

Accurate determination of the binding energy of the formic acid dimer: The importance of geometry relaxation

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(Received 15 December 2013; accepted 12 February 2014; published online XX XX XXXX)

The formic acid dimer in its C_{2h} -symmetrical cyclic form is stabilized by two equivalent H-bonds. The currently accepted interaction energy is 18.75 kcal/mol whereas the experimental binding energy D_0 value is only 14.22 ± 0.12 kcal/mol [F. Kollipost, R. W. Larsen, A. V. Domanskaya, M. Nörenberg, and M. A. Suhm, *J. Chem. Phys.* **136**, 151101 (2012)]. Calculation of the binding energies D_e and D_0 at the CCSD(T) (coupled-cluster single double triple)/CBS (Complete Basis Set) level of theory, utilizing CCSD(T)/CBS geometries and the frequencies of the dimer and monomer, reveals that there is a 3.2 kcal/mol difference between interaction energy and binding energy D_e , which results from (i) not relaxing the geometry of the monomers upon dissociation of the dimer and (ii) approximating CCSD(T) correlation effects with MP2. The most accurate CCSD(T)/CBS values obtained in this work are $D_e = 15.55$ and $D_0 = 14.32$ kcal/mol where the latter binding energy differs from the experimental value by 0.1 kcal/mol. The necessity of employing augmented VQZ and VPZ calculations and relaxing monomer geometries of H-bonded complexes upon dissociation to obtain reliable binding energies is emphasized. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4866696>]

I. INTRODUCTION

One of the challenges of both experimental and theoretical chemistry is the accurate description of hydrogen-bonded complexes^{1,2} in such a way that the electronic factors of H-bonding can be separated from vibrational, temperature, pressure, and entropic effects. Much work has been devoted to the application of sophisticated quantum chemical methods, which can correctly assess the properties of H-bonded complexes.^{3–8} The ability of a quantum chemical method to accurately describe non-covalent interactions, especially H-bonds, is assessed by applying the method in question to a suitable test set of small complexes, for which reliable interaction energies are known. Such a test set is Set 22 (S22) originally defined by Hobza and co-workers,⁹ which contains typical H-bonded complexes, complexes with predominantly dispersion interactions, or those with weak electrostatic interactions.

These authors based their calculated interaction energies on CCSD(T) (coupled cluster method including all single (S) and double (D) excitations augmented by a perturbative treatment of the triple (T) excitations¹⁰) and MP2 (second order perturbation theory calculations with the Møller-Plesset perturbation operator^{11,12}). The latter level of theory was used to extrapolate CCSD(T) correlation energies to the complete basis set (CBS) limit in the sense of a focal point analysis.¹³ The original S22 interaction energies have been confirmed (with the inclusion of slight, but significant improvements)^{14–17} and are generally accepted by the quantum chemistry community. This is based on two cornerstones of computational chemistry: (i) CCSD(T) is considered to be the *gold standard* of

quantum chemical methodology. (ii) The focal point analysis leads to reasonable estimates of CCSD(T)/CBS interaction energies when calculating the CBS limit of the correlation energy with a low level method such as MP2.

Although the S22 interaction energies were originally thought to be reliable reference energies for the testing of new approximate quantum chemical methods, the fact that S22 coupled cluster energies of increasing accuracy have been published,^{14–17} can lead experimental and computational chemists to the assumption that any effect not considered in the calculation of the S22 interaction energies is of minor importance and that S22 energies can be directly taken as complex binding energies.

A key complex for the H-bonded examples of the S22 set is the formic acid dimer (**FAD**) in its cyclic, C_{2h} -symmetrical form, which is held together by two equivalent H-bonds (see Figure 1). When dissociating **FAD**, two formic acid molecules each in its trans form (*t*-**FA**) are obtained.¹⁸ **FAD** is significantly more stable than any of the other single or double H-bonded formic acid dimer.^{19–29} This has been confirmed by extended quantum chemical investigations.^{13,30–43} There have been reliable spectroscopic investigations of **FAD** in the gas phase, which have led to the determination of all its vibrational frequencies and an increasing amount of spectroscopic data at low temperatures.^{28,44–46}

The accepted interaction energy of **FAD** is 18.75 kcal/mol.^{14–17} In a recent publication, Suhm and co-workers²⁹ presented FTIR spectra of the hydrogen bond fundamentals of **FAD**, which were recorded in a supersonic slit jet expansion. Based on these data, the authors presented for the first time an accurate binding energy D_0 at 0 K of 14.22 kcal/mol for **FAD**. This value differs by 4.5 kcal/mol from the best value of the interaction energy published so far (18.75 kcal/mol^{16,17}).

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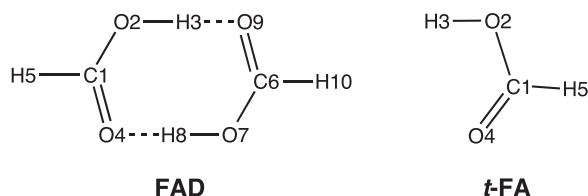


FIG. 1. Numbering of the atoms in the formic acid dimer (**FAD**) and in *trans* formic acid (**t-FA**).

84 Considering the high accuracy of quantum chemical
 85 calculations, which can be reached with modern methodologies,
 86 and considering the wealth of spectroscopic data for **FAD**, on
 87 which the measured D_0 value is based,²⁹ even a 1 kcal/mol
 88 difference between theory and experiment, let alone a
 89 4 kcal/mol difference is not acceptable. Of course, the ex-
 90 perimental binding energy at 0 K includes the effect of zero-
 91 point energies (ZPE) of **FAD** and **t-FA** monomers, whereas
 92 the quantum chemical values do not. However, it is the ques-
 93 tion whether this is the only reason for the large difference
 94 between the experimental binding energy D_0 and the calcu-
 95 lated interaction energies.

96 In this work, we will demonstrate that it requires an accu-
 97 rate calculation of geometry and vibrational frequencies at the
 98 CCSD(T)/CBS level of theory for both dimer and monomer
 99 to determine a reliable value for the binding energy of **FAD**.
 100 Especially, we will show that one has to base the CBS calcu-
 101 lations of the energy in this particular case on quadruple and
 102 pentuple zeta basis sets to obtain reliable energy differences.

103 II. COMPUTATIONAL METHODS

104 The procedure used in this work to obtain a reliable
 105 **FAD** binding energy D_0 consists of 5 steps. (i) First, bind-
 106 ing energy D_e , geometry, and harmonic vibrational frequen-
 107 cies of **FAD** and **t-FA** were calculated at the CCSD(T) level
 108 of theory¹⁰ utilizing up to four augmented correlation con-
 109 sistent Dunning basis sets: aug-cc-pVXZ with X = D, T, Q,
 110 and P (augmented double zeta: aD; augmented triple zeta:
 111 aT; augmented quadruple zeta: aQ; augmented pentuple zeta:
 112 aP).^{47,48} (ii) The influence of the basis set superposition er-
 113 ror (BSSE) was investigated for the calculated binding en-
 114 ergies by employing the counterpoise method of Boys.^{49,50}
 115 (iii) Formulas for 2- and 3-point extrapolations⁵¹⁻⁵³ were
 116 used to obtain reliable CCSD(T)/CBS values for D_e , geom-
 117 etry, and harmonic vibrational frequencies of both **FAD** and
 118 **t-FA**. The various CBS extrapolations are given by the fol-
 119 lowing notation: CBS(m,aX,aY,aZ) where m = 2 or 3 de-
 120 notes the 2- or 3-point extrapolations and is followed by the
 121 basis sets used. (iv) CCSD(T)/CBS results were compared
 122 with explicitly correlated CCSD(T)-F12 energies where the
 123 F12a and F12b approximations of Werner and co-workers
 124 were used.^{54,55} In these approaches, simplifications are em-
 125 ployed, which partly use MP2-F12 methodology only that
 126 the MP2 amplitudes are replaced by the CCSD amplitudes.
 127 CCSD-F12b differs from CCSD-F12a by a stronger cou-
 128 pling between the conventional and the explicitly correlated
 129 coupled cluster parts. The triples part is calculated in the
 130 conventional way, i.e., via perturbation theory. An approx-
 131 imate correction for the triple part by scaling with a fac-

132 tor Ecor(MP2-F12)/Ecor(MP2) determined by the correlation
 133 energies (Ecor) of a second order Møller-Plesset (MP2)^{11,12}
 134 and a MP2-F12 treatment,^{54,56} which has to be determined
 135 for the complex and applied to both the complex and the
 136 monomer to guarantee size-extensivity.^{55,57} (v) ZPE, needed
 137 for the calculation of D_0 values, were determined utilizing
 138 harmonic frequencies. Harmonic ZPE values were improved
 139 by obtaining B3LYP/aug-cc-pVTZ anharmonicity corrections
 140 for the harmonic frequencies.⁵⁸ The latter were compared
 141 with the experimental frequencies.^{29,59}

142 Conventional coupled cluster calculations were carried
 143 out with the program package CFOUR⁶⁰ whereas for the
 144 explicitly correlated CCSD(T)-F12 calculations the package
 145 MOLPRO⁶¹ was used.

146 III. RESULTS AND DISCUSSION

147 Results of this investigation are summarized in Table I
 148 (geometries), Table II (vibrational frequencies), and Table III
 149 (binding energies).

150 A. Use of the correct equilibrium geometry

151 The CCSD(T) geometries of both **FAD** and **t-FA** vary
 152 significantly for bond lengths when increasing the basis set
 153 size from aD to aT whereas the differences between aT and
 154 aQ are small. Changes in the bond angles are generally much
 155 smaller. The well-known shortening of the bond lengths with
 156 increasing basis set size can be observed, which is sometimes
 157 accompanied with a slight widening of the angles between
 158 adjoint bonds. One might argue that by augmenting a VDZ
 159 by a full set of diffuse functions (i.e., for both H and heavy
 160 atoms), the VDZ basis nearly adopts triple zeta quality and
 161 therefore the change in the geometries from aD to aT and aQ
 162 is moderate and regular. However, this is not the case because
 163 the diffuse functions do not improve the valence and bond-
 164 ing region significantly. Accordingly, CBS geometries deter-
 165 mined by a 2-point extrapolation based on just aug-cc-pVDZ
 166 and aug-cc-pVTZ basis sets, i.e., a CBS(2,aD,aT) geometry
 167 is unreliable and differs significantly from the 3-point extrap-
 168 olated CBS geometry including also the aug-cc-pVQZ result,
 169 i.e., CBS(3,aD,aT,aQ). The latter geometry is far more reli-
 170 able and verified by the CBS(2,aT,aQ) geometry, which be-
 171 comes obvious when comparing the H-bond length and the 2
 172 non-bonded distances O2...O9 and O2...O4 also given in
 173 Table I.

174 At all levels of theory, there is a relatively large change
 175 in the geometry of the monomer upon dimerization. The C–O
 176 bond lengths decrease from 1.340 to 1.307 Å, which is accom-
 177 panied by an increase of the C=O and OH bond lengths from
 178 1.197 to 1.215 Å and 0.965 to 0.994 Å, respectively. These
 179 bond length changes lead to a widening of the angles H3-C1-
 180 O2 (from 107.0° to 109.9°) and O2-C1=O4 (from 124.8° to
 181 126.1°, see Table I) and a corresponding change in the exter-
 182 nal angles (H5-C1-O2: 110.2 to 112.1; H5-C1=O4: 125.0°
 183 to 121.9°), where in all cases the CBS(2,aT,aQ) results are
 184 compared. Hence, H-bonding has not only a lengthening ef-
 185 fect on the OH donor bond, but also a shortening (lengthen-
 186 ing) effect on the C–O (C=O) bond, which are related to

TABLE I. Calculated and experimental bond lengths (in Å) and angles (in degree) are given for the formic acid dimer (**FAD**)⁶² and *trans* formic acid (*t*-**FA**).^{63–65} The calculated data are given at the CCSD(T)¹⁰ level of theory using the Dunning basis sets aug-cc-pVXZ where X = D, T, Q (aD, aT, aQ).^{47,48}

Molecule	Parameter	CCSD(T) aD	CCSD(T) aT	CCSD(T) aQ	CBS (2,aD,aT)	CBS (3,aD,aT,aQ)	CBS (2,aT,aQ)	Expt.
FAD	C1–H5	1.104	1.090	1.091	1.084	1.092	1.092	1.079
	C1–O2	1.328	1.311	1.309	1.304	1.307	1.307	1.320
	C1=O4	1.232	1.218	1.216	1.212	1.216	1.215	1.217
	O2–H3	0.997	0.992	0.993	0.989	0.994	0.994	1.033
	O4...H8	1.698	1.670	1.669	1.658	1.669	1.668	
	O2 O9	2.695	2.661	2.662	2.647	2.663	2.663	2.696
	O2 O4	2.284	2.257	2.252	2.246	2.249	2.248	2.262
	H5–C1–O2	111.6	111.6	111.9	111.7	112.0	112.1	
	H5–C1=O4	122.1	122.1	121.9	122.0	121.9	121.9	115.4
	O2–C1=O4	126.3	126.3	126.2	126.3	126.1	126.1	126.2
	C1–O2–H3	109.3	109.8	109.9	110.0	109.9	109.9	108.5
	C1=O4...H8	124.6	124.3	125.0	124.3	125.4	125.5	
O2–H3...O9	179.9	179.6	179.0	179.4	178.6	178.6	180.0	
<i>t</i> - FA	C1–H5	1.105	1.090	1.092	1.084	1.093	1.093	1.097
	C1–O2	1.360	1.343	1.341	1.336	1.340	1.340	1.343
	C1=O4	1.214	1.200	1.198	1.194	1.197	1.197	1.202
	O2–H3	0.974	0.967	0.966	0.964	0.965	0.965	0.972
	H4–C1–O2	109.8	109.7	110.0	109.7	110.2	110.2	
	H5–C1=O4	125.2	125.2	125.1	125.2	125.0	125.0	124.1
	O2–C1=O4	125.0	125.1	124.9	125.1	124.8	124.8	124.6
	C1–O2–H3	106.5	106.8	106.9	106.9	107.0	107.0	106.3

the strength of the H-bond. We calculate that these changes in the monomer geometry upon complex formation account for 2 times 1.26 kcal/mol yielding a change of 2.52 kcal/mol in total. Hence, any quantum chemical study that does not consider the effect of geometry relaxation upon dissociation of the complex will be inaccurate by this rather large energy change.

Comparison of the CCSD(T) geometries with the experimental geometry of both **FAD** and *t*-**FA** is only meaningful in a limited way, because the experimental geometries are based on microwave spectroscopy and electron diffraction (ED) data with uncertainties in the bond lengths up to 0.01 Å and in the bond angles up to 1°. An exception is the angle H5–C1–O4, where a standard deviation of 3.1° is given in the ED investigation.⁶² As for the position of H5, assumptions had to be made, which may cause this large uncertainty. In this connection, we note that there is a 6.5° difference between the CBS value of 121.9° and the ED value of 115.4°, which seems to confirm the problems of the ED investigations with regard to the exact position of H5. Apart from this, the O2–H3...O9 angle of **FAD** was assumed to be 180°. Hence, the corresponding r_o and r_a geometries of the target molecules can hardly be used to decide on the reliability of the r_e geometries obtained with different CBS-procedures. Test calculations show that, by using experimental geometries, the binding energy may differ as much as 4–5 kcal/mol (CCSD(T)/aT: $D_e = 13.11$ kcal/mol; CCSD(T)-F12a/aT: $D_e = 12.51$ kcal/mol; CCSD(T)-F12b/aT: $D_e = 12.49$ kcal/mol compared 18.12, 16.47, and 16.47 kcal/mol obtained with optimized geometries; see below). Obviously, the use of experimental geometries based on different techniques and

being derived by assuming specific parameters cannot be recommended.

B. Use of the correct zero-point energy

In Table II, CCSD(T) harmonic frequencies calculated with the aD and aT basis sets, the corresponding CBS(2,aD,aT) limit values, B3LYP/aT harmonic frequencies and their anharmonicity corrections, estimated anharmonically corrected CCSD(T) frequencies, and the corresponding experimental frequencies for both **FAD**²⁹ and *t*-**FA**⁵⁹ are compared. Since for the calculation of the D_0 binding energy the change in ZPE has to be known accurately, ZPE and Δ ZPE values (corrections) are also given in Table II for each set of frequencies. The dependence of the CCSD(T) Δ ZPE on the basis set is moderate despite of the strong dependence of the CCSD(T) normal mode frequencies ω_μ on the basis set. Hence, the CBS value of -2.13 kcal/mol for Δ ZPE can be predicted based on the harmonic approximation.

The anharmonically corrected B3LYP/aT frequencies lead to a Δ ZPE correction of -1.23 kcal/mol. This value is in line with the corresponding ZPE correction based on measured vibrational frequencies (-1.20 kcal/mol; see Table II). If the density functional theory (DFT) anharmonicity corrections are combined with the CCSD(T)/CBS harmonic frequencies a somewhat larger Δ ZPE correction of -1.52 kcal/mol is obtained. Since a CCSD(T)/CBS calculation of anharmonicity effects is beyond the scope of this investigation, we utilize for the calculation of the Δ ZPE value and the D_0 binding energy of **FAD** the B3LYP/aT harmonic and anharmonically corrected frequencies.

TABLE II. CCSD(T) and B3LYP harmonic vibrational frequencies ω_μ are given for the formic acid dimer (**FAD**) and *trans* formic acid (**t-FA**). CBS values of ω_μ were calculated using a 2-point extrapolation of the CCSD(T)/aug-cc-pVDZ (aD) and CCSD(T)/aug-cc-pVTZ (aT) frequencies. The anharmonic corrections (anh. cor.) were calculated using VPT2⁵⁸ at the B3LYP/aug-cc-pVTZ (aT) level of theory yielding a Δ ZPE of -1.23 kcal/mol. For the calculation of ZPE and Δ ZPE values, see text.

Molecule	μ	Sym	B3LYP aT	CCSD(T) aD	CCSD(T) aT	CBS (2,aD,aT)	B3LYP anh. cor.	CBS anh. est.	Exp.
FAD	24	B _u	3160	3307	3308	3309	-301	3008	3084
	23	A _g	3066	3210	3202	3199	-175	3024	2949
	22	B _u	3054	3116	3098	3091	-169	2922	2939
	21	A _g	3039	3112	3095	3088	-340	2748	2900
	20	B _u	1766	1750	1785	1799	-42	1757	1746
	19	A _g	1692	1691	1718	1730	-42	1688	1670
	18	B _u	1478	1481	1497	1504	-24	1480	1454
	17	A _g	1449	1455	1466	1471	-31	1439	1415
	16	A _g	1404	1387	1409	1418	-35	1383	1375
	15	B _u	1402	1384	1406	1415	-34	1381	1364
	14	B _u	1260	1231	1265	1279	-26	1253	1218
	13	A _g	1256	1224	1260	1275	-28	1247	1214
	12	B _g	1101	1091	1131	1148	-39	1109	1060
	11	A _u	1079	1067	1105	1121	-27	1094	1050
	10	A _u	1002	973	1018	1036	-36	1001	922
	9	B _g	982	952	994	1012	-52	960	911
	8	B _u	723	698	716	724	-8	716	698
7	A _g	689	668	688	697	-8	690	677	
6	B _u	281	272	280	283	-13	270	264	
5	B _g	260	252	259	263	-19	244	242	
4	A _g	212	209	214	216	-26	190	194	
3	A _u	186	172	190	197	-15	182	168	
2	A _g	175	169	166	165	-12	153	161	
1	A _u	77	68	72	74	-29	45	69	
ZPE (kcal/mol):			44.02	44.23	44.81	45.05	-2.19	42.87	42.52
t-FA	9	A'	3716	3725	3767	3785	-186	3599	3554
	8	A'	3048	3101	3098	3096	-156	2940	2956
	7	A'	1811	1779	1818	1835	-33	1802	1844
	6	A'	1402	1392	1414	1423	-18	1404	1384
	5	A'	1298	1304	1318	1323	-42	1281	1306
	4	A'	1121	1113	1141	1152	-33	1119	1101
	3	A''	1052	1036	1069	1083	-20	1063	1037
	2	A''	675	662	671	675	-56	618	639
	1	A'	629	618	632	638	-7	631	628
ZPE (kcal/mol):			21.09	21.06	21.34	21.46	-0.79	20.67	20.66
Δ ZPE (kcal/mol):			-1.84	-2.11	-2.13	-2.13	0.61	-1.52	-1.20

TABLE III. Calculated binding energies D_e and D_0 in kcal/mol are given for the formic acid dimer (**FAD**) and compared with the experimental D_0 value. The calculated D-values are based on CCSD(T),¹⁰ CCSD(T)-F12a, and CCSD(T)-F12b⁵⁷ using the Dunning basis sets aug-cc-pVXZ where X = D, T, Q, P (aD, aT, aQ, aP).^{47,48}

Property	CCSD(T) aD//aD	CCSD(T) aT//aT	CCSD(T) aQ//aQ	CCSD(T)/aP //CBS(2,aT,aQ)	CBS (2,aD,aT)	CBS (3,aD,aT,aQ)	CBS (2,aT,aQ)	CBS (3,aT,aQ,aP)	CBS (2,aQ,aP)	Expt.	Ref.
D_e (CCSD(T)-F12a)	16.75	16.47	16.25	16.17	16.36	16.11	16.08	16.12	16.09		
D_e (CCSD(T)-F12b)	16.57	16.47	16.29	16.21	16.44	16.19	16.16	16.16	16.13		
D_e (CCSD(T))	16.71	18.12	17.00	16.29	18.72	16.33	16.19	15.88	15.55		
D_0 (CCSD(T)-F12a)	15.54	15.26	15.04	14.96	15.12	14.91	14.88	14.91	14.88		
D_0 (CCSD(T)-F12b)	15.36	15.26	15.08	15.00	15.21	14.97	14.95	14.95	14.92		
D_0 (CCSD(T))	15.50	16.91	15.79	15.08	17.49	15.12	14.97	14.67	14.32	14.22 \pm 0.12	29

247 Within the VPT2 description of the ZPE, the following
248 formula is used:⁵⁸

$$ZPE(VPT2) = \chi_0 + \frac{1}{2} \sum_i^{N_{vib}} \left(\omega_i + \frac{1}{2} \chi_{ii} + \frac{1}{2} \sum_{j>i}^{N_{vib}} \chi_{ij} \right), \quad (1)$$

249 where ω denotes the harmonic vibrations, χ the anharmonic
250 constants, and $N_{vib} = 3N - L$ the number of vibrations with
251 N being the number of atoms and L the number of translations
252 and rotations of the molecule. Equation (1) can be simplified
253 to

$$ZPE(VPT2) = \frac{1}{2}(ZPEH + ZPEF) + \chi_0 - \frac{1}{4} \sum_i^{N_{vib}} \chi_{ii} \quad (2)$$

254 by defining the harmonic ZPE (ZPEH) and fundamental ZPE
255 (ZPEF) according to

$$ZPEH = \frac{1}{2} \sum_j^{N_{vib}} \omega_j \quad (3)$$

256 and

$$ZPEF = \frac{1}{2} \sum_j^{N_{vib}} \nu_j, \quad (4)$$

257 where the fundamental frequencies ν_i are defined by

$$\nu_i = \omega_i + 2\chi_i + \frac{1}{2} \sum_{j \neq i}^{N_{vib}} \chi_{ij}. \quad (5)$$

258 In this work, we have chosen to use Eq. (4) because the
259 corresponding DFT ZPE correction ΔZPE is close to
260 that obtained for measured fundamental frequencies (-1.23
261 vs. -1.20 kcal/mol). The corresponding B3LYP result
262 for ZPE(VPT2) is -1.53 kcal/mol and would become
263 -1.83 kcal/mol if the ZPEH value from the CCSD(T)/CBS
264 calculations is used. The accuracy of ZPE(VPT2) depends
265 first of all on ZPEH and ZPEF where at least the latter term
266 is satisfactorily reproduced at the B3LYP level. Generally, the
267 last two terms of Eq. (2) are considered to be less important.⁵⁸
268 This is confirmed by our calculations as the contributions
269 from these terms to ΔZPE are just 0.15 kcal/mol. Hence, the
270 accuracy of ZPE(VPT2) depends on the accuracy of ZPEH.
271 This will have to be considered when using ΔZPE to deter-
272 mine the binding energy D_0 from the calculated D_e (see be-
273 low).

274 C. Determination of the coupled cluster CBS 275 limit energy

276 CCSD(T) binding energies D_e calculated in this work
277 with the aug-cc-pVXZ basis sets for $X = D, T, Q, P$
278 (Table III) are 16.71, 18.12, 17.00, and 16.29 kcal/mol. By
279 using the 2-point extrapolation a CBS(2,aD,aT) value of
280 18.72 kcal/mol is obtained, which suffers from the deficien-
281 cies of the aug-cc-pVDZ basis set.⁶⁶⁻⁶⁹

282 These deficiencies are also reflected by the binding ener-
283 gies in Table III. The aD and aT results suggest an increase

284 in the binding energy with increasing number of basis func-
285 tions whereas the aT, aQ, and aP results indicate that the bind-
286 ing energy D_e decreases with an improvement of the basis
287 set. Accordingly, the CBS values based on the aQ and aP
288 basis, CBS(3,aT,aQ,aP): (15.88 kcal/mol) and CBS(2,aQ,aP)
289 (15.55 kcal/mol), predict significantly lower binding energies
290 (Table III), which differ from all previously published interac-
291 tion energies obtained at a similarly high level of theory.^{9,14-17}

292 D. Pros and cons of a basis set superposition 293 corrections

294 BSSE corrections were obtained with the aD and
295 aT basis sets. By including these corrections (1.43 and
296 1.45 kcal/mol, respectively) a CBS(2,aD,aT) binding energy
297 of just 15.80 kcal/mol is obtained. The BSSE is unusually
298 large and does not decrease with the size of the basis set. This
299 is in line with the observations made by other authors⁷⁰⁻⁷²
300 and results from the fact that for highly correlated methods
301 calculated with incomplete basis sets two effects are encoun-
302 tered: (i) The BSSE implies an unbalanced description of the
303 monomers relative to that of the dimer, which benefits from
304 the mutual complementation of the monomer basis sets. This
305 error decreases with increasing basis set so that its correction
306 becomes superfluous in the CBS limit provided the CBS ex-
307 trapolation has been carried out with a sufficiently large basis
308 set. (ii) There is an intramolecular BSSE correction, which
309 results from an artificial improvement of electron correlation
310 effects. This contribution leads to an unbalanced description
311 of electron correlation and significantly increases the inter-
312 molecular BSSE. It slightly increases with the size of the basis
313 set and significantly changes the convergence behavior of the
314 electron correlation method in dependence of the basis set.

315 In view of the undesirable intramonomer effects, the
316 BSSE corrections obtained at the CCSD(T) level of theory
317 are questionable. Therefore, we have refrained from includ-
318 ing any BSSE corrections for CCSD(T) results at all thus
319 following the recommendations given in the literature.⁷² By
320 utilizing the aQ and aP energies for the extrapolation any
321 residual BSSE should be small whereas use of the calculated
322 aD and aT BSSE corrections would lead most likely to a steep
323 convergence causing an underestimation of the D_e value.

324 E. Explicit correlation at the coupled cluster level

325 Explicitly correlated wave functions can obtain high
326 accuracy with basis sets of moderate size. For example,
327 Marchetti and Werner⁷³ showed that high accuracy bind-
328 ing energies can be obtained for noncovalently bonded com-
329 plexes with an aug-cc-pVDZ basis set. In this work, we use
330 the CCSD(T)-F12a and CCSD(T)-F12b approximations of
331 Werner and co-workers.^{55,57} Contrary to the CCSD(T) bind-
332 ing energies, the CCSD(T)-F12 results show (i) a steady
333 convergence with increasing number of basis functions and
334 (ii) a strongly reduced dependence on the size of the ba-
335 sis set. At the CCSD(T)/aug-cc-pVDZ level of theory, inclu-
336 sion of the explicit correlation leads to a similar improvement
337 for monomer and dimer energies so that the binding energy

338 does not change much (F12a: 16.75; F12b: 16.57 kcal/mol;
339 Table III). With the aT and aQ basis sets, the corresponding
340 D_e values are slightly reduced to 16.47 and 16.25 kcal/mol.
341 Use of the aP-basis causes only a marginal improvement to
342 16.17 and 16.21 kcal/mol thus being close to the CCSD(T)
343 value of 16.29 kcal/mol.

344 Due to the moderate basis set dependence of the
345 CCSD(T)-F12 energies, CBS values cluster between 16.08
346 and 16.44 kcal/mol (Table III). The best value at the
347 CBS(2,aQ,aP) of CCSD(T)-F12a is 16.09 kcal/mol and by
348 this 0.54 kcal/mol larger than the best CCSD(T)/CBS value
349 of 15.55 kcal/mol for D_e .

350 The CBS limit energies obtained with CCSD(T)-F12
351 vary in a small range between 16.08 (CCSD(T)-F12a-
352 CBS(2,aQ,aP)) and 16.13 kcal/mol (CCSD(T)-F12b-CBS
353 (2,aq,aP); see Table III) if one excludes CBS values from a
354 2-point, DZ-based extrapolation (16.36 and 16.44 kcal/mol).
355 CCSD(T)-F12a has been described as the more reliable
356 method as long as relatively small basis sets are used (aug-cc-
357 pVXZ with $X < Q$ ⁵⁷), whereas CCSD(T)-F12b as the method
358 with a somewhat less approximate approach should be better
359 for larger basis sets.⁵⁷ However, in connection with the cal-
360 culation of D_e for **FAD**, there is little difference between the
361 two methods. We note that the convergence behavior of CCSD
362 (T)-F12a and CCSD(T)-F12b requires more investigations.

363 The different approximations used for CCSD(T)-F12a
364 or CCSD(T)-F12b make it difficult to get a reasonable
365 CBS value close to the conventional CCSD(T) limit. Since
366 the triples are not explicitly correlated, we used also the
367 CCSD(T*)-F12 method, which scales the triples according
368 to the correlation energies of MP2-F12 and MP2. However,
369 neither CCSD(T*)-F12a nor CCSD(T*)-F12b led to any im-
370 provement. These results suggest that too little is known about
371 the influence of the approximations made at the CCSD-F12
372 level and the consequences of not having a genuine CCSD(T)-
373 F12 approach.

374 Actually, CCSD(T)-F12/CBS limits were determined by
375 various authors^{74–76} where in general the F12b approach was
376 found to lead to more reliable data. Feller *et al.*⁷⁵ report resid-
377 ual errors in the mhartree range (0.5 kcal/mol for C_2) result-
378 ing from the lack of an explicit correlation for the noniterative
379 triples. We note that a deviation of this magnitude is found for
380 the D_e of **FAD**.

381 F. Comparison of measured and calculated 382 binding energies

383 The best D_e value for **FAD** calculated in this work
384 is 15.55 obtained at the CCSD(T)/CBS(2,aQ,aP) using a
385 CCSD(T)/CBS(2,aT,aQ) geometry. Since the ZPE correction
386 is -1.23 kcal/mol (B3LYP result; -1.20 kcal/mol when using
387 measured vibrational frequencies), the D_0 -value obtained in
388 this work is 14.32 kcal/mol and by this just 0.1 kcal/mol larger
389 than the experimental D_0 value of 14.22 ± 0.12 kcal/mol of
390 Suhm and co-workers,²⁹ i.e., it is within the error bars of the
391 experimental binding energy D_0 .

392 If $\Delta ZPE(VPT2)$ is used, a D_0 value of 14.02 kcal/mol
393 results for the CCSD(T)/CBS(2,aQ,aP) limit of D_e and of

14.56 and 14.60 kcal/mol, respectively, for the corresponding
CCSD(T)-F12a and CCSD(T)-F12b CBS limits. Using for
the latter limit value the $\Delta ZPE(VPT2)$ result based on the
harmonic CCSD(T)/CBS frequencies (-1.83 kcal/mol, see
above), $D_0 = 14.31$ kcal/mol is obtained. Hence, the various
calculated D_0 values suggest 14.3 ± 0.3 kcal/mol in excellent
agreement with experiment.

The interaction energy of **FAD** was repeatedly calculated
to be in the 18–19 kcal/mol range and by this more than 3
kcal/mol larger than the D_e value obtained in this work.^{14,15}
Our investigation reveals that several reasons are responsible
for this relatively large discrepancy:

- (i) The assumption made in previous S22 investigations is
that the geometry relaxation effect upon dissociation is
small. This is definitely correct for dispersion stabilized
complexes. In the case of H-bonded or even double H-
bonded complexes such as **FAD**, this is no longer correct.
The internal coordinates listed in Table I reveal that there
is a significant change in the CO bond lengths, which
leads to an energy change by more than 2 kcal/mol.
When describing **FAD** dissociation with a frozen
monomer geometry, D_e values are exaggerated. We ob-
tain geometry relaxation energies of 2.25 (aD), 2.44 (aT),
2.61 (aQ), and 2.65 kcal/mol (aP), i.e., the D_e values
for rigid monomers are 18.96, 20.57, 19.61, and 18.94
kcal/mol (see Table IV). This leads to CBS(2,aD,aT),
CBS(3,aD,aT,aQ), CBS(2,aT,aQ), CBS(3,aT,aQ,aP),
and CBS(2,aQ,aP) values of 21.24, 19.03, 18.90, 18.55,
and 18.24 kcal/mol clearly approaching the interaction
energies of those investigations, which are based on the
unrelaxed monomer geometry.
- (ii) Early investigations by Jurečka and Hobza⁷⁷ suggested
that the energy difference between the MP2 and the
CCSD(T) binding energies D_e of **FAD** are largely
independent of the basis set used (MP2/cc-pVTZ: 17.24;
CCSD(T)/cc-pVTZ: 17.28 kcal/mol). In this connection,
one has to consider that improvements in the basis set
can change the energy in two different ways: (i) directly
by an improved description of the electronic structure
of the target molecule; (ii) indirectly, by an improved
description of the geometry. If the latter effect is ex-
cluded by using frozen monomer geometries, the basis
set dependence of the MP2-CCSD(T) energy difference
might be indeed small. This was the observation made
in most **FAD** investigations^{9,14,15,67,68} and was recently
confirmed in an investigation, which also considered
the interplay between BSSE and MP2-CCSD(T) energy
difference.⁷⁸ In this study, the largest change in the
interaction energies in dependence of the basis set was
found to be 0.3 kcal/mol.

In Table IV, the basis set dependence of the difference
 $D_e(\text{CCSD(T)}) - D_e(\text{MP2})$ is analyzed. There is a sig-
nificant dependence on the size of the basis set chang-
ing from 1.35 kcal/mol (aT basis) to -0.05 kcal/mol
(aP basis). Accordingly, the CBS estimates change from
1.80 to -0.60 kcal/mol. If the monomer geometries
are optimized as done in this work, aQZ or better an
aP difference is needed to get from MP2 reasonable

TABLE IV. Dependence of the binding energies D_e (in kcal/mol) on the freezing of the monomer geometry, the CCSD(T)-MP2 difference, and the basis set used. Monomer stabilization denotes the energy change in D_e upon relaxing a rigid monomer geometry during dissociation.

Property	CCSD(T) aD//aD	CCSD(T) aT//aT	CCSD(T) aQ//aQ	CCSD(T)/aP //CBS(2,aT,aQ)	CBS (2,aD,aT)	CBS (3,aD,aT,aQ)	CBS (2,aT,aQ)	CBS (3,aT,aQ,aP)	CBS (2,aQ,aP)
D_e (CCSD(T), rigid monomer)	18.96	20.57	19.61	18.94	21.24	19.03	18.90	18.55	18.24
Monomer stabilization	2.25	2.44	2.61	2.65	2.51	2.69	2.72	2.68	2.70
D_e (MP2, relaxed monomer)	16.42	16.77	16.53	16.34	16.92	16.38	16.35	16.23	16.14
D_e (MP2, rigid monomer)	18.91	19.56	19.32	19.10	19.83	19.17	19.14	19.00	18.90
Monomer stabilization	2.49	2.79	2.79	2.76	2.91	2.78	2.79	2.77	2.76
CCSD(T)-MP2	0.29	1.35	0.47	-0.05	1.80	-0.05	-0.16	-0.36	-0.60
Monomer stabilization	0.05	1.01	0.29	-0.16	1.41	-0.14	-0.24	-0.45	-0.66

estimates for the D_e (CCSD(T)) value of **FAD**. We note that MP2 even at the CBS(2,aQ,aP) level predicts a D_e value, which is 0.6 kcal/mol higher than the corresponding CCSD(T) value. We note that in a recent study of **FAD** based on MP2, CCSD, CCSD(T), G4, and CBS-QB3 too low D_0 values ranging from 12.12 to 13.23 kcal/mol were obtained.⁷⁹ This confirms the necessity of using CCSD(T) with aQ and aP basis sets. Apart from this the basis set dependence for the difference D_e (CCSD(T)) - D_e (MP2) is more than 4 times larger, which leads to another deviation of the binding energy of **FAD** from the corresponding interaction energies published in the literature.^{9,14-16,67,68,78}

(iii) Finally, the assumption made by Hobza and co-workers⁹ that a cc-pVTZ basis set is sufficient to describe **FAD** underestimates the errors in binding energy and geometry, which result when a diffuse charge distribution in connection with H-bonding is described by a too rigid basis set. But even the aT basis used in this work is not sufficient to provide a reliable estimate of D_e or the difference D_e (CCSD(T)) - D_e (MP2) in the case of **FAD**. An aug-cc-pVXZ basis set with X = Q or P is essential to obtain a reliable CBS-2-point extrapolation value for D_e , which is in line with other investigations of the last years.^{14-16,78}

IV. CONCLUSIONS

This work shows that the binding energy D_e of **FAD** is significantly smaller than the previously published interaction energies, which are all in the 18 kcal/mol range. The D_e value obtained in this work at the CCSD(T)/CBS(2,aQ,aP) level of theory based on a CCSD(T)/CBS(2,aT,aQ) geometry is 15.55 kcal/mol and by this more than 3 kcal/mol smaller than the best interaction energies published so far. The ZPE difference changes this value by -1.23 kcal/mol to a D_0 binding energy of 14.32 kcal/mol, which is within the error bars of the experimental value $D_0 = 14.22 \pm 0.12$ kcal/mol derived by Suhm and co-workers²⁹ on the basis of measured data.

The major reason for the 3.3 kcal/mol difference between the high level interaction energies of previous studies and the binding energy D_e obtained in this work is the use of a rigid monomer model for the **FAD** dissociation, which is used in all S22 and related investigations.

The assumption that the energy difference D_e (MP2) - D_e (CCSD(T)) is largely independent of the basis set used is only

acceptable for the rigid monomer model. When the monomer geometries are relaxed in the dissociation process, the basis set dependence becomes significant. Then, the CCSD(T) dependence on the basis set is clearly more distinct than that of the MP2 method. In the case of CCSD(T), the D_e value first increases from 16.71 to 18.12 and then decreases to 16.29 kcal/mol whereas the corresponding MP2 values slowly decrease from 16.77 (aT) to 16.34 kcal/mol (aP).

In view of the results obtained in this work, we consider it important to calculate the binding energies of the S22 set with reliable methods and relaxed monomer geometries. In view of the sophisticated methods and computational resources available today, the rigid monomer model is outdated. It would be much more rewarding if the interaction energies discussed for the S22 and other sets could be used by experimentalists for comparison with measured data as discussed in this work for the case of **FAD**.

ACKNOWLEDGMENTS

This work was financially supported by the National Science Foundation, Grant No. CHE 1152357. We thank SMU for providing computational resources.

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