates of the expected errors in these calculations. These calculations serve to increase the precision of previous calculations significantly. They are also expected to complement experimental work, which ultimately should produce a gold standard of measurement for $\Delta E_{TS}$. We believe that our calculations are sufficiently precise to guide in a detailed fashion experimental planning and ultimately to aid the acceptance or rejection of various experimental interpretations of the measured spectra.

The first direct spectroscopic observation of HCCl/DCCl in the gas phase was reported in 1966 by Merer and Travis,[6] who have assigned the band system between 550 and 820 nm to the $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$ transition. This pioneering work was followed by numerous spectroscopic studies on the $\tilde{A} \leftarrow \tilde{X}$ transition both in the gas phase[8–17] and in Ar matrix.[7] All of these studies revealed strong and complicated perturbations caused by the Renner–Teller effect and spin–orbit coupling with the low-lying $\tilde{a}^3A''$ state.

The first data on the $\tilde{X}$ state vibrational levels of HCCl, more specifically the $\nu_2$ (HCCl bend) and the $\nu_3$ (CCl stretch) fundamentals were provided by matrix isolation infrared (IR) studies.[7,18] These data were notably complemented by Chang *et al*,[13,14] who have identified six and 11 vibrational levels in the dispersed fluorescence spectra of HCCl and DCCl, respectively. A few years later the same group has re-recorded these spectra and assigned 19/24 vibrational levels of HCCl/DCCl in the $\tilde{X}$ state.[17] Besides the rotationally resolved $\tilde{X}(0,0,1) \leftarrow (0,0,0)$ transition,[19] pure rotational transitions of the $\tilde{X}(0,0,0)$ vibrational level have also been observed recently for $H^{35}CCl$ and $H^{37}CCl$.[20] The analysis of these spectra resulted in effective rotational constants, centrifugal distortion constants, nuclear quadrupole interaction constants, and spin-rotation constants for these species. One of the interesting observations of ref. 20 was that the spin-rotation constants make a significant contribution to the hyperfine structure due to the relatively low-lying $\tilde{A}$ state.

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† Electronic supplementary information (ESI) available: Triplet–singlet energy splittings, enthalpies of formation, and $\tilde{X}$ and $\tilde{a}$ state vibrational energy levels. See http://dx.doi.org/10.1039/b506790a

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The $\tilde{a}^3A''$ – $\tilde{X}^1A'$ energy splitting, $\Delta E_{TS}$, was estimated experimentally first by the analysis of the negative ion photoelectron spectrum of $HCCl^-$ by Lineberger *et al*[21,22] In their first report they obtained 11 ± 0.3 kcal $mol^{-1}$.[21] Later they revised this number to 4.2 ± 2.5 kcal $mol^{-1}$.[22] The analysis of the dispersed fluorescence spectra also resulted in triplet–singlet energy splitting values for HCCl and DCCl. In their first dispersed fluorescence reports Chang *et al*,[13,14] due to the lack of perturbations in the observed $\tilde{X}$ state vibrational levels, determined the low limits of the triplet–singlet energy splitting for HCCl/DCCl as ≈8/11 kcal $mol^{-1}$ with an error estimate of ±2 kcal $mol^{-1}$. In their recently published paper,[17] which presented the analysis of new dispersed fluorescence spectra with much better signal-to-noise ratio, they have not only observed perturbations, but assigned some weak bands to the $\tilde{a}^3A''$ state. The new, revised $\Delta E_{TS}$ values were 6.20 ± 0.05 kcal $mol^{-1}$ for HCCl and 6.25 ± 0.05 kcal $mol^{-1}$ for DCCl. At present these values seem to be the most dependable experimental estimates of $\Delta E_{TS}$ of HCCl.

The first reliable *ab initio* study on $\Delta E_{TS}$ of HCCl was published by Bauschlicher *et al* in 1977.[56] Although these calculations were carried out at a relatively low level of electronic structure theory, the singlet and triplet states were treated in a balanced manner, *i.e.* Hartree–Fock theory was used for the triplet and the generalized valence bond (GVB 1/2) method for the singlet. These calculations resulted in $\Delta E_{TS}$ = 1.6 kcal $mol^{-1}$. After this work the *ab initio* prediction of the triplet–singlet gap of HCCl has evolved in the following way: 5.4 kcal $mol^{-1}$ (1986),[57] {5.8, 6.7, 5.6 ± 0.7, 9.3} kcal $mol^{-1}$ (1987),[58,59] {6.0, 6.4 ± 0.7} kcal $mol^{-1}$ (1990),[60] 6.39 kcal $mol^{-1}$ (1992),[61] 4.8 kcal $mol^{-1}$ (1993),[62] 5.8 kcal $mol^{-1}$ (1996),[63] 6.2 kcal $mol^{-1}$ (1997),[64] {9.0, 5.7} kcal $mol^{-1}$ (1999),[65] {0.9–6.6} kcal $mol^{-1}$ (2000),[66] {6.1, 6.6} kcal $mol^{-1}$ (2000),[67] {6.1, 6.8, 5.9} kcal $mol^{-1}$ (2001).[68] Considering the most dependable results[67,68] among these calculations the computational estimate of $\Delta E_{TS}$ is 6.4 ± 0.8 kcal $mol^{-1}$.

The enthalpy of formation, $\Delta_f H_{298}{}^{\circ}$, of HCCl was obtained experimentally by ion cyclotron resonance (ICR)[45,46] and collision induced dynamics (CID)[47] techniques, which resulted in 71 ± 5 kcal $mol^{-1}$ (1985),[45] 75.7 ± 4.8 kcal $mol^{-1}$ (1994),[46] and 80.4 ± 2.8 kcal $mol^{-1}$ (1997).[47] All the available quantum chemical calculations[47,65,77,82] are consistent with these results, scattering between 75.3 and 77.4 kcal $mol^{-1}$. Among these predictions for $\Delta_f H_{298}{}^{\circ}$ the most reliable, 76.5 ± 1 kcal $mol^{-1}$, was obtained by basis set extrapolation of CCSD(T) energies and inclusion of scalar relativistic corrections.[77]

The first spectroscopic study on $CCl_2$ was carried out in 1967 in an Ar matrix by Milligan and Jacox.[23] In this matrix isolation IR study the symmetric and the antisymmetric stretching frequencies, 748 and 721 $cm^{-1}$ for $C^{35}Cl_2$ and 726 and 700 $cm^{-1}$ for $C^{35}Cl^{37}Cl$, respectively, were obtained, but without an unambiguous assignment of which is which. A year later Andrews[24] performed a similar experiment and assigned the lower of these frequencies to the symmetric stretch ($\nu_1$). Some further Ne,[41] Ar,[18,25] and Kr[18] matrix IR studies have confirmed this assignment, while fluorescence studies in cryogenic matrices[26–28] resulted in a value for the bending fundamental ($\nu_2$) of 333 $cm^{-1}$ in Ar, for the first time. The $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ excitation energies have also been obtained, $T_0$=17 092 $cm^{-1}$ in Ar, first from matrix isolation experiments.[23,25–28]

In 1977 Huie *et al*[29] recorded the laser-induced fluorescence (LIF) excitation spectrum of the $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ transition of $CCl_2$ in the gas phase. This was followed by several other gas-phase laser[30–36,44] and synchrotron[37,38] fluorescence excitation studies. Among these probably the most notable are the first rotationally resolved jet-cooled studies of Clouthier and Karolczak,[34,35] which yielded structural and vibrational parameters of the two lowest-lying singlet states. Since in these works the ground-state vibrational parameters were determined from the observed hot bands of the excitation spectra, these data were substantially refined by the analysis of the recently recorded[43,44] dispersed fluorescence spectra. These two papers together report 83 and 40 assigned $\tilde{X}$-state vibrational levels for $C^{35}Cl_2$ and $C^{35}Cl^{37}Cl$, respectively. Two microwave studies[39,40] on $C^{35}Cl_2$ provided not only accurate rotational constants but also centrifugal distortion constants, elements of the complete nuclear quadrupole coupling tensor, and nuclear spin-rotation constants.

Similarly to HCCl, the triplet–singlet energy splitting of $CCl_2$ was first estimated reliably *ab initio* by Bauschlicher *et al*[56] Including this work the theoretical predictions between 1977 and 1999 started to converge to around 19–23 kcal $mol^{-1}$ as follows: 13.5 kcal $mol^{-1}$ (1977),[56] 19.1 kcal $mol^{-1}$ (1979),[70] 21.9 kcal $mol^{-1}$ (1985),[71] {21.1, 23.2, 21.6 ± 1.4, 25.9} kcal $mol^{-1}$ (1987),[58,59] 20.5 kcal $mol^{-1}$ (1990),[60] 23.7 kcal $mol^{-1}$ (1991),[72] 20.0 kcal $mol^{-1}$ (1992),[61] 23.7 kcal $mol^{-1}$ (1992),[73] 20.5 ± 1 kcal $mol^{-1}$ (1993),[62] 19.7 kcal $mol^{-1}$ (1996),[63] 21.0 kcal $mol^{-1}$ (1999),[74] and {23.1, 19.6} kcal $mol^{-1}$ (1999).[65] In 1999 Lineberger *et al* have published a report on the photoelectron spectrum of $CCl_2{}^-$.[42] In this work they have determined the triplet–singlet energy splitting of $CCl_2$ to be 3 ± 3 kcal $mol^{-1}$. This has ignited a huge trepidation in the community of theoretically oriented chemists and inspired several groups to perform more accurate theoretical predictions and publish papers on the "surprising difference"[75] or on the "remarkable discrepancy between theory and experiment"[66] including these new estimates for the triplet–singlet splitting: 19.5 ± 2 kcal $mol^{-1}$ (2000),[75] 20.0 ± 1 kcal $mol^{-1}$ (2000),[76] {19.2, 20.9} kcal $mol^{-1}$ (2000),[77] {14.7–21.5} kcal $mol^{-1}$ (2000),[66] {21.0, 21.5, 19.9} kcal $mol^{-1}$ (2001),[68] 19.8 kcal $mol^{-1}$ (2003).[80] Ideas have been put forward to reinterpret the "mystery state"[75] of the photoelectron spectrum. Lee *et al*[76] suggested that it could be an excited state of the anion or that the discrepancy could come from the errors fitting the Franck–Condon factors. McKee and Michl assumed,[81] and supported it with calculations, that the "mystery" band corresponds to the quartet state of $CCl_2{}^-$. Efforts to obtain a new experimental value for the triplet–singlet energy gap have also been made by analyzing the laser-induced dispersed fluorescence spectrum of $CCl_2$.[43] Although the spectrum of $CCl_2$ has been recorded up to 8500 $cm^{-1}$, due to its complexity, *e.g.*, the occurrence of Fermi resonances and an unfavorable signal-to-noise ratio, in the high-energy region it could be fully and unambiguously assigned to $\tilde{X}$-state vibrational levels "only" up to 5000 $cm^{-1}$. Hence, only a lower limit of 14 kcal $mol^{-1}$ could be determined from this experiment.

The enthalpy of formation, $\Delta_f H_{298}{}^{\circ}$, of $CCl_2$ has been obtained experimentally in numerous ways including kinetic studies,[48] electron impact experiments,[49,53] ion cyclotron resonance techniques,[45,50–52] collision induced dynamics studies,[47,54] and by determination of the ionization potential.[55] Some of these studies, especially the earlier ones, resulted in values below 50 kcal $mol^{-1}$: 47 ± 3 kcal $mol^{-1}$ (1967),[48] 44 ± 2 kcal $mol^{-1}$ (1976),[50] 47.8 ± 2 kcal $mol^{-1}$ (1978),[52] 37 ± 7 kcal $mol^{-1}$ (1980),[53] 39 ± 3 kcal $mol^{-1}$ (1985).[45] In contrast to these, other measurements, including the most recent ones scatter between 51 and 57 kcal $mol^{-1}$: 56.5 ± 5 kcal $mol^{-1}$ (1968),[49] 53.8 ± 2 kcal $mol^{-1}$ (1977),[51] 52.1 ± 3.4 kcal $mol^{-1}$ (1991),[54] 51.0 ± 2.0 kcal $mol^{-1}$ (1993),[55] 55.0 ± 2.0 kcal $mol^{-1}$ (1985).[47] All the theoretical results[47,65,77–79,82,83] favor the higher value and predict $\Delta_f H_{298}{}^{\circ}$ between 51 and 56 kcal $mol^{-1}$. The highest-level calculation so far was performed by Demaison *et al*[79] using the Weizmann 2 (W2) model chemistry.[84,85] In this study 54.48 ± 0.4 kcal $mol^{-1}$ was obtained for $\Delta_f H_0{}^{\circ}$, which, when combined with other reliable results,[77] gives 54.8 ± 0.4 kcal $mol^{-1}$ for $\Delta_f H_{298}{}^{\circ}$.

For an even more detailed summary of the experimental and theoretical evaluations of the triplet–singlet energy splittings and enthalpies of formation of HCCl and $CCl_2$ see Tables S1–S4 of the electronic supplementary information (ESI).†

The purpose of this paper is to reduce the uncertainty of the theoretical predictions for the above-discussed spectroscopic and thermochemical properties of the HCCl and $CCl_2$ radicals by using sophisticated theoretical techniques. Indeed we aim to approach "near-spectroscopic" accuracy, *i.e.*, $\pm\sim 50\ \mathrm{cm}^{-1}$ for $\Delta E_{\mathrm{TS}}$. After the detailed description of the methodologies applied (Section II), we report in Section III the theoretical determination of the triplet–singlet energy gap [$T_0$ (ã)] of HCCl and $CCl_2$ by employing the focal-point approach (FPA).[86,87] Beyond the apparent accuracy of the FPA method its other advantage is that the uncertainty of its final energy predictions can be estimated reliably due to the systematic build-up of its composite calculations. In Section IV vibrational energy levels calculated both perturbationally and variationally from an accurate quartic force field representation of the potential energy surfaces (PESs) of HCCl and $CCl_2$ are presented. It is shown that due to the accuracy of these vibrational calculations they can help the further analysis of the dispersed fluorescence spectra, including the possible identification of the triplet state of $CCl_2$. In Section V accurate *ab initio* determination of the enthalpies of formation, $\Delta_f H_T^\circ$, of HCCl and $CCl_2$ is described, utilizing FPA results of this study and related existing high-quality thermochemical data.[88–92] The paper is concluded by a short summary detailing the possible impact of the new theoretical data on subsequent experiments.

## II. Computational details

### II.1. Electronic structure calculations

As it is mentioned in the Introduction the electronic structure calculations have been carried out according to the recipe of the so-called focal-point approach documented well in recent publications.[86,87] Therefore, it is not described here in detail. However, the structure of the rest of this section is organized in a way to follow the major steps of FPA and give insight for a reader not familiar with this approach. The electronic structure calculations reported in this paper have been performed with the help of the ACES II,[93,94] PSI 2,[95] Gaussian03,[96] and MRCC[97,98] program packages.

Reference electronic wave functions have been determined by the single-configuration restricted-open-shell Hartree–Fock (ROHF) method. In the case of $CCl_2$ the computations have been repeated using an unrestricted Hartree–Fock (UHF) reference, as well. Electron correlation was accounted for by standard methods of electronic structure theory: second-order Møller–Plesset (MP2) perturbation theory,[99] and the coupled cluster (CC) series, including single and double (CCSD),[100] single, double and perturbatively estimated triple [CCSD(T)],[101] single, double and triple (CCSDT),[102,103] and single, double, triple and quadruple excitations (CCSDTQ).[104,105] In the valence-only correlated-level calculations the 1s orbital of C and the 1s, 2s, and 2p orbitals of Cl were kept doubly occupied. No virtual molecular orbitals were kept frozen in any of the calculations.

Relativistic electronic energy corrections were determined by the 1-electron mass-velocity–Darwin (MVD1)[106,107] and the second-order Douglas–Kroll–Hess [DKH(2)][108–112] methods. Corrections beyond the Dirac–Coulomb theory[113] (*e.g.*, the Breit term) and quantum electrodynamics (QED) contributions (Lamb-shift),[114] which supposed to be much smaller than the remaining uncertainty of the non-relativistic calculations, were neglected in this study.

Computation of the mass-dependent diagonal Born–Oppenheimer correction (DBOC) was performed by the BORN program operating within the PSI 2 program package at the Hartree–Fock level, using the formalism of Handy, Yamaguchi and Schaefer.[115]

The one-particle basis sets chosen for the frozen-core correlation calculations include the correlation-consistent (aug)-cc-pV$X$Z, $X = 2$(D), 3(T), 4(Q), 5, and 6, basis sets developed by Dunning and co-workers.[116,117] If not noted otherwise, the improved version[118] of these basis sets have been employed for Cl, which include more d-functions than the original version.[119] All-electron correlation calculations have been carried out using the (aug)-cc-pCV$X$Z sets,[120,121] which are able to describe the core region adequately. Estimation of the complete basis set (CBS) limits have been performed by well-established extrapolation formulas, namely by an exponential formula,[122]

$$E^X = E_{\mathrm{CBS}} + a\exp(-bX) \qquad (1)$$

in the case of HF and an inverse power formula,[123]

$$E^X = E_{\mathrm{CBS}} + cX^{-3} \qquad (2)$$

for both the frozen-core and all-electron correlated energy increments. For DBOC energy correction calculations the Dunning–Huzinaga-type DZP and TZ2P basis sets[124] have been used.

Reference geometries of $CCl_2$ and HCCl for the single-point energy calculations within the focal-point approach and for the force field calculations have been obtained by geometry optimization at the all-electron CCSD(T)/aug-cc-pCVTZ level of theory. The related structural parameters are collected in Table 1.

Quartic (and partial sextic) force fields in (stretch, stretch, bend) internal coordinates have been determined by finite differentiation of frozen-core CCSD(T)/aug-cc-pVQZ energy values. This level of electronic structure theory was chosen because it represents a well-known Pauling-point in the computational armamentarium, and according to our experience it provides an almost as good local PES as the best state-of-the-art *ab initio* surfaces (*i.e.* CBS extrapolated and augmented by auxiliary corrections).[125]

### II.2. Vibrational energy level calculations

Vibrational energy levels were computed using formulas based on second-order vibrational perturbational theory (VPT2)[126–129] and by an approximately variational discrete variable representation (DVR)[130–132] technique.[133]

The VPT2 calculations were performed using the ANHARM[128] program package. Since the geometry optimizations and the force field calculations have been performed at different levels of theory, the force fields included non-zero forces. The (stretch, stretch, bend) quartic force fields were first transformed to (SPF, SPF, bend) coordinates, where SPF stands for Simons–Parr–Finlan[134] coordinates, where the forces were neglected, then to Cartesian coordinates, the necessary inputs of ANHARM.

The variational calculations were performed with the program DOPI3,[133] where DOPI stands for DVR (D)—Hamiltonian in orthogonal (O) coordinates—direct product (P) basis—iterative (I) sparse Lanczos eigensolver. The PES for the variational calculations was built using force constants in the quartic (SPF, SPF, bend) representation, where the non-zero forces were not neglected in the expansion of the potential. The use of the quartic force field in SPF coordinates was chosen

**Table 1** Born–Oppenheimer equilibrium structural parameters of HCCl and $CCl_2$ in their X̃ and ã states, optimized at the all-electron CCSD(T)/aug-cc-pCVQZ level of theory

| Parameter | HCCl | | $CCl_2$ | |
|---|---|---|---|---|
| | X̃ | ã | X̃ | ã |
| $\theta_{\mathrm{HCCl/ClCCl}}/^\circ$ | 102.331 | 126.482 | 109.256 | 127.853 |
| $r_{\mathrm{CCl}}$/Å | 1.69506 | 1.65927 | 1.71896 | 1.67386 |
| $r_{\mathrm{HCl}}$/Å | 1.10880 | 1.08181 | — | — |

**Table 2** The effect of basis set size and electron correlation on the valence-only triplet–singlet energy gap of HCCl[a]

| Aug-cc-pV*XZ* | $\Delta E_{\mathrm{TS}}$(ROHF) | δMP2 | δCCSD | δCCSD(T) | δCCSDT | δCCSDTQ | $\Delta E_{\mathrm{TS}}$ |
|---|---|---|---|---|---|---|---|
| D (64) | −3634 | +4259 | +638 | +612 | +43 | +*47*[c] | 1965 |
| T (124) | −3864 | +4835 | +362 | +677 | +25 | [+*47*] | 2082 |
| Q (215) | −3898 | +5055 | +234 | +684 | [+25] | [+*47*] | 2147 |
| 5 (343) | −3907 | +5150 | +169 | +688 | [+25] | [+*47*] | 2172 |
| 6 (488) | −3909 | +5192 | +140 | [+689] | [+25] | [+*47*] | 2184 |
| CBS[b] | −3910 | +5236 | +116 | +691 | [+25] | [+*47*] | **2205** |

[a] For each basis set the total number of contracted Gaussian functions is given in parentheses. For correlated-level calculations the symbol δ denotes the increment in relative energy, $\Delta E_{\mathrm{TS}}$, with respect to the preceding level of theory. Brackets signify assumed increments from smaller basis set results. All values are given in $\mathrm{cm}^{-1}$. [b] Aug-cc-pVDZ results were not included in the extrapolation to the CBS. [c] The δCCSDTQ increment was obtained using the 'old' version[119] of the cc-pVDZ basis set.

because according to previous results[133,134] (i) employing an SPF representation instead of the simple stretch representation results in better agreement between the variationally computed and the experimental energy levels; and (ii) the quartic and sextic force fields in SPF coordinates result in highly similar energy levels. All the vibrational energies presented were converged to better than 0.01 $\mathrm{cm}^{-1}$. In some variational calculations the quintic and sextic diagonal bending internal coordinate force constants have also been included to improve the description of the bending motion.

All the necessary force field transformations both for the VPT2 and the variational calculations have been carried out with the help of the INTDER[135–137] program.

# III. Triplet–singlet energy gap

## III.1. HCCl and DCCl

The valence-only FPA results for the triplet–singlet energy splitting of HCCl are summarized in Table 2. From the data presented the following conclusions, similar to those found for $\mathrm{CH_2}$,[138] can be drawn: (i) Both the extension of the one-particle basis set and the electron correlation treatment systematically lowers the energy of the singlet state with respect to the triplet state. (ii) The HF triplet–singlet energy splitting is fairly independent of the size of the one-particle basis set, it changes only 276 $\mathrm{cm}^{-1}$ between the aug-cc-pVDZ and the CBS limit. Convergence of the higher-order electron correlation contributions, δCCSD(T)[139] and above, with the one-particle basis set is even faster. (iii) The δMP2 and δCCSD contributions converge rather slowly, the change of their absolute value from the aug-cc-pCVDZ basis set to the CBS limit is 977 and 522 $\mathrm{cm}^{-1}$, respectively. (iv) The well-known imbalanced treatment of the two electronic states at the HF level of theory is slowly corrected as the single-reference electron correlation treatment is improved. This is well demonstrated by the extremely large δCCSD(T) contribution, 691 $\mathrm{cm}^{-1}$ at the CBS limit. Nevertheless, the δCCSDTQ increment is comfortably small, +47 $\mathrm{cm}^{-1}$. Our final estimate for the valence-only triplet–singlet energy gap is 2205 ± 35 $\mathrm{cm}^{-1}$.

Furthermore, again similarly to observations for $\mathrm{CH_2}$,[138] inclusion of core correlation is important, it considerably stabilizes the triplet state with respect to the singlet state (see Table 3). It is also in good correspondence with the observations for $\mathrm{CH_2}$ and other previous studies that, due to the opposite signs of the δCCSD and the δCCSD(T) contributions the MP2 level of theory, with a large enough (*e.g.*, cc-pCVQZ) basis set, estimates well the converged core correlation contribution, which is determined in this study to be −146 ± 20 $\mathrm{cm}^{-1}$.

**Table 3** Contribution of core correlation to the triplet–singlet energy gap of HCCl[a]

| cc-pCV*XZ* | MP2 | δCCSD | δCCSD(T) | $\Delta\Delta E_{\mathrm{TS}}$ (CC) |
|---|---|---|---|---|
| D (50) | 0 | −53 | +3 | −30 |
| T (116) | −71 | −67 | +38 | −100 |
| Q (223) | −115 | −69 | +44 | −141 |
| CBS | −120 | −72 | +46 | **−146** |

[a] See footnote *a* of Table 2.

Since the contribution of the relativistic effects is expected to be more important in the case of HCCl than in $\mathrm{CH_2}$ it was computed in a somewhat more careful manner. First, the one-electron scalar contribution was obtained by the MVD1 perturbation method using the ROHF wave function. This was then augmented by the difference of the DKH(2) and the MVD1 results calculated also at the ROHF level. Although the two methods approximate the Dirac–Coulomb Hamiltonian by different partitioning schemes, due to the effective treatment of the first- and second-row elements by these relativistic perturbation techniques this difference basically covers the two-electron scalar and spin–orbit relativistic corrections within the Dirac–Coulomb Hamiltonian. Finally, the electron correlation contribution to the one-electron scalar terms were obtained as the difference of the ROHF and CCSD(T) MVD1 results. As can be seen from Table 4 the relativistic correction calculated by MVD1 perturbation theory and an ROHF wave function estimates the final result well, both the two-electron and the electron-correlation contributions to the total relativistic correction are small. Our final estimate of the relativistic corrections to $\Delta E_{\mathrm{TS}}$ is +54 ± 10 $\mathrm{cm}^{-1}$.

As expected, the diagonal Born–Oppenheimer correction (DBOC) to the triplet–singlet energy gap of HCCl/DCCl is smaller (see Table 5) than it was found for $\mathrm{CH_2}$.[138] Our best estimate is +10 ± 4 $\mathrm{cm}^{-1}$ and +8 ± 4 $\mathrm{cm}^{-1}$ for HCCl and DCCl, respectively. (The isotopologs containing $^{35}\mathrm{Cl}$ and $^{37}\mathrm{Cl}$ have the same BODC energy corrections to within 1 $\mathrm{cm}^{-1}$.)

The zero-point vibrational energy (ZPE) corrections have been computed both by the VPT2 and the variational methods (see Table 6). The total VPT2 ZPE value can be calculated by the following formula:

$$E_{\mathrm{ZPE}} = G_0 + \sum_i \frac{\omega_i}{2} + \sum_{i \geq j} \frac{\chi_{ij}}{4} \tag{3}$$

where the three terms are the $G_0$, the harmonic, and the anharmonic contributions, respectively. (A correct analytic formula for the computation of the $G_0$ term from quartic force fields for asymmetric tops has been derived by Allen *et al*[140]). As can be seen from Table 6, the anharmonic and the $G_0$ contributions to the triplet–singlet energy splitting are only on the order of 1–2 $\mathrm{cm}^{-1}$. Furthermore, the total VPT2 ZPE correction agrees with the variational results to about 1 $\mathrm{cm}^{-1}$. Similarly to findings for $\mathrm{CH_2}$,[138] the ZPE correction is larger for the triplet state, the numerical results for the HCCl and DCCl radicals are 47 and 50 $\mathrm{cm}^{-1}$, respectively. Our error estimate for the ZPE correction is ±5 $\mathrm{cm}^{-1}$.

**Table 4** Contribution of relativistic effects to the triplet–singlet energy gap of HCCl[a]

| Basis | ROHF | | δCCSD(T) | |
|---|---|---|---|---|
| | MVD1 | δDKH(2) | MVD1 | $\Delta\Delta E_{TS}$ (Rel) |
| cc-pCVDZ (50) | +52 | −4 | +3 | +51 |
| Aug-cc-pCVDZ (72) | +51 | −4 | +3 | +50 |
| cc-pCVTZ (116) | +45 | −4 | +6 | +47 |
| Aug-cc-pCVTZ (148) | +46 | +2 | +5 | +53 |
| cc-pCVQZ (223) | +48 | −4 | +5 | +49 |
| Aug-cc-pCVQZ (289) | +48 | +1 | [+5] | **+54** |

[a] For each basis set the total number of contracted Gaussian functions is given in parenthesis. δDKH(2) is the relativistic energy increment to the MVD1 results using ROHF reference wave function for both calculations. δCCSD(T) MVD1 is the energy increment of the (MVD1) relativistic correction due to the inclusion of electron-correlation. All values are given in cm$^{-1}$.

**Table 5** Contribution of diagonal Born–Oppenheimer correction (DBOC) to the triplet–singlet energy gap of HC$^{35}$Cl, DC$^{35}$Cl, and C$^{35}$Cl$_2$[a]

| Level | HC$^{35}$Cl | DC$^{35}$Cl | C$^{35}$Cl$_2$ |
|---|---|---|---|
| ROHF/DZP (43/61) | +7.7 | +6.9 | +5.0 |
| ROHF/TZ2P (64/86) | **+9.5** | **+8.0** | **+5.1** |

[a] For each basis set the total number of contracted Gaussian functions for (HCCl/CCl$_2$) is given in parenthesis. All values are given in cm$^{-1}$.

To obtain the best estimate for $T_0$ (ã), one sums the lowest, rightmost numbers in Tables 2–4 and the corresponding bottommost numbers in Tables 5 and 6. The resulting values of HCCl and DCCl are 2170 ± 40 cm$^{-1}$ (6.204 ± 0.114 kcal mol$^{-1}$) and 2171 ± 40 cm$^{-1}$ (6.207 ± 0.114 kcal mol$^{-1}$), respectively. These estimates are in an excellent agreement with the recently revised experimental value, 2167/2187 ± 18 cm$^{-1}$ for HCCl/DCCl, of Chang *et al*[17] On the other hand, the experimentally obtained difference of $T_0$(ã) of HCCl and DCCl is considerably larger than the theoretically computed difference. A possible source of this apparent discrepancy is the assigned error bar of the experimental observations, which is comparable to the difference of the two $T_0$(ã) values. An alternative explanation is offered if a relatively large spin–vibronic perturbation existed between the singlet and triplet states, and it is different for the two species. Although this perturbation is not included in our theoretical treatment, the estimation of the magnitude of this perturbation, based on the comparison of the computed and the experimentally observed vibrational levels, will be discussed in Section V.1.

## III.2. CCl$_2$

Since the technical details and the qualitative observations during determination of the triplet–singlet energy gap of CCl$_2$ by the FPA were similar to those for CH$_2$ and HCCl, here we mostly concentrate on the differences and the tendencies in the CH$_2$/HCCl/CCl$_2$ substitution series.

Convergence of the valence-only energy difference of the singlet and triplet states of CCl$_2$ with the correlation level is similarly slow (see Table 7) as observed for CH$_2$ and HCCl. Consequently, to get accurate valence-only estimates higher-order electron correlation contributions have to be determined in this case, as well. At the same time, it is much more demanding to perform higher-order correlation calculations for CCl$_2$ than for the smaller HCCl and CH$_2$ systems. Practically we were able to carry out CCSDT calculations only with the aug-cc-pVDZ and the 'old' (*i.e.* one less d orbital on Cl) cc-pVTZ basis set, while CCSDTQ calculations were limited to the 'old' cc-pVDZ basis set of Dunning. Although for CH$_2$ and HCCl we found that the post-CCSD(T) electron-correlation contributions are small, and their CBS values can be estimated relatively accurately using small basis sets, it is desirable to check in an independent way whether the same holds for CCl$_2$. A well-established way to do this is the comparison of the correlation series using ROHF and UHF references.[141] It was found in many cases that the convergence with the correlation level is significantly different in the two cases. In these situations, since both series converge ultimately to the same valence-only limit, the difference of the restricted and unrestricted methods at the same computational level indicates the uncertainty of the calculations due to the neglect of higher-order correlations. In the case of CCl$_2$ the obtained CBS result for {$\Delta E_{TS}$(HF), $\Delta E_{TS}$(MP2), $\Delta E_{TS}$(CCSD), $\Delta E_{TS}$[CCSD(T)]} is {–22, 6660, 5896, 6997} cm$^{-1}$ using an ROHF reference (see Table 7), and {–1710, 6922, 5864, 7021} cm$^{-1}$ when an UHF reference is used. This reveals that in spite of the large deviation, 1688 cm$^{-1}$, observed at the HF level, the two CBS CCSD(T) values agree within 24 cm$^{-1}$. From this we expect that the contribution of the post-CCSD(T) electron correlation is on the order of a few tens of cm$^{-1}$. Since this contribution is relatively small and the δCCSD(T) contribution converges relatively fast with the basis set size to CBS limit, it is expected that post-CCSD(T) electron correlation contributions are well estimated by CCSDT and CCSDTQ calculations even using small basis sets. Consequently, we allocate an 50 cm$^{-1}$ error bar to the 7050 cm$^{-1}$ valence-only result of the triplet–singlet energy splitting of CCl$_2$.

Inclusion of core correlation (Tables 3 and 8) and relativistic effects (Tables 4 and 9) are becoming more and more important as one goes from the lighter to the heavier species. Together with this the contribution of their cross term, namely the difference between the correlated and non-correlated one-electron scalar relativistic effects, is also increasing. This cross term is three times larger in CCl$_2$ than in HCCl. Our best numerical estimates for the core correlation and the relativistic correction of the triplet–singlet energy gap of CCl$_2$ are −176 ± 25 cm$^{-1}$ and +91 ± 15 cm$^{-1}$, respectively.

As expected, the DBOC contribution (see Table 5) to the triplet–singlet energy gap is decreasing in the CH$_2$, HCCl (DCCl), and CCl$_2$ series. The DBOC contribution, in the case of CCl$_2$, is only 5 ± 2 cm$^{-1}$. In contrast to this, the ZPE contribution of the total $T_0$(ã) value, +75 ± 5 cm$^{-1}$ (see Table 6), of CCl$_2$ is in between the corresponding values obtained for CH$_2$ and HCCl/DCCl.

The final estimate of this study for $T_0$(ã) of CCl$_2$ is obtained by summing the lowest, rightmost numbers in Tables 5–9. The resulting value is 7045 ± 60 cm$^{-1}$ (20.13 ± 0.17 kcal mol$^{-1}$). This estimate is in good agreement with other recent *ab initio* predictions, but the assigned error bar of the theoretical prediction is reduced by an order of magnitude. This result further supports the alternative reassignments[76,81] of the photodetachment spectrum of CCl$_2^-$ over the original assignment.[42]

**Table 6** Zero-point vibrational energy correction of the triplet–singlet energy gap of HC$^{35}$Cl, DC$^{35}$Cl, and C$^{35}$Cl$_2$[a]

| Method | HC$^{35}$Cl | DC$^{35}$Cl | C$^{35}$Cl$_2$ |
|---|---|---|---|
| VPT2 (Harmonic) | +49.1 | +51.4 | +75.4 |
| VPT2 (Harmonic+anharmonic) | +50.1 | +50.5 | +75.2 |
| VPT2 (Harmonic+anharmonic+$G_0$) | +48.4 | +51.5 | +74.3 |
| Variational | **+47.3** | **+50.1** | **+74.7** |

[a] All values are given in cm$^{-1}$.

**Table 7** The effect of basis set size and electron correlation on the valence-only triplet–singlet energy gap of $CCl_2$[a]

| Aug-cc-pV$XZ$ | $\Delta E_{TS}$(ROHF) | δMP2 | δCCSD | δCCSD(T) | δCCSDT | δCCSDTQ | $\Delta E_{TS}$ |
|---|---|---|---|---|---|---|---|
| D (87) | 380 | +5749 | −108 | +971 | −2 | *+69*[c] | 7059 |
| T (156) | 55 | +6300 | −490 | +1073 | *−16*[c] | [*+69*] | 6991 |
| Q (258) | 1 | +6504 | −633 | +1088 | [*−16*] | [*+69*] | 7013 |
| 5 (399) | −15 | +6594 | −704 | +1095 | [*−16*] | [*+69*] | 7023 |
| 6 (546) | −21 | +6647 | −738 | [+1099] | [*−16*] | [*+69*] | 7040 |
| CBS[b] | −22 | +6682 | −764 | +1101 | [*−16*] | [*+69*] | **7050** |

[a] See footnote *a* of Table 2. [b] Aug-cc-pVDZ results were not included in the extrapolation to the CBS. [c] Numbers in italics were determined by using the 'old' version of the cc-pV$XZ$ basis set.[119]

## IV. Vibrational energy levels

The VPT2 vibrational parameters of the $\tilde{X}$ and $\tilde{a}$ states of $HC^{35}Cl$, $DC^{35}Cl$, and $C^{35}Cl_2$ are listed in Table 10. The vibrational levels obtained by substituting these parameters into the anharmonic oscillator equation of a triatomic molecule,

$$G(v_1, v_2, v_3) = G_0 + \sum_{i=1,2,3} \omega_i \left(v_i + \frac{1}{2}\right) + \sum_{i \geq j, i=1,2,3} x_{ij} \left(v_i + \frac{1}{2}\right)\left(v_j + \frac{1}{2}\right) \tag{4}$$

are given in Tables 11–16.[142] These tables also contain the vibrational levels obtained by variational calculations and from experiments. Some further converged variational results as well as results for other isotopologs can be found in the ESI.†

### IV.1. HCCl and DCCl

The vibrational energy levels of singlet HCCl and DCCl computed variationally from the quartic force field (see the Var4 columns of Tables 11 and 13) show excellent agreement with the experimentally observed levels up to 3000 $cm^{-1}$. The root-mean-square (rms) errors calculated from the first eight and 12 vibrational levels of HCCl and DCCl are 3.6 and 4.5 $cm^{-1}$, respectively. Although the corresponding rms errors of the perturbationally obtained energy levels are somewhat larger, 5.4 and 5.9 $cm^{-1}$, this still can be considered as a fine performance for a simple, purely theoretical treatment.

Above 3000 $cm^{-1}$ the situation is, however, quite different. The Var4 results for the vibrational energy levels involving small bending quantum numbers still agree very well with the experimental data, while highly excited bending modes show significant (>15 $cm^{-1}$) deviation from the experimental observations. In order to understand the source of this error we have added the pure fifth- and sixth-order bending force constants to the quartic force field and reran the variational calculations using this augmented force field (see the Var4$^+$ columns of Tables 11 and 13). As it is expected, the predicted Var4 and Var4$^+$ vibrational energy levels are the same within 1 $cm^{-1}$ for modes with small $n_2$ vibrational quantum numbers. On the other hand, the Var4 and Var4$^+$ results for highly excited bending modes are rather different, the Var4$^+$ energy levels are 15–40% closer to the experimental values than the corresponding Var4 ones. The importance of the inclusion of the higher order bending force constants is connected to the fact that the barrier to linearity of HCCl in its $\tilde{X}$ state is relatively low, 17 766 $cm^{-1}$ at the all-electron CCSD(T)/aug-cc-pCVTZ level. Somewhat surprisingly the perturbational predictions, which of course utilize the quartic force fields only, are better for the highly excited bending modes than the variational results. Nevertheless, this seems to be a consequence of fortuitous cancellation of errors in this region, since the errors of the perturbationally obtained vibrational energy levels of modes with low bending excitation have opposite signs.

**Table 8** Contribution of core correlation to the triplet–singlet energy gap of $CCl_2$[a]

| cc-pCV$XZ$ | ΔMP2 | δCCSD | δCCSD(T) | $\Delta\Delta E_{TS}$ (CC) |
|---|---|---|---|---|
| D (72) | +4 | −76 | +40 | −32 |
| T (161) | −68 | −92 | +58 | −102 |
| Q (302) | −121 | −98 | +64 | −154 |
| CBS | −143 | −100 | +67 | **−176** |

[a] See footnote of Table 3.

In ref. 17 Chang *et al* discussed the spin–vibronic coupling and the perturbation between certain vibrational levels of the $\tilde{X}$ and $\tilde{a}$ states. They have estimated the magnitude of these perturbations by the difference between the experimentally determined vibrational levels and the vibrational levels calculated from fitted effective spectroscopic parameters, when only the unperturbed levels were included in the preceding fit. In this paper we estimate these spin–vibronic perturbations a similar way, but instead of the fitted expansion we use the Var4$^+$ results. Although the variationally obtained vibrational levels have somewhat larger errors than the levels obtained by the use of the fitted expansion, determination of the perturbations from the variational results has certain advantages. First, one does not need to consider prior to the fit which levels are perturbed and which are not and hence all appropriate levels can be considered. Second, the variational method, unlike the second-order expansion of the anharmonic oscillator model, treats exactly the resonances between the vibrational levels belonging to the same electronic state. Finally, it is noted that larger errors can be by-passed if they are systematic for a given series.

Chang *et al*[17] pointed out large perturbations with given $\tilde{a}$-state vibrational levels for the $\tilde{X}$(0,2,0), $\tilde{X}$(0,2,1), and $\tilde{X}$(0,2,2) vibrational levels of HCCl and for the $\tilde{X}$(0,4,0) and the $\tilde{X}$(0,4,1) levels of DCCl. From our calculations the errors of the Var4$^+$ results for the $\tilde{X}(0,n_2,0)$ energy levels of HCCl (Table 11) are {+5, −2, +8, +11} $cm^{-1}$ for $n_2$={1,2,3,4}. If the trend in the errors is systematic, one would expect a

**Table 9** Contribution of relativistic effects to the triplet–singlet energy gap of $CCl_2$[a]

| Basis | ROHF | | δCCSD(T) | |
|---|---|---|---|---|
| | MVD1 | δDKH(2) | MVD1 | $\Delta\Delta E_{TS}$ (Rel) |
| cc-pCVDZ (72) | +86 | −6 | +9 | +89 |
| cc-pCVTZ (161) | +79 | [−6] | +14 | +87 |
| Aug-cc-pCVTZ (209) | +82 | [−6] | +14 | +90 |
| cc-pCVQZ (302) | +83 | [−6] | +14 | **+91** |

[a] See footnote of Table 4.

**Table 10** Calculated (VPT2) vibrational parameters, in $\mathrm{cm}^{-1}$, of $HC^{35}Cl$, $DC^{35}Cl$, and $C^{35}Cl_2$

| | HCCl | | DCCl | | $CCl_2$ | |
|---|---|---|---|---|---|---|
| | $\tilde{X}$ | ã | $\tilde{X}$ | ã | $\tilde{X}$ | ã |
| $\omega_1$ | 2924.00 | 3203.29 | 2148.50 | 2358.85 | 733.37 | 686.30 |
| $\omega_2$ | 1223.14 | 893.02 | 909.14 | 720.94 | 336.92 | 300.86 |
| $\omega_3$ | 821.39 | 970.47 | 809.94 | 890.63 | 772.17 | 1005.99 |
| $x_{11}$ | −68.77 | −63.67 | −37.09 | −34.34 | −3.21 | −3.72 |
| $x_{12}$ | −8.53 | −3.09 | 1.49 | −6.89 | −1.34 | −1.46 |
| $x_{13}$ | 1.11 | −9.71 | −1.39 | 2.08 | −4.80 | −3.96 |
| $x_{22}$ | −8.54 | −5.05 | −6.50 | −3.04 | −0.19 | 0.22 |
| $x_{23}$ | −7.74 | −1.56 | −4.12 | −8.35 | −4.64 | −4.24 |
| $x_{33}$ | −5.07 | −10.69 | −4.74 | −5.33 | −5.15 | −6.66 |
| ZPVE | 2450.3 | 2498.7 | 1914.6 | 1965.1 | 917.7 | 992.0 |

+6 – +7 $\mathrm{cm}^{-1}$ error for the $\tilde{X}(0,2,0)$ mode. From this we can deduce an 8–9 $\mathrm{cm}^{-1}$ perturbation between the $\tilde{X}(0,2,0)$ level at 2383 $\mathrm{cm}^{-1}$ (experimental, Table 11) and the close-lying ã(0,0,0) level at 2167 $\mathrm{cm}^{-1}$ (experimental). This perturbation lowers the energy of ã(0,0,0), in other words the unperturbed $T_0$(ã) of HCCl is larger than the experimentally observed value. Consequently the difference (see Section III.1) between the experimentally determined (20 $\mathrm{cm}^{-1}$) and the calculated (1 $\mathrm{cm}^{-1}$) difference of the $T_0$(ã) of HCCl and DCCl would be slightly smaller if the computed values included spin–vibronic interactions.

**Table 11** Experimental and calculated vibrational energy levels, in $\mathrm{cm}^{-1}$, for the $\tilde{X}$ state of $HC^{35}Cl$

| Vibrational level $(v_1,v_2,v_3)$[a] | Exp. | VPT2 (–Exp.) | Var4 (–Exp.)[b] | Var4$^+$ (–Exp.)[b] |
|---|---|---|---|---|
| (0,0,1) | 810 | −2 | 0 | 0 |
| (0,1,0) | 1195 | +3 | +5 | +5 |
| (0,0,2) | 1613 | −7 | −3 | −3 |
| (0,1,1) | 1999 | −1 | +3 | +3 |
| (0,2,0)* | 2383 | −4 | −1 | −2 |
| (0,0,3) | 2402 | −9 | −3 | −3 |
| (0,1,2) | 2791 | −8 | −6 | −6 |
| (1,0,0) | 2791 | −3 | +4 | +4 |
| (0,0,4) | | 3171 | 3177 | 3176 |
| (0,2,1)* | 3181 | −10 | −1 | −1 |
| (0,3,0) | 3538 | +5 | +11 | +8 |
| (0,1,3) | 3575 | −7 | −1 | −1 |
| (1,0,1) | 3604 | −12 | −5 | −5 |
| (0,0,5) | | 3938 | 3950 | 3950 |
| (0,2,2)* | 3976 | −22 | −16 | −17 |
| (1,1,0) | | 3972 | 3979 | 3979 |
| (0,3,1) | 4329 | +2 | −7 | +4 |
| (0,1,4) | | 4338 | 4346 | 4346 |
| (1,0,2) | | 4391 | 4399 | 4399 |
| (0,4,0) | 4684 | +5 | +17 | +11 |
| (0,0,6) | | 4696 | 4710 | 4711 |
| (0,2,3) | 4729 | −3 | +5 | +4 |
| (1,1,1) | | 4773 | 4782 | 4781 |
| (0,1,5) | | 5107 | 5108 | 5108 |
| (0,3,2) | 5107 | −5 | +5 | +3 |
| (1,2,0) | | 5144 | 5146 | 5144 |
| (1,0,3) | | 5179 | 5190 | 5190 |
| (2,0,0) | | 5428 | 5447 | 5446 |
| (0,0,7) | | 5466 | 5462 | 5462 |
| (0,4,1) | 5466 | 0 | +15 | +9 |
| (0,2,4) | | 5488 | 5498 | 5497 |
| (1,1,2) | | 5565 | 5575 | 5574 |
| (0,5,0) | | 5819 | 5841 | 5830 |
| (0,1,6) | | 5847 | 5861 | 5861 |
| (0,3,3) | | 5866 | 5879 | 5876 |
| (1,2,1) | | 5938 | 5942 | 5940 |
| (1,0,4) | | 5958 | 5971 | 5971 |

[a] Levels strongly perturbed by spin–vibronic interactions are labeled by an asterisk. See text for details. [b] Var4 results were obtained by varitional method using the complete quartic force field, while Var4$^+$ results utilized the quartic force field augmented with the diagonal quintic and sextic bending force constants. When experimental observations are available the calculated – experimental values are given in the theoretical columns.

In a similar way, considering the error series of the calculated $\tilde{X}(0,n_2,1)$ vibrational levels ({0, +3, −4, +4} for $n_2$ = 0,1,2,3), a smaller, roughly +4 $\mathrm{cm}^{-1}$ energy increase would be obtained for the $\tilde{X}(0,2,1)$ vibrational level at 3181 $\mathrm{cm}^{-1}$ (experimental, Table 11) due to the interaction with the ã(0,1,0) and/or the ã(0,0,1) vibrational levels at 3050 $\mathrm{cm}^{-1}$ and 3110 $\mathrm{cm}^{-1}$ (experimental $T_0$(ã) + Var4$^+$ vibrational level), respectively.

It is evident that the $\tilde{X}(0,2,2)$ level of HCCl at 3976 $\mathrm{cm}^{-1}$ can be perturbed by the close-lying ã(0,2,0) and the ã(0,1,1) vibrational levels at 3915 $\mathrm{cm}^{-1}$ and 3983 $\mathrm{cm}^{-1}$ (experimental $T_0$(ã) + Var4$^+$ vibrational level), respectively. Unfortunately, the fourth member of the $\tilde{X}(0,n_2,2)$ series already falls in the region where the accuracy of the variational calculations is not sufficient to be included in the error series. From the fist three members, {−3, −6, −17}, of this error series only a very rough estimate of the perturbation effects can be determined, for $\tilde{X}(0,2,2)$, 6–10 $\mathrm{cm}^{-1}$. Similarly to this, both the $\tilde{X}(0,4,0)$ and the $\tilde{X}(0,4,1)$ levels of DCCl fall in the energy region where the accuracy of the present variational calculations starts to deteriorate, consequently no reliable estimate

**Table 12** Calculated vibrational energy levels, in $\mathrm{cm}^{-1}$, for the ã state of $HC^{35}Cl$[a]

| Vibrational level $(v_1,v_2,v_3)$ | VPT2 | Var4 | Var4$^+$ |
|---|---|---|---|
| (0,1,0) | 881 | 883 | 883 |
| (0,0,1) | 943 | 943 | 943 |
| (0,2,0) | 1751 | 1756 | 1756 |
| (0,1,1) | 1822 | 1825 | 1825 |
| (0,0,2) | 1866 | 1864 | 1864 |
| (0,3,0) | 2611 | 2620 | 2620 |
| (0,2,1) | 2691 | 2696 | 2696 |
| (0,1,2) | 2743 | 2742 | 2742 |
| (0,0,3) | 2766 | 2764 | 2764 |
| (1,0,0) | 3070 | 3071 | 3071 |
| (0,4,0) | 3462 | 3472 | 3472 |
| (0,3,1) | 3550 | 3557 | 3557 |
| (0,2,2) | 3610 | 3607 | 3607 |
| (0,1,3) | 3642 | 3626 | 3626 |
| (0,0,4) | 3646 | 3654 | 3654 |
| (1,1,0) | 3947 | 3951 | 3951 |

[a] See footnote *b* of Table 11.

**Table 13** Experimental and calculated vibrational energy levels, in $cm^{-1}$, for the $\tilde{X}$ state of $DC^{35}Cl$[a]

| Vibrational level $(v_1,v_2,v_3)$ | Exp. | VPT2(–Exp.) | Var4(–Exp.) | $Var4^+$(–Exp.) |
|---|---|---|---|---|
| (0,0,1) | 801 | −3 | −1 | −1 |
| (0,1,0) | 893 | +2 | +3 | +3 |
| (0,0,2) | 1594 | −8 | −4 | −4 |
| (0,1,1) | 1690 | −2 | +1 | +1 |
| (0,2,0) | 1772 | +5 | +7 | +7 |
| (1,0,0) | 2081 | −7 | −5 | −5 |
| (0,0,3) | 2377 | −12 | −6 | −6 |
| (0,1,2) | 2478 | −5 | −1 | −1 |
| (0,2,1) | 2565 | +1 | +5 | +5 |
| (0,3,0) | 2644 | +1 | +7 | +6 |
| (1,0,1) | 2880 | −9 | −6 | −6 |
| (1,1,0) | 2975 | −4 | −2 | −2 |
| (0,0,4) | | 3134 | 3142 | 3142 |
| (0,1,3) | | 3247 | 3253 | 3253 |
| (0,2,2) | 3349 | −3 | +3 | +2 |
| (0,3,1) | 3434 | −3 | +4 | +3 |
| (0,4,0) | 3497 | 4 | +16 | +14 |
| (1,0,2) | | 3658 | 3662 | 3662 |
| (1,1,1) | 3768 | −5 | −2 | −2 |
| (1,2,0) | 3850 | +4 | +2 | +1 |
| (0,0,5) | | 3894 | 3904 | 3904 |
| (0,1,4) | | 4012 | 4020 | 4020 |
| (2,0,0) | | 4075 | 4084 | 4084 |
| (0,2,3) | | 4117 | 4123 | 4123 |
| (0,3,2) | 4214 | +7 | +1 | 0 |
| (0,4,1) | 4278 | −5 | +18 | +15 |
| (0,5,0) | 4350 | +6 | +17 | +12 |
| (1,0,3) | | 4435 | 4441 | 4441 |
| (1,1,2) | | 4546 | 4550 | 4550 |
| (1,2,1) | 4641 | −1 | 0 | 0 |
| (0,0,6) | | 4644 | 4657 | 4657 |
| (1,3,0) | 4715 | −9 | +1 | 0 |
| (0,1,5) | | 4768 | 4777 | 4777 |
| (2,0,1) | | 4870 | 4878 | 4878 |
| (0,2,4) | | 4878 | 4886 | 4885 |
| (2,1,0) | | 4972 | 4982 | 4981 |
| (0,3,3) | | 4973 | 4987 | 4987 |

[a] See footnote *b* of Table 11.

of the perturbation effects can be determined based on the present data.

There are no experimental data available on the vibrational energy levels of triplet HCCl, and only two vibrationally excited energy levels in the ã state of DCCl were observed experimentally.[17] For these two vibrational levels of DCCl the calculated data and the experimental values agree to within 6–15 $cm^{-1}$. Again, this discrepancy, at least partially, might be caused by spin–vibronic interaction between the singlet and triplet states.

### IV.2. $CCl_2$

As expected, the variationally calculated vibrational levels of singlet $CCl_2$ show an even better agreement with the experimental observations than it was found for HCCl and DCCl. Comparing the Var4 energy levels up to 4000 $cm^{-1}$ to the experimental data of Liu *et al*[43] results in an rms error of 2.6 $cm^{-1}$, which is even less than the assigned uncertainty, ±3 $cm^{-1}$, of the experimental data. The deviation of the Var4 results from the experimental data set of Kable *et al*[44] is somewhat worse, the rms error is 6.9 $cm^{-1}$ for the same region. The rms error calculated from comparing the Liu *et al*[43] data set with the VPT2 results is even larger, it is 9.7 $cm^{-1}$. In the former case the larger rms error is probably due to the lower precision of the experimental data set, while in the latter case it is the consequence of the less accurate theoretical treatment, *i.e.*, perturbational *vs.* variational, of the nuclear motion problem.

**Table 14** Experimental and calculated vibrational energy levels, in $cm^{-1}$, for the ã state of $DC^{35}Cl$[a]

| Vibrational level $(v_1,v_2,v_3)$ | Exp. | VPT2(–Exp.) | Var4(–Exp.) | $Var4^+$(–Exp.) |
|---|---|---|---|---|
| (0,1,0) | | 707 | 708 | 707 |
| (0,0,1) | | 876 | 879 | 879 |
| (0,2,0) | 1414 | −8 | −6 | −8 |
| (0,1,1) | | 1575 | 1579 | 1578 |
| (0,0,2) | | 1742 | 1748 | 1748 |
| (0,3,0) | 2110 | −7 | −9 | −15 |
| (0,2,1) | | 2268 | 2271 | 2268 |
| (1,0,0) | | 2288 | 2289 | 2289 |
| (0,1,2) | | 2432 | 2440 | 2439 |
| (0,0,3) | | 2596 | 2607 | 2607 |
| (0,4,0) | | 2792 | 2785 | 2770 |
| (0,3,1) | | 2955 | 2956 | 2949 |
| (1,1,0) | | 2988 | 2990 | 2990 |
| (0,2,2) | | 3117 | 3125 | 3121 |
| (1,0,1) | | 3166 | 3170 | 3170 |
| (0,1,3) | | 3278 | 3291 | 3290 |
| (0,0,4) | | 3439 | 3456 | 3426 |
| (0,5,0) | | 3475 | 3458 | 3455 |
| (0,4,1) | | 3635 | 3633 | 3615 |
| (1,2,0) | | 3682 | 3685 | 3683 |
| (0,3,2) | | 3795 | 3803 | 3793 |
| (1,1,1) | | 3858 | 3863 | 3862 |
| (0,2,3) | | 3954 | 3969 | 3964 |

[a] See footnote *b* of Table 11.

As it is expected, no perturbation due to spin–vibronic interaction with the triplet state can be found up to 4000 $cm^{-1}$, since the calculated triplet–singlet energy gap is well above this energy region. Although further converged Var4 results are available in the ESI,† due to the high density of vibrational levels above 4000 $cm^{-1}$ the assignment of these energy states to given vibrational quantum numbers is ambiguous without detailed wave function analysis. This was omitted in the present study.

The calculated vibrational levels of triplet $C^{35}Cl_2$ are summarized in Table 15. Considering the excellent performance of the Var4 results for the singlet state, the predictions for the triplet state are expected to be similarly good, which could help the further analysis of the experimental data, including the determination of $T_0(\tilde{a})$. Some suggested directions for future experiments utilizing these computed data will be discussed briefly in Section VI.

## V. Enthalpies of formation

Utilizing the high-quality *ab initio* results described above, the enthalpies of formation of $HCCl(\tilde{X}^1A')$ and $CCl_2(\tilde{X}^1A_1)$ at 0 K have been determined by calculating the enthalpy change of the reactions

$$CH_2(\tilde{a}^1A_1) + HCl(\tilde{X}^1\Sigma^+) \rightarrow HCCl(\tilde{X}^1A') + H_2(\tilde{X}^1\Sigma_g) \quad (5)$$

and

$$CH_2(\tilde{a}^1A_1) + 2HCl(\tilde{X}^1\Sigma^+) \rightarrow CCl_2(\tilde{X}^1A_1) + 2\,H_2(\tilde{X}^1\Sigma_g) \quad (6)$$

For the enthalpies of formation of $HCl(\tilde{X}^1\Sigma^+)$, $H_2(\tilde{X}^1\Sigma_g)$, and $CH_2(\tilde{a}^1A_1)$, required to evaluate $\Delta_fH_0^\circ$ (HCCl) and $\Delta_fH_0^\circ$ ($CCl_2$), see Table 17. The advantages of this procedure over calculating the appropriate atomization energies lies in that (i) the contribution of the spin–orbit effect can be neglected since it is much smaller for a non-linear open-shell species than for an atom; and (ii) the errors due to neglecting higher-order correlation effects (*e.g.* δCCSDTQP) is expected to cancel out in a proper reaction scheme.

**Table 15** Experimental and calculated vibrational energy levels, in cm$^{-1}$, for the $\tilde{X}$ state of $C^{35}Cl_2$[a]

| Vibrational level ($v_1$,$v_2$,$v_3$) | Exp.#1[43] | Exp.#2[44] | VPT2(–Exp.#1) | Var4(–Exp.#1) | Var4(–Exp.#2) |
|---|---|---|---|---|---|
| (0,1,0) | 334 | 335 | 0 | +1 | 0 |
| (0,2,0) | 668 | 669 | +1 | +1 | 0 |
| (1,0,0) | 726 | 727 | +2 | +1 | 0 |
| (0,0,1) | 757.9[b] | | 757 | 760 | |
| (0,3,0) | 1003 | 1003 | +3 | 0 | 0 |
| (1,1,0) | 1058 | 1059 | +2 | +3 | +2 |
| (0,1,1) | | | 1086 | 1090 | |
| (0,4,0) | 1337 | 1337 | +5 | 0 | 0 |
| (1,2,0) | 1394 | 1391 | +6 | 0 | +3 |
| (0,2,1) | | | 1415 | 1420 | |
| (2,0,0) | 1448 | 1445 | +7 | +1 | +4 |
| (1,0,1) | | | 1476 | 1481 | |
| (0,0,2) | | 1509 | 1504 | 1511 | +2 |
| (0,5,0) | 1670 | 1668 | +6 | 0 | +2 |
| (1,3,0) | 1727 | 1723 | +8 | 0 | +4 |
| (0,3,1) | | | 1743 | 1750 | |
| (2,1,0) | 1779 | 1775 | +7 | +2 | +6 |
| (1,1,1) | | | 1804 | 1810 | |
| (0,1,2) | | 1839 | 1828 | 1837 | −2 |
| (0,6,0) | 2002 | 2002 | +6 | +1 | +1 |
| (1,4,0) | 2057 | 2053 | +7 | +2 | +6 |
| (2,2,0) | 2111 | 2106 | +8 | +1 | +6 |
| (3,0,0) | 2161 | 2159 | +9 | +2 | +4 |
| (1,0,2) | | 2227 | 2218 | 2229 | +2 |
| (0,7,0) | 2336 | 2333 | +9 | −1 | +2 |
| (1,5,0) | 2389 | 2386 | +8 | +2 | +5 |
| (2,3,0) | 2442 | 2437 | +9 | +2 | +7 |
| (3,1,0) | 2492 | 2489 | +10 | +3 | +6 |
| (1,1,2) | | 2549 | 2541 | 2554 | +5 |
| (0,8,0) | 2668 | 2663 | +10 | −1 | +4 |
| (1,6,0) | 2721 | 2717 | +9 | +2 | +6 |
| (2,4,0) | 2772 | 2766 | +9 | +3 | +9 |
| (3,2,0) | 2823 | 2817 | +12 | +2 | +8 |
| (4,0,0) | 2870 | 2866 | +13 | +4 | +8 |
| (0,9,0) | 2997 | 2993 | +9 | 0 | +4 |
| (1,7,0) | 3051 | 3046 | +10 | +3 | +8 |
| (2,5,0) | 3102 | 3097 | +10 | +4 | +9 |
| (3,3,0) | 3151 | 3145 | +11 | +4 | +10 |
| (4,1,0) | 3199 | 3194 | +14 | +3 | +8 |
| (0,10,0) | 3329 | 3323 | +10 | −1 | +5 |
| (1,8,0) | | 3375 | 3371 | 3385 | +10 |
| (2,6,0) | 3431 | 3425 | +10 | +5 | +11 |
| (3,4,0) | 3480 | 3474 | +12 | +5 | +11 |
| (4,2,0) | 3528 | 3521 | +15 | +4 | +11 |
| (5,0,0) | 3573 | 3567 | +18 | +4 | +10 |
| (0,11,0) | 3656 | 3649 | +8 | +1 | +8 |
| (1,9,0) | | 3703 | 3700 | 3708 | +5 |
| (2,7,0) | | 3752 | 3750 | 3765 | +13 |
| (3,5,0) | 3808 | 3802 | +12 | +6 | +12 |
| (4,3,0) | 3852 | 3849 | +11 | −2 | +1 |
| (5,1,0) | 3901 | 3891 | +19 | +3 | +14 |
| (0,12,0) | 3987 | 3979 | +9 | 0 | +8 |

[a] See footnote *b* of Table 11. All vibrational levels are listed up to 2000 cm$^{-1}$. Between 2000 cm$^{-1}$ and 4000 cm$^{-1}$ only the vibrational levels included for which experimental observations are available. [b] Measured in Ne matrix, from ref. 41.

## V.1. HCCl

The enthalpy of formation of HCCl($\tilde{X}^1A'$) at 0 K, $\Delta_f H_0^o$ (HCCl), calculated from the enthalpy change of reaction (5) and $\Delta_f H_0^o$ of $CH_2(\tilde{a}^1A_1)$,[138] $HCl(\tilde{X}^1\Sigma^+)$,[91] and $H_2(\tilde{X}^1\Sigma_g)$[90] is 76.28 kcal mol$^{-1}$. Due to the abovementioned error compensation of the total energy of $CH_2(\tilde{a}^1A_1)$ and HCCl($\tilde{X}^1A'$) the enthalpy change of reaction (5) is expected to be estimated to better than ±0.1 kcal mol$^{-1}$. A larger part of the uncertainty of the present calculation comes from the uncertainty of $\Delta_f H_0^\circ$ of $CH_2(\tilde{a}^1A_1)$ and a smaller portion from the uncertainty of $\Delta_f H_0^\circ$ of $HCl(\tilde{X}^1\Sigma^+)$. Since these uncertainties are ±0.16 and ±0.024 kcal mol$^{-1}$, respectively, we allocate a ±0.20 kcal mol$^{-1}$ uncertainty to our final value of $\Delta_f H_0^\circ$ (HCCl). Utilizing the calculated thermal correction, $\Delta_f H_{298}^\circ - \Delta_f H_0^\circ = 0.07$ kcal mol$^{-1}$, of ref. 77. results in 76.35 ± 0.20 kcal mol$^{-1}$ for $\Delta_f H_{298}^\circ$ of HCCl($\tilde{X}^1A'$).

The uncertainty of the present result is smaller by a factor of five than the uncertainty of the former highest-level calculation,[77] and more than an order of magnitude smaller than the values obtained by experiments[45–47] or reported in the available thermochemical databases.[143–146]

**Table 16** Calculated vibrational energy levels, in $\text{cm}^{-1}$, for the $\tilde{a}$ state of $C^{35}Cl_2$[a]

| Vibrational level ($v_1$,$v_2$,$v_3$) | VPT2 | Var4 |
|---|---|---|
| (0,1,0) | 298 | 299 |
| (0,2,0) | 597 | 599 |
| (0,0,1) | 676 | 679 |
| (0,3,0) | 897 | 900 |
| (0,1,1) | 973 | 977 |
| (1,0,0) | 989 | 991 |
| (0,4,0) | 1196 | 1200 |
| (2,0,1) | 1271 | 1276 |
| (1,1,0) | 1283 | 1287 |
| (0,0,2) | 1345 | 1352 |
| (5,0,0) | 1497 | 1502 |
| (3,0,1) | 1568 | 1574 |
| (2,1,0) | 1577 | 1583 |
| (1,0,2) | 1640 | 1648 |
| (0,1,1) | 1661 | 1666 |
| (6,0,0) | 1797 | 1804 |
| (4,0,1) | 1867 | 1874 |
| (3,1,0) | 1873 | 1879 |
| (2,0,2) | 1936 | 1945 |
| (1,1,1) | 1954 | 1960 |
| (0,2,0) | 1964 | 1970 |

[a] See footnote *b* of Table 11.

### V.2. $CCl_2$

The enthalpy of formation of $CCl_2(\tilde{X}^1A_1)$ at 0 K, $\Delta_f H_0^\circ$ ($CCl_2$), calculated through Reaction (6), is 54.54 kcal $\text{mol}^{-1}$. From considerations analogues to those given in Section V.1. the uncertainty of this value is ±0.20 kcal $\text{mol}^{-1}$.

The thermal correction of the enthalpy of formation of $CCl_2(\tilde{X}^1A_1)$ can be obtained as follows: $\Delta_f H_{298}^\circ - \Delta_f H_0^\circ[CCl_2](\tilde{X}^1A_1)] = \{H_{298} - H_0[CCl_2(\tilde{X}^1A_1)]\} - \{H_{298}{-}H_0[C_{\text{graphite}}]\} - \{[Cl_2\ (\tilde{X}^1\Sigma_g)]\} = \{2.737\}^{90} - \{2.194\}^{90} - \{0.251\}^{79}$ kcal $\text{mol}^{-1} = 0.292$ kcal $\text{mol}^{-1}$. This value is equal to the calculated value of ref. 77, and it results in 54.83 ± 0.20 kcal $\text{mol}^{-1}$ for $\Delta_f H_{298}^\circ$ of $CCl_2(\tilde{X}^1A_1)$.

The present result is in excellent agreement with the recent W2 computation of Demaison *et al*[79] Furthermore, due to the inclusion of higher-order correlation effects in its computation in this study and utilization of a reaction scheme instead of atomization energies it was possible to reduce the uncertainty of the theoretical predictions by a factor of two. Note that the present value, as well as recently published theoretical values,[78,79] have at least an order of magnitude smaller uncertainty than the values given in the available thermochemical databases.[143–148]

## VI. Summary and outlook

In this paper the best technically feasible values for the triplet–singlet energy gap of the HCCl/DCCl and $CCl_2$ radicals have been determined through the focal-point approach. The final estimates for the triplet–singlet energy gap, $T_0(\tilde{a})$, are 2170 ± 40/2171 ± 40 $\text{cm}^{-1}$ for HCCl/DCCl and 7045 ± 60 $\text{cm}^{-1}$ for $CCl_2$. The estimate for HCCl is in very good agreement with the recently revised experimental value, 2167/2187 ± 18 $\text{cm}^{-1}$ for HCCl/DCCl, of Chang *et al*,[17] while the estimate for $CCl_2$ supports alternative reassessments[76,81] of the photodetachment spectrum of $CCl_2^-$ over the original assignment,[42] as well as the experimental lower limit value of $T_0(\tilde{a})$ suggested by Liu *et al.*[43]

Complete quartic force fields in internal coordinates have been computed for both the $\tilde{X}$ and $\tilde{a}$ states of both radicals at the frozen-core CCSD(T)/aug-cc-pVQZ level. Using these force fields vibrational energy levels were computed both by second-order vibrational perturbation theory and variationally. These results, especially the variational ones, show excellent agreement with the experimentally determined energy levels. The accuracy of these calculations and the systematic behavior of errors of vibrational progressions allowed us to determine the extent of perturbations due to spin–vibronic coupling between singlet and triplet vibrational levels of HCCl. In agreement with Chang *et al*,[17] significant perturbations, as much as 4–12 $\text{cm}^{-1}$ are observed for the $\tilde{X}(0,2,0)$, $\tilde{X}(0,2,1)$, and $\tilde{X}(0,2,2)$ vibrational levels.

From the accurate theoretical values the enthalpies of formation of $HCCl(\tilde{X}^1A')$ and $CCl_2(\tilde{X}^1A_1)$ were determined at 0 K, which are 76.28 ± 0.20 and 54.54 ± 0.20 kcal $\text{mol}^{-1}$, respectively. These results are in good agreement with other recent calculations. Furthermore, the uncertainties of the present results are smaller by a factor of 2–5 than the uncertainties of even the best of the former theoretical values, and more than an order of magnitude smaller than $\Delta_f H_0^\circ$ given in the available thermochemical databases.

It is worthwhile checking if the available dispersed fluorescence spectrum above 7000 $\text{cm}^{-1}$ (see Fig. 1) is consistent or inconsistent with the computed $T_0(\tilde{a})$ and the $\tilde{a}$ state vibrational levels of $CCl_2$. Within the error bar of the theoretically determined $T_0(\tilde{a})$, three–four peaks can be assigned to the vibrational origin of the triplet state; namely, A: 6954 ± 5 $\text{cm}^{-1}$, B: 7012 ± 5 $\text{cm}^{-1}$, C: 7033 ± 5 $\text{cm}^{-1}$, and D: 7071 ± 10 $\text{cm}^{-1}$. Marking the calculated triplet state $n_2$ vibrational progressions (and the first $n_3$ level) in the same figure (Fig. 1) it is

**Table 17** Components of and total electronic energies, in $E_h$, and enthalpies of formation at 0 K, $\Delta_f H_0^o$ in kcal $\text{mol}^{-1}$, of HCl, $H_2$, $CH_2$, HCCl, and $CCl_2$

| Term[a] | $HCl(\tilde{X}^1\Sigma^+)$ | $H_2(\tilde{X}^1\Sigma_g)$ | $CH_2(\tilde{a}^1A_1)$ | $HCCl(\tilde{X}^1A')$ | $CCl_2(\tilde{X}^1A_1)$ |
|---|---|---|---|---|---|
| HF | −460.1128048 | −1.1336211 | −38.8960759 | −497.8630432 | −956.8213197 |
| δCCSD(T) | −0.2653072 | −0.0409409 | −0.1817536 | −0.4221569 | −0.6629700 |
| δCCSDT | −0.0004920 | −0.0000000 | −0.0008128 | −0.0012263 | −0.0012721 |
| δCCSDTQ | −0.0002651 | −0.0000000 | −0.0001826 | −0.0006356 | −0.0011468 |
| ΔCC | −0.4096884 | — | −0.0549573 | −0.4644786 | −0.8947332 |
| ΔRel | −1.4057415 | −0.0000105 | −0.0150137 | −1.4209184 | −2.8269971 |
| ΔDBOC | +0.0061455 | +0.0085133 | +0.0037202 | +0.0078903 | +0.0128108 |
| ΔZPVE | +0.0067805 | +0.0098838 | +0.0164575 | +0.0011174 | +0.0041950 |
| **Sum** | **−462.1813730** | **−1.1561753** | **−39.1286182** | **−500.1634513** | **−961.1914331** |
| $\Delta_f H_0^\circ$ | **−22.018 ± 0.024**[b] | **−2.0239 ± 0.0002**[c] | **102.32 ± 0.16**[d] | **76.28 ± 0.20**[e] | **54.54 ± 0.20**[e] |

[a] The definition of the different terms are as follows, HF: CBS HF; δCCSD(T): CBS CCSD(T)(fc) – HF; δCCSDT: CCSDT(fc)/cc-pVTZ – CCSD(T)(fc)/cc-pVTZ; δCCSDTQ: CCSDTQ(fc)/cc-pVDZ – CCSDT(fc)/cc-pVDZ; ΔCC: CBS CCSD(T)(ae) – CBS CCSD(T)(fc); ΔRel: MVD1 CCSD(T)/cc-pCVQZ; ΔDBOC: DBOC HF/TZ2P; ΔZPVE: variational or VPT2 results. fc: frozen-core, ae: all-electron. [b] From ref. 91. [c] From ref. 90. [d] Data taken from refs. 88, 89 and 138. [e] Obtained from the other values of the table through reactions 5 and 6. See text for details.

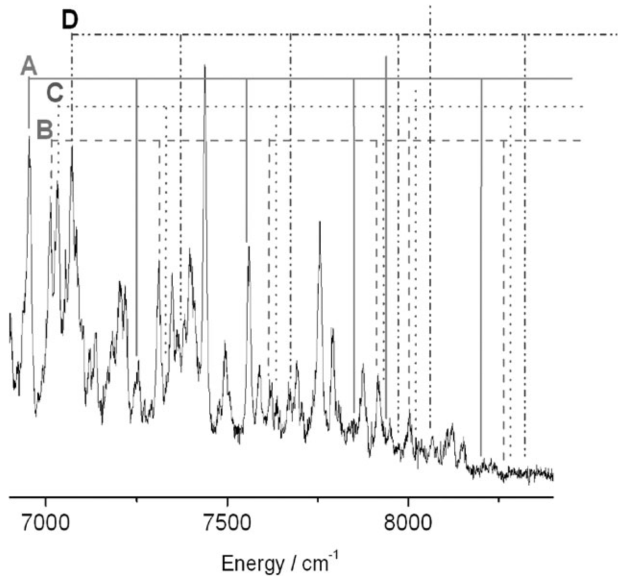

**Fig. 1** Possible assignments of ã state vibrational levels in the dispersed fluorescence spectrum of $C^{35}Cl_2$ as obtained by pumping the $1_0^2 2_0^3$ $\tilde{A} \leftarrow \tilde{X}$ transition. (The spectrum has been recorded at Ohio State University. See ref. 43 for technical details.)

apparent that progressions starting from peaks A and B match the other peaks of the spectrum best. Since peak A is slightly out of the error bar of the computed $T_0(\tilde{a})$, peak B becomes the most probable candidate for the ã(0,0,0) energy level. Of course, this assignment should be considered only very preliminary and tentative. It really just demonstrates that there are transitions in this spectral region consistent with the presence of the ã state. It is unlikely that these transitions are attributable to highly excited $\tilde{X}$ vibrational levels due to the poor Franck–Condon factors involved. Because of the high density of states in this region, spectra obtained at higher resolution and with better signal-to-noise ratio could notably facilitate arguments about the assignment.

Another problem making the above assignment ambiguous is related to spin–vibronic coupling. If the coupling is too small, the emissions to triplet state levels might not appear in the dispersed fluorescence spectrum at all. On the other hand, if the coupling is large, the triplet state vibrational levels computed using the triplet-state PES only could be significantly different from their experimental counterparts. Hence, it would be advisable to utilize other experiments to determine $T_0(\tilde{a})$ of $CCl_2$. Since the bond angles, and consequently the rotational constants are remarkably different in the singlet and triplet states (see Table 1), one possibility would be to record the rotationally resolved stimulated emission pumping (SEP) spectrum of $CCl_2$. Another possibility would be to record the absorption spectrum, *e.g.*, by the cavity ring-down spectroscopy (CRDS) technique. In this case the high-energy $\tilde{X}$ state vibrational overtones ($n_2 > 20$ or $n_1 > 10$) are not expected to appear in the spectrum, while the intensity of the triplet state levels is determined by the spin–vibronic coupling.

## Note added in proof

After submission of the paper we have received a manuscript from H.-G. Xu, T. Sears and J. T. Muckerman entitled "Potential energy surfaces and vibrational energy levels of DCCl and HCCl in three low-lying states". The MRCI calculations reported in this paper are in good agreement with our results. The only smaller difference between our and their results is in the numerical value (4 *vs.* 22 cm$^{-1}$, respectively) of the perturbation between the ã(0,1,0) and $\tilde{X}$(0,2,1) levels of HCCl.

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$$G(v_1, v_2, v_3) = \sum_{i=1,2,3} \omega_i^0 v_i + \sum_{i \geq j, i=1,2,3} x_{ij}^0 v_i v_j.$$

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