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Vibrational Frequencies and Ideal Gas Heat Capacities of Fluorochloro-Derivatives of Methane as Calculated from Quantum Mechanical Methods

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In a previous paper various quantum mechanical methods were applied to difluoromethane in order to find a suitable path to accurate ideal gas heat capacities. Now, these calculations are extended to all fluorochloro-derivatives of methane. Reliable experimental heat capacity data reveal that the combination of quantum mechanics and statistical thermodynamics facilitates a prediction of ideal gas heat capacities with an accuracy of ±1% and better. This is very close to the range of accuracy, which is observed for the best experimental zero pressure heat capacity data from different sources of the literature.

KEY WORDS: halogenated methanes; heat capacity; ideal gas; molecular structure; vibrational frequencies.

1. INTRODUCTION

Accurate ideal gas properties are accessible by means of statistical thermodynamics [1]. Based on the rigid rotator-harmonic oscillator (RRHO) model of the molecules, the ideal gas state functions result from the individual contributions of translation, external rotation, and vibrations. Additional terms correct for deviations of molecular behavior from the RRHO approximation, e.g., for anharmonicity of vibrations. But, as shown

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in Ref. 1 and can be seen from the previous paper on difluoromethane [2], the main contribution of anharmonicity to the heat capacity is already taken into account, if the vibrational part is evaluated with anharmonic vibrational frequencies. Then, for temperatures up to 600 K, the contributions of corrections are of less importance.

In the absence or in the case of conflicting molecular data from different literature sources, the calculation of heat capacities is no longer routine. If this situation is encountered, a method is required that yields the molecular data with high accuracy. This is accomplished from the combination of quantum mechanics and statistical thermodynamics. In a previous paper [2] we reported the results for ideal gas heat capacities of difluoromethane obtained from various quantum mechanical methods and basis sets of different quality. It was observed that the equilibrium structure and harmonic vibrational frequencies are predicted best by applying high quality basis sets and taking into account electron correlation as much as possible. However, available computational power is the limiting factor.

The scientific route to anharmonic vibrational frequencies must include cubic and quartic force constants in frequency calculations. But at present, this quantum mechanical treatment is restricted to molecules of smaller size than those of interest here.

In this paper we present results obtained from quantum mechanical treatment of all fluorochloro-derivatives of methane in order to find out which method and basis set is best suited for the prediction of heat capacities.

2. RESULTS

For all fluorochloro-derivatives of methane we calculated the molecular properties at the HF-, B3LYP- and MP2-levels with different basis sets using GAUSSIAN 98 [3]. ACES II [4] was used for CCSD(T) calculations, which could only be performed for a few molecules because of the lack of required computational power.

In order to assess the quality of the predicted vibrational frequencies, they have to be compared to experimental harmonic data. Unfortunately, these data are not available for all of the molecules considered here. For CH_4, CH_3F, CH_2F_2, and CH_3Cl, experimental vibrational frequencies corrected to their harmonic values can be found in the literature. These data are collected in Table I. As can be seen, their numerical values scatter in the range of nearly 2%. This uncertainty yields calculated heat capacities, which, e.g., for CH_3Cl, differ by up to 0.8% from each other. In view of missing harmonic data for all the molecules, these data are ruled out as a suitable reference for the assessment of the predictions.

Table I. Harmonic Vibrational Frequencies ω_i (cm^{-1}) from the Literature

CH_4

Ref.	ω_1 $\{A_1\}$	ω_2 $\{E\}$	ω_3 $\{F_2\}$	ω_4 $\{F_2\}$
[10]	3026	1583	3157	1367
[11]	3143	1573	3154	1357

CH_2F_2

Ref.	ω_1 $\{A_1\}$	ω_2 $\{A_1\}$	ω_3 $\{A_1\}$	ω_4 $\{A_1\}$	ω_5 $\{A_2\}$	ω_6 $\{B_1\}$	ω_7 $\{B_1\}$	ω_8 $\{B_2\}$	ω_9 $\{B_2\}$
[12]	3071	1539	1124	539	1288	3140	1202	1464	1101

CH_3F

Ref.	ω_1 $\{A_1\}$	ω_2 $\{A_1\}$	ω_3 $\{A_1\}$	ω_4 $\{E\}$	ω_5 $\{E\}$	ω_6 $\{E\}$
[13]	3055	1500	1067	3165	1510	1212
[14]	2995	1493	1064	3166	1509	1214
[15]	3005	1500	1067	3165	1510	1212
[16]	3031	1490	1059	3132	1498	1206

CH_3Cl

Ref.	ω_1 $\{A_1\}$	ω_2 $\{A_1\}$	ω_3 $\{A_1\}$	ω_4 $\{E\}$	ω_5 $\{E\}$	ω_6 $\{E\}$
[14]	3045	1388	741	3220	1492	1048
[15]	3062	1398	733	3209	1510	1049
[17]	3088	1396	751	3183	1496	1037

Although frequency data obtained from spectroscopic investigations differ from their corresponding harmonic values due to anharmonicity of molecular vibrations, they offer a unique basis for comparison. For all of the 15 fluorochloro-derivatives of methane, their numerical values can be found in the literature and are collected in Table II. These frequency data were already selected by Rodgers et al. [5] and Chen et al. [6] for their calculation of ideal gas properties and are chosen here as reference data for the following discussions. The only exception is $CHClF_2$, for which we selected the observed frequencies from the more recent work of Magill et al. [7]. As an example, we present the results of frequency calculations from the HF-, MP2-, and B3LYP-methods with a cc-pVDZ basis set first. The deviations of the calculated harmonic frequencies from the observed

Table II. Observed Vibrational Frequencies ν_i (cm^{-1}) from the Literature

		Symmetry								
		A_1	E	F_2						
Molecule	Ref.	ν_1	ν_2	ν_3	ν_4					
CH_4	[18]	2917	1534	3019	1306					
CF_4	[18]	909	435	1281	632					
CCl_4	[18]	459	217	776	314					
		A_1			E					
		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6			
CH_3F	[18]	2930	1464	1049	3006	1467	1182			
CHF_3	[18]	3036	1117	700	1372	1152	507			
CH_3Cl	[18]	2937	1355	732	3039	1452	1017			
$CHCl_3$	[18]	3034	680	363	1220	774	261			
$CClF_3$	[21]	1105	781	476	1212	563	350			
CCl_3F	[21]	1085	535	350	847	394	241			
		A_1				A_2	B_1		B_2	
		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
CH_2F_2	[19]	2949	1508	1116	529	1262	3012	1176	1436	1090
CH_2Cl_2	[18]	2999	1467	717	282	1153	3040	898	1268	758
CCl_2F_2	[21]	1101	667	458	262	322	1159	446	902	437
		A'						A''		
		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
CH_2ClF	[20]	2993	1470	1351	1068	760	385	3048	1236	1004
$CHClF_2$	[7]	3021	1313	1109	809	596	413	1351	1128	365
$CHCl_2F$	[6]	3026	1316	1083	742	456	274	1240	802	365

values are displayed as a departure plot in Fig. 1. Only CCSD(T) results are omitted, because, as previously mentioned, they were not performed for all the molecules. As can be seen, at the HF-level all vibrational frequencies are overestimated, ranging up to 15% around 1000 cm^{-1} and up to nearly 10% for the CH-stretching frequencies around 3000 cm^{-1}. Although at HF level, due to its variational principle and the approximation of harmonic oscillations, the vibrational frequencies are expected to be lower than their appropriate experimental data, one frequency around 1100 cm^{-1} is

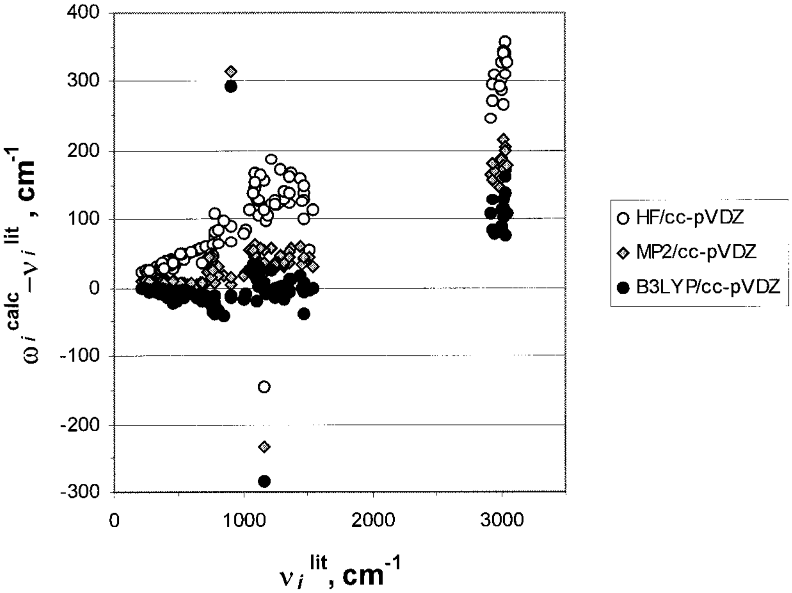

Fig. 1. Deviation of calculated and observed vibrational frequencies.

obviously underestimated. Taking into account electron correlation by the MP2 method again, all frequencies are predicted higher than their experimental values, except for the one mentioned before. Now the mean deviation is reduced to 3 %. Using B3LYP density functional theory, good overall agreement is achieved, but overestimation is observed for the predicted frequencies as well as underestimation. The resulting mean absolute deviation is 2.5 %.

The vibrational frequency, which is predicted too low, belongs to CCl_2F_2. The observed and the calculated fundamentals of difluorodichloromethane are collected in Table III. All calculations with different basis sets show the same tendency, i.e., indicating a possible wrong assignment of the highest B_1 and B_2 frequency. In order to improve certainty about assignment, we performed CCSD(T) calculations with basis sets of cc-pVDZ and aug-cc-pVDZ quality, additionally. But, as can be seen from the last two rows of Table III, these results are in agreement with the assignments of the literature. Such an interchange of assignment was not observed in the calculations of the other molecules. Especially these vibrational modes seem to be very sensitive to the shape of the intramolecular energy, i.e., the method to be applied. Further investigations will be necessary to give certainty about the assignment for this molecule and to reveal the influencing quantities. From a scientific point of view, this situation

Table III. Observed and Calculated Vibrational Frequencies of CCl_2F_2

	Symmetry								
	A_1				A_2	B_1		B_2	
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
Observed [21]	1101	667	458	262	322	1159	446	902	437
HF/cc-pVDZ	1254	726	497	286	354	1013	474	1347	471
MP2/cc-pVDZ	1137	673	464	269	328	926	445	1217	444
B3LYP/cc-pVDZ	1113	659	445	257	317	875	425	1195	428
CCSD(T)/cc-pVDZ	1138	665	457	265	324	1222	437	918	438
CCSD(T)/aug-cc-pVDZ	1088	647	450	264	320	1140	435	913	435

is unsatisfactory to some degree, but the prediction of the heat capacity is not affected, because these modes are nondegenerate.

In the following we discuss the impact of the various methods and basis sets on heat capacity. The reader, who is interested in the results of vibrational frequencies, IR intensities, and molecular geometries from the various methods and basis sets, is referred to Ref. 8, where the results are given in detail. The resulting deviations of the predictions are shown as departure plots in the next four figures. For all departure plots, the reference line represents the ideal heat capacity calculated from the observed frequencies of Table II, i.e., those of Refs. 5 and 6 except for $CHClF_2$ as mentioned previously. In order to give an overall impression only, different symbols for the individual molecules are omitted. At HF level, cf. Fig. 2, the heat capacities are underestimated up to a maximum of -7% due to an overestimation of vibrational frequencies. Moreover, dependence on the basis set is weak, except for the aug-cc-pVDZ basis set. But at MP2 level a distinct dependence on basis set is seen from Fig. 3. Again, the heat capacities are underestimated but now only up to a maximum of -2.5%. The only exception is the results obtained from the aug-cc-pVDZ basis set. At MP2 level this basis set is the only one of the basis sets used that leads to underestimated vibrational frequencies, resulting in an overestimation up to 2.5% for the heat capacity of CF_4.

It should be mentioned that Fig. 3 may be misleading regarding the accuracy achieved for higher basis sets than cc-pVTZ, because these calculations were not performed for all the molecules of the series. Best agreement is achieved from B3LYP calculations and the cc-pVDZ basis set, cf. Fig. 4. All the other basis sets lead to a broader range of deviations. Finally, Fig. 5 depicts the results obtained from CCSD(T) calculations. As

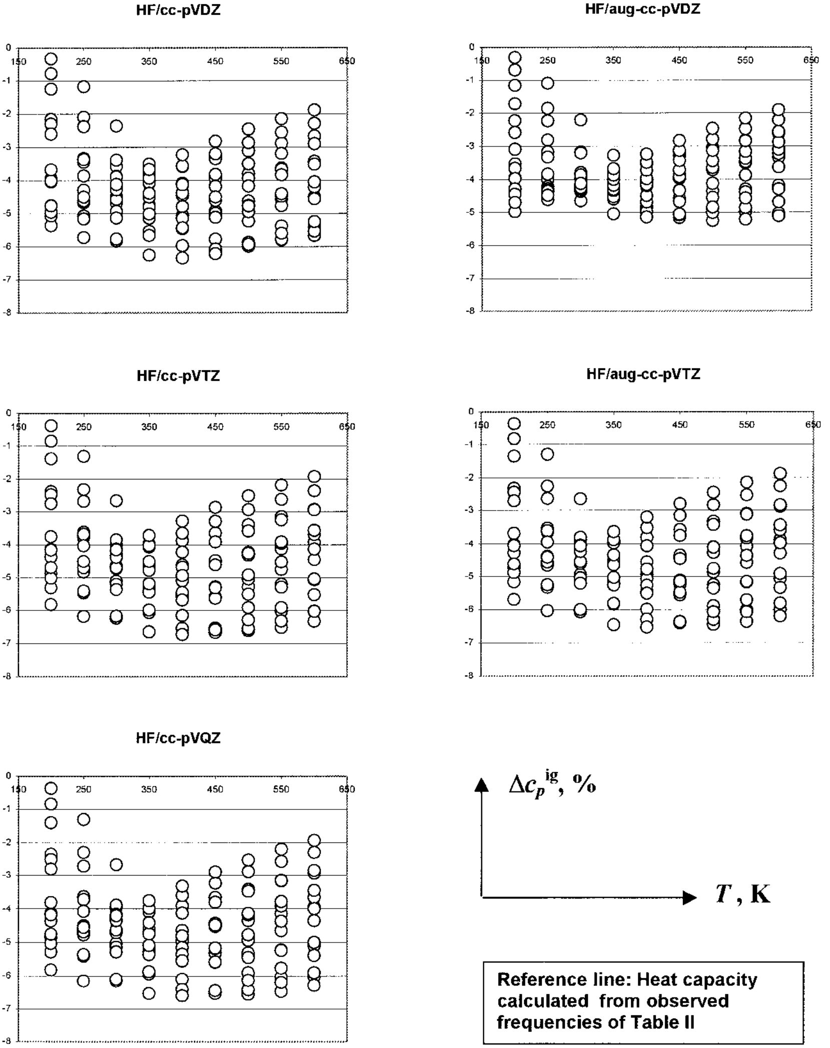

Fig. 2. Deviation of quantum mechanically calculated heat capacities: HF.

expected, the heat capacities from cc-pVDZ and cc-pVTZ basis sets are lower than their corresponding calculations from experimental frequencies. Here again the aug-cc-pVDZ basis set yields higher heat capacities due to an underestimation of vibrational frequencies. From this, we conclude that the B3LYP/cc-pVDZ method is well suited for the prediction of heat capacities.

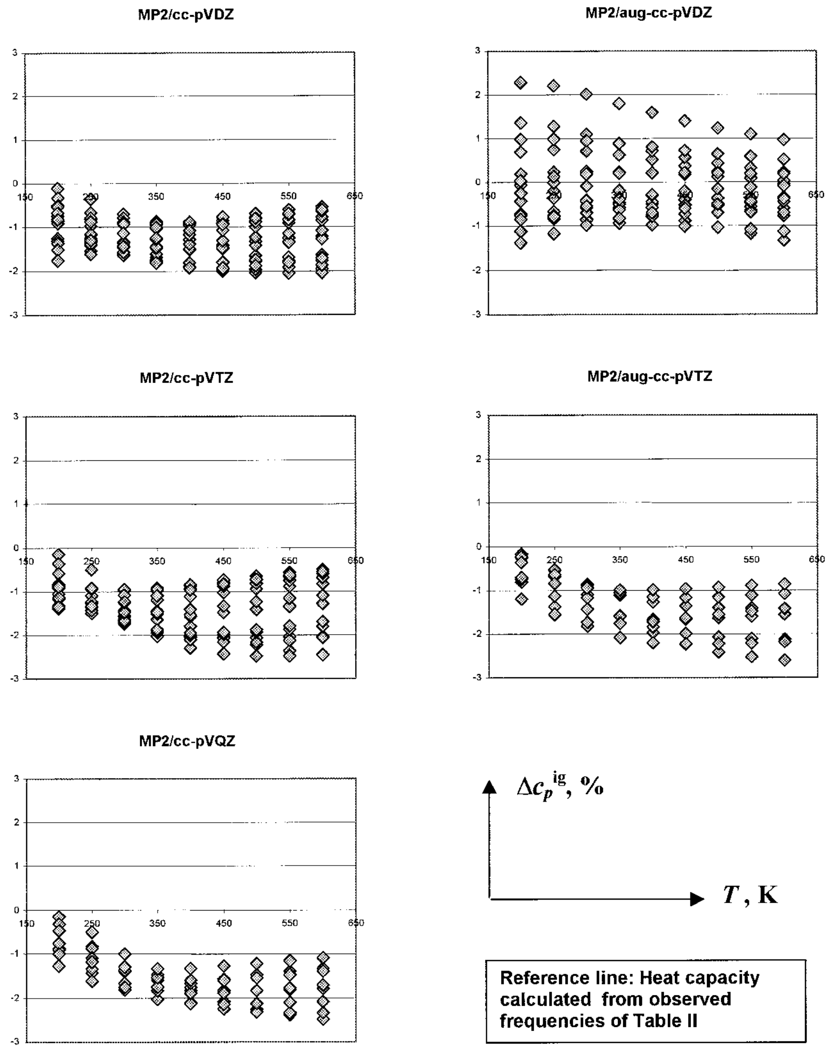

Fig. 3. Deviation of quantum mechanically calculated heat capacities: MP2.

In order to confirm this conclusion, B3LYP/cc-pVDZ predictions are compared to experimental heat capacity data obtained from speed-of-sound or calorimetric measurements extrapolated to zero pressure. The results are given in Figs. 6 to 13, where older heat capacity data are omitted, which were proven to be of less quality [9] and the reference line again represents ideal gas heat capacities calculated from the observed frequencies of Table II. For the molecules on which we performed MP2/cc-pVQZ

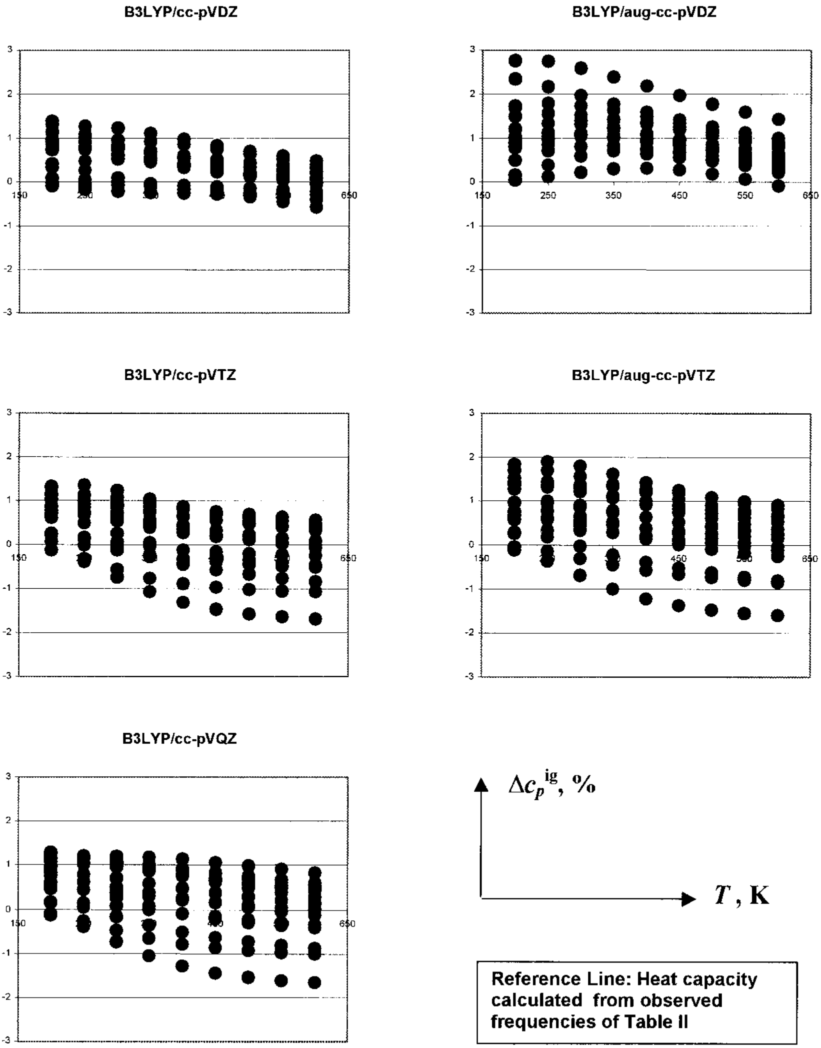

Fig. 4. Deviation of quantum mechanically calculated heat capacities: B3LYP.

and CCSD(T)/cc-pVTZ calculations, these results are also included. As can be seen, these two methods yield heat capacities that are up to 2.5% lower. Good agreement, however, with the experimental data in the range of ±1% is observed for B3LYP/cc-pVDZ predictions. From the departure plots it is seen that this is very close to the range of accuracy of the best experimental investigations, which sometimes differ by up to 1%.

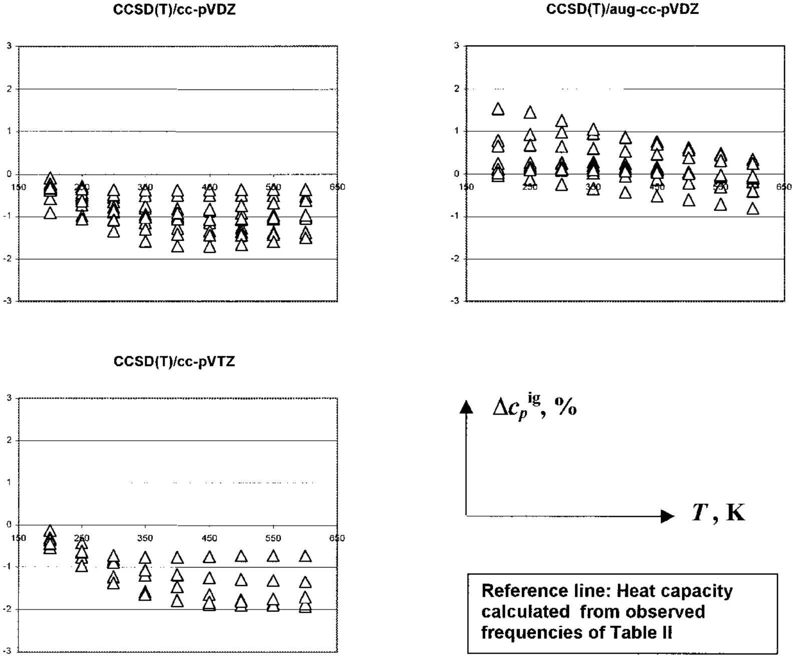

Fig. 5. Deviation of quantum mechanically calculated heat capacities: CCSD(T).

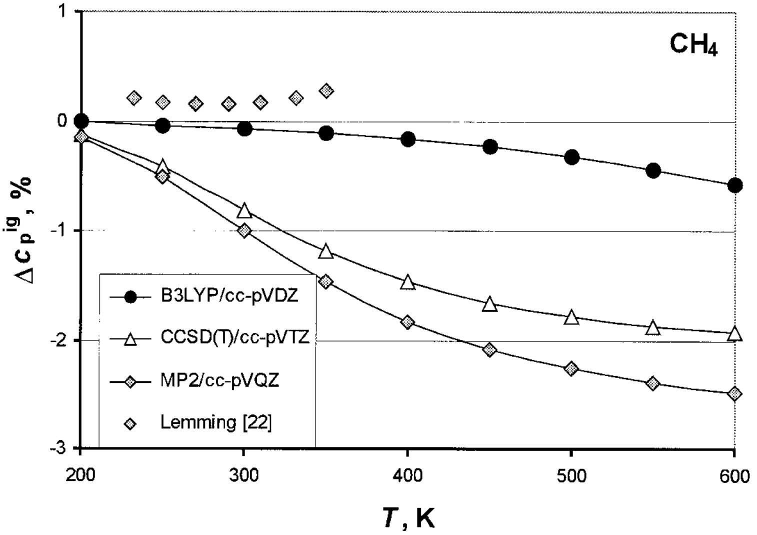

Fig. 6. Experimental and predicted heat capacity of CH_4.

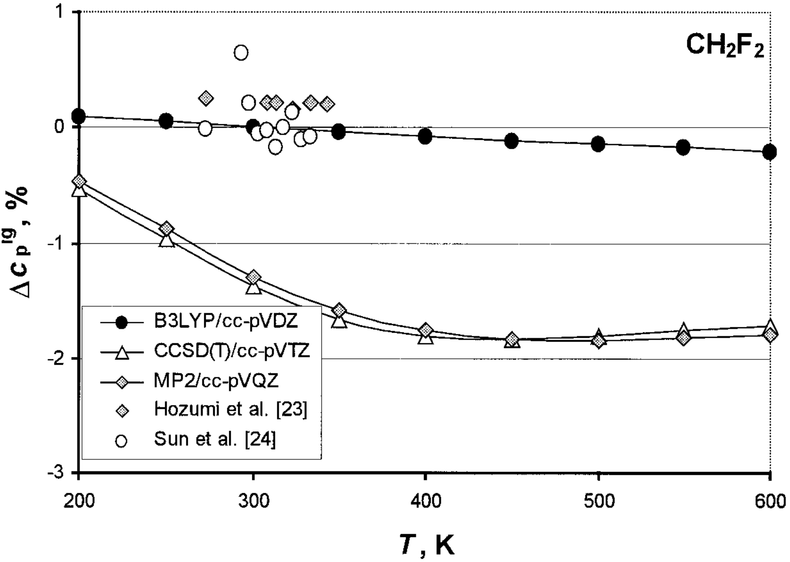

Fig. 7. Experimental and predicted heat capacity of CH_2F_2 (R32).

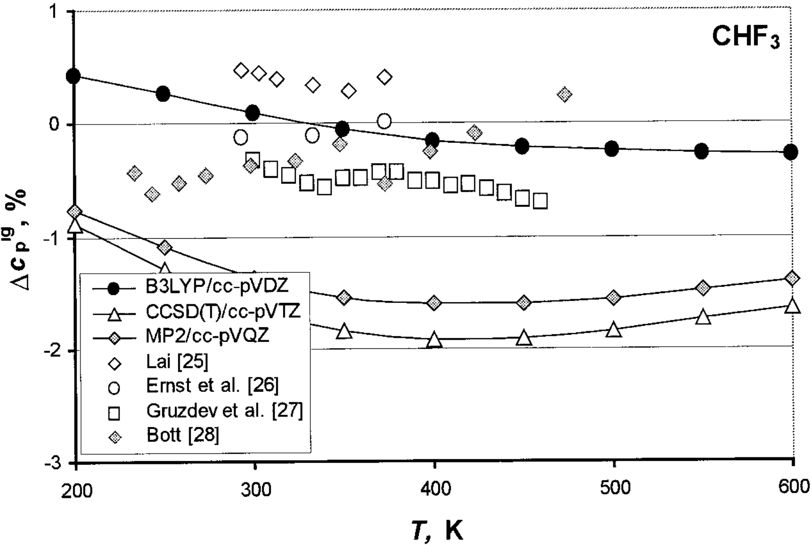

Fig. 8. Experimental and predicted heat capacity of CHF_3 (R23).

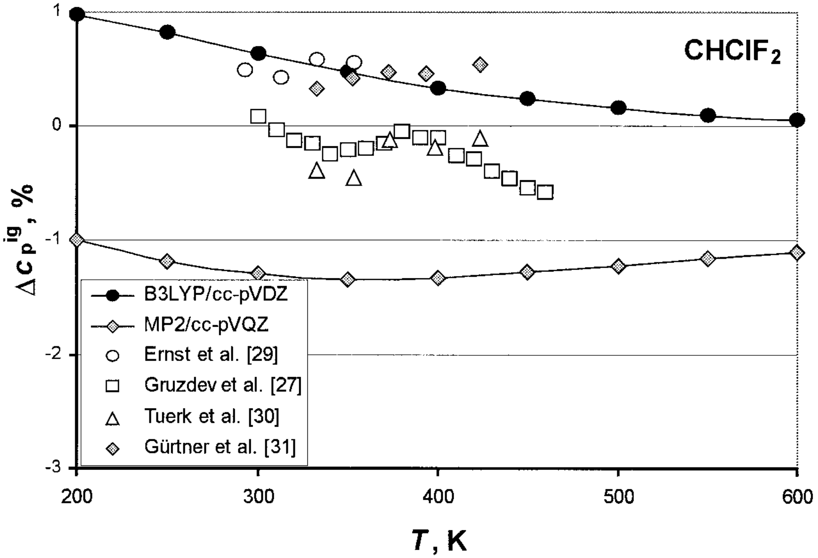

Fig. 9. Experimental and predicted heat capacity of CHClF$_2$ (R22).

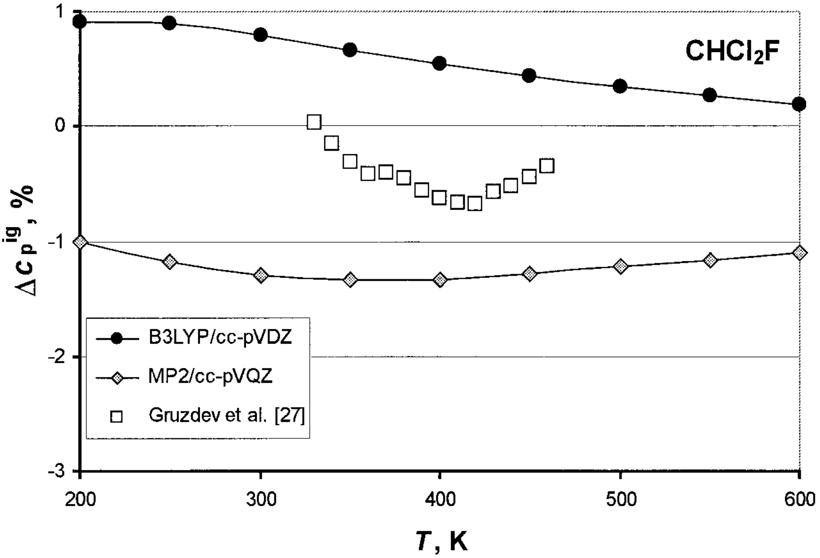

Fig. 10. Experimental and predicted heat capacity of CHCl$_2$F (R21).

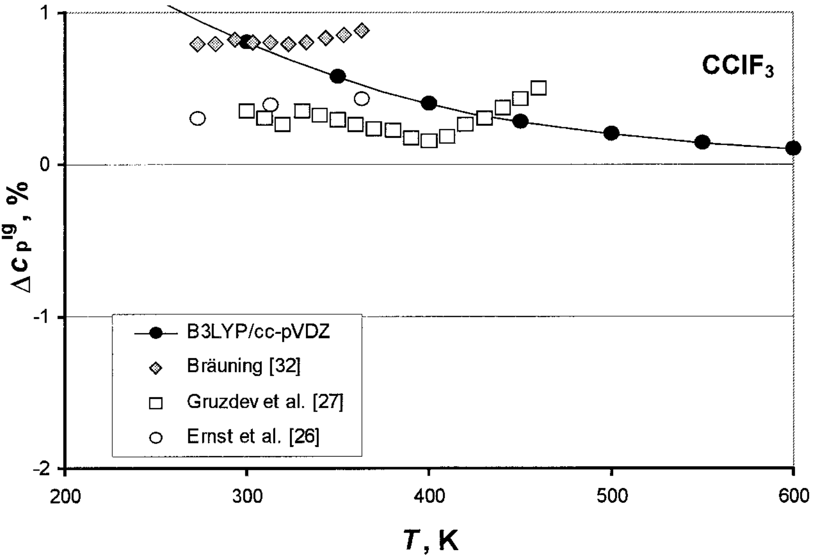

Fig. 11. Experimental and predicted heat capacity of $CClF_3$ (R13).

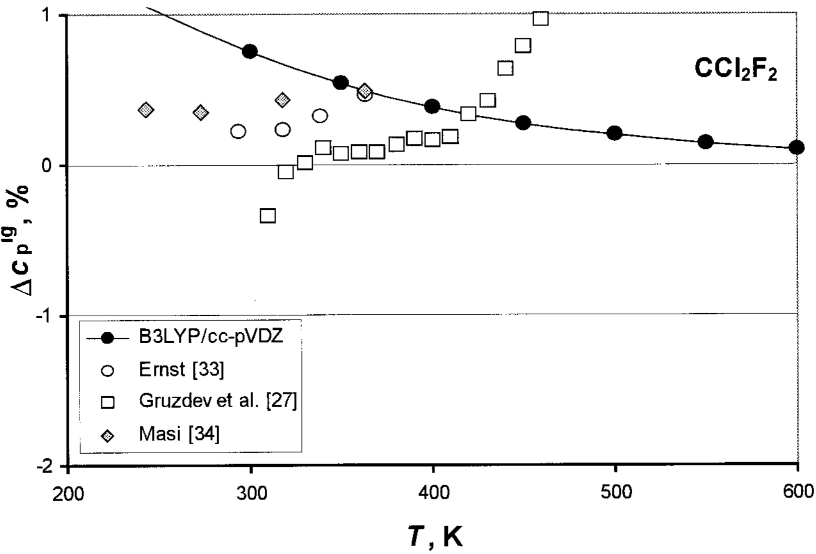

Fig. 12. Experimental and predicted heat capacity of CCl_2F_2 (R12).

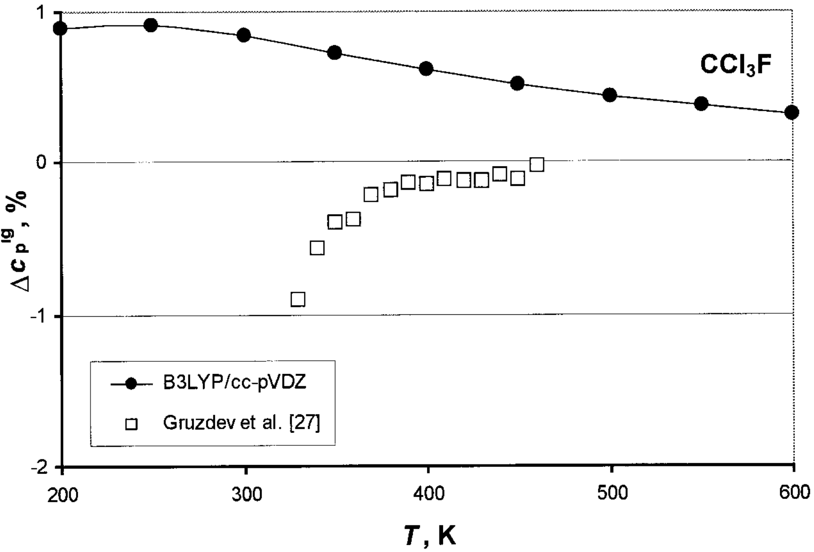

Fig. 13. Experimental and predicted heat capacity of CCl_3F (R11).

3. CONCLUSION

We performed quantum mechanical calculations with different methods and basis sets for all fluorochloro-derivatives of methane. It turned out that the B3LYP/cc-pVDZ method is a rational path to the prediction of heat capacities without any use of experimental information. Finally, reliable experimental heat capacity data reveal that the combination of quantum mechanics and statistical thermodynamics yields a prediction of ideal gas heat capacities with an accuracy of $\pm 1\%$ and better. This is very close to the range of accuracy, which is observed for the best experimental zero-pressure heat capacity data from different literature sources. In a following paper we will present the results obtained from this method for molecules of the series of ethane.

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