Supplementary Material (ESI) for PCCP

Electronic Supplementary Information

Peter BOTSCHWINA* and Rainer OSWALD

Institut für Physikalische Chemie, Universität Göttingen, Tammannstrasse 6, D-37077 Göttingen, Germany

Guntram RAUHUT*

Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Explicitly correlated coupled cluster calculations for the propargyl cation ($H_2C_3H^+$) and related species

5 tables

Tables S1 and S2 report the parameters of the five-dimensional potential energy function (PEF) and electric dipole moment (EDMF) for $H_2C_3H^+$, as obtained by CCSD(T*)-F12a with the VTZ-F12 basis. PEF and EMDF are represented in polynomial form according to eq. (2) of the printed version. The mass-independent curvilinear symmetry coordinates S_1 – S_5 are defined as follows:

$$S_1 = \frac{1}{\sqrt{2}} (\Delta r_1 + \Delta r_1') \qquad \text{methylenic symmetric CH stretch} \qquad (2a)$$

$$S_2 = -\sqrt{\frac{3}{2}}\, \Delta\alpha \qquad CH_2 \text{ scissoring} \qquad (2b)$$

$$S_3 = \Delta R_1 \qquad \text{C - C stretch} \qquad (2c)$$

$$S_4 = \Delta R_2 \qquad \text{C} \equiv \text{C stretch} \qquad (2d)$$

$$S_5 = \Delta r_2 \qquad \text{acetylenic CH stretch} \qquad (2e)$$

S_1 – S_5 are difference coordinates, taken with respect to the CCSD(T*)-F12a/VTZ-F12 equilibrium geometrical parameters as given in Table 1 of the printed version.

Table S1. Coefficients of 5D potential energy function (PEF) for $H_2C_3H^+$. [a]

i	j	k	l	m	coefficient	i	j	k	l	m	coefficient
2	0	0	0	0	0.1770689	2	1	0	0	0	0.0039397
3	0	0	0	0	-0.1256960	1	2	0	0	0	-0.0160126
4	0	0	0	0	0.0600174	0	2	1	0	0	-0.0037637
5	0	0	0	0	-0.0244255	0	1	2	0	0	-0.0059236
6	0	0	0	0	0.0066142	0	0	2	1	0	-0.0307133
0	2	0	0	0	0.0521693	0	0	1	2	0	-0.0065767
0	3	0	0	0	0.0056291	0	0	0	2	1	0.0003306
0	4	0	0	0	0.0004121	0	0	0	1	2	0.0043960
0	5	0	0	0	0.0003519	2	0	1	0	0	0.0031125
0	6	0	0	0	-0.0002270	1	0	2	0	0	-0.0095736
0	7	0	0	0	0.0000541	0	2	0	1	0	-0.0026580
0	8	0	0	0	0.0002058	0	1	0	2	0	-0.0004677
0	0	2	0	0	0.2680148	0	0	2	0	1	0.0002574
0	0	3	0	0	-0.2573037	0	0	1	0	2	-0.0001220
0	0	4	0	0	0.1643201	2	0	0	1	0	-0.0006594
0	0	5	0	0	-0.0903022	1	0	0	2	0	-0.0016470
0	0	6	0	0	0.0356508	0	2	0	0	1	0.0000399
0	0	0	2	0	0.4563055	0	1	0	0	2	0.0000004
0	0	0	3	0	-0.4712624	2	0	0	0	1	-0.0001226
0	0	0	4	0	0.3062221	1	0	0	0	2	-0.0001470
0	0	0	5	0	-0.1697592	1	1	1	0	0	-0.0088369
0	0	0	6	0	0.0751946	1	1	0	1	0	-0.0021949
0	0	0	0	2	0.1926275	1	1	0	0	1	-0.0001012
0	0	0	0	3	-0.1934798	1	0	1	1	0	0.0081386
0	0	0	0	4	0.1313124	1	0	1	0	1	0.0000643
0	0	0	0	5	-0.0756881	1	0	0	1	1	0.0012679
0	0	0	0	6	0.0397474	0	1	1	1	0	0.0043768
0	0	0	0	7	-0.0196507	0	1	1	0	1	0.0001938
0	0	0	0	8	0.0070239	0	1	0	1	1	-0.0015843
1	1	0	0	0	-0.0065340	0	0	1	1	1	-0.0002205
0	1	1	0	0	0.0286910	2	2	0	0	0	0.0052035
0	0	1	1	0	0.0305250	0	2	2	0	0	-0.0001063
0	0	0	1	1	-0.0115982	0	0	2	2	0	-0.0056274
1	0	1	0	0	0.0066935	0	0	0	2	2	0.0009509
0	1	0	1	0	0.0040744	2	0	2	0	0	0.0076077
0	0	1	0	1	0.0011230	0	2	0	2	0	0.0039281
1	0	0	1	0	-0.0000411	0	0	2	0	2	0.0086602
0	1	0	0	1	-0.0001516	2	0	0	2	0	0.0097254
1	0	0	0	1	0.0003860	0	2	0	0	2	-0.0009022
						2	0	0	0	2	0.0059986

[a] CCSD(T*)-F12a / VTZ-F12. Coefficients are given in atomic units.

Table S1, continued.

i	j	k	l	m	coefficient	i	j	k	l	m	coefficient
3	1	0	0	0	-0.0002350	0	0	1	1	2	-0.0001936
1	3	0	0	0	-0.0023922	2	1	0	1	0	-0.0008883
0	3	1	0	0	0.0028866	1	2	0	1	0	-0.0001997
0	1	3	0	0	-0.0011169	1	1	0	2	0	0.0001980
0	0	3	1	0	0.0264671	2	1	0	0	1	0.0000463
0	0	1	3	0	0.0088461	1	2	0	0	1	0.0001002
0	0	0	3	1	0.0007843	1	1	0	0	2	-0.0000125
0	0	0	1	3	-0.0001105	2	0	1	1	0	0.0005281
3	0	1	0	0	-0.0022351	1	0	2	1	0	-0.0028491
1	0	3	0	0	0.0023068	1	0	1	2	0	-0.0011332
0	3	0	1	0	-0.0030161	2	0	1	0	1	0.0000418
0	1	0	3	0	-0.0021194	1	0	2	0	1	0.0000472
0	0	3	0	1	-0.0000178	1	0	1	0	2	0.0000375
0	0	1	0	3	0.0009683	2	0	0	1	1	-0.0000264
3	0	0	1	0	0.0013584	1	0	0	2	1	-0.0000337
1	0	0	3	0	0.0030377	1	0	0	1	2	0.0000019
0	3	0	0	1	-0.0005133	0	2	1	0	1	-0.0004873
0	1	0	0	3	-0.0008969	0	1	2	0	1	-0.0001216
3	0	0	0	1	0.0002088	0	1	1	0	2	-0.0000071
2	1	1	0	0	0.0008659	0	2	0	1	1	0.0000605
1	2	1	0	0	0.0033659	0	1	0	2	1	0.0001412
1	1	2	0	0	0.0012252	0	1	0	1	2	-0.0000606
0	2	1	1	0	0.0063591	1	1	1	1	0	-0.0014025
0	1	2	1	0	0.0051556	0	1	1	1	1	-0.0002673
0	1	1	2	0	-0.0025989	1	1	1	0	1	0.0001860
0	0	2	1	1	0.0002008	1	1	0	1	1	-0.0000830
0	0	1	2	1	0.0003406	1	0	1	1	1	-0.0002498

Table S2. Coefficients of 5D electric dipole moment function (EDMF) for $H_2C_3H^+$. [a]

i	j	k	l	m	coefficient	i	j	k	l	m	coefficient
1	0	0	0	0	-0.22893	0	1	1	0	0	0.02665
2	0	0	0	0	0.01081	0	2	1	0	0	0.08884
3	0	0	0	0	-0.00121	0	1	2	0	0	-0.04804
4	0	0	0	0	0.01024	0	0	1	1	0	0.45576
5	0	0	0	0	-0.00182	0	0	2	1	0	0.14738
6	0	0	0	0	0.00040	0	0	1	2	0	-0.38466
0	1	0	0	0	-0.18213	0	0	0	1	1	0.20257
0	2	0	0	0	0.00997	0	0	0	2	1	-0.04029
0	3	0	0	0	-0.04682	0	0	0	1	2	0.05693
0	4	0	0	0	-0.01230	1	0	1	0	0	-0.12363
0	5	0	0	0	-0.00589	2	0	1	0	0	-0.00521
0	6	0	0	0	-0.00112	1	0	2	0	0	-0.08741
0	7	0	0	0	0.00022	0	1	0	1	0	0.03382
0	8	0	0	0	0.00073	0	2	0	1	0	-0.02990
0	0	1	0	0	-0.85537	0	1	0	2	0	-0.02450
0	0	2	0	0	-0.13988	0	0	1	0	1	0.00815
0	0	3	0	0	0.20043	0	0	2	0	1	0.04016
0	0	4	0	0	-0.07564	0	0	1	0	2	-0.01087
0	0	5	0	0	0.01341	1	0	0	1	0	-0.06550
0	0	6	0	0	-0.03681	2	0	0	1	0	0.00504
0	0	0	1	0	0.84789	1	0	0	2	0	-0.01259
0	0	0	2	0	-0.28363	0	1	0	0	1	0.01586
0	0	0	3	0	0.10239	0	2	0	0	1	0.00236
0	0	0	4	0	0.12673	0	1	0	0	2	0.00559
0	0	0	5	0	0.02215	1	0	0	0	1	0.00713
0	0	0	6	0	-0.02586	2	0	0	0	1	0.00346
0	0	0	0	1	0.46308	1	0	0	0	2	0.00000
0	0	0	0	2	0.07773	1	1	1	0	0	-0.03284
0	0	0	0	3	-0.00033	1	1	0	1	0	0.01254
0	0	0	0	4	-0.02956	1	1	0	0	1	0.00792
0	0	0	0	5	0.00085	1	0	1	1	0	0.07184
0	0	0	0	6	-0.00467	1	0	1	0	1	-0.01943
0	0	0	0	7	0.01466	1	0	0	1	1	0.00301
0	0	0	0	8	-0.01047	0	1	1	1	0	0.09465
1	1	0	0	0	-0.07294	0	1	1	0	1	0.00025
2	1	0	0	0	-0.02525	0	1	0	1	1	0.01992
1	2	0	0	0	-0.00361	0	0	1	1	1	0.02484

[a] CCSD(T*)-F12a / VTZ-F12. Coefficients are given in atomic units. Electric dipole moments were evaluated in the molecular centre-of-mass coordinate system.

Table S3. Nuclear cartesian coordinates of $H_2C_3H^+ \cdot Ar$ complexes (in atomic units).[a]

Coordinate	C_s Min 1	C_s Min 2	C_{2v}
YC1	0.018540	-0.002418	
ZC1	-2.514027	-2.516659	-2.548959
YC2	0.022109	0.012211	
ZC2	0.040040	0.030459	0.000000
YC3	0.000938	0.017280	
ZC3	2.363266	2.358609	2.324858
XH1	1.771504	1.773180	1.773162
YH1	-0.004108	-0.009154	
ZH1	-3.553181	-3.554663	-3.445649
XH2	-1.771504	-1.773180	-1.773162
YH2	-0.004108	-0.009154	
ZH2	-3.553181	-3.554663	-3.445649
YH3	-0.022165	-0.012168	
ZH3	4.392306	4.387401	4.360653
YAr	5.425735	5.692193	
ZAr	-4.122429	3.918084	9.087767

[a] CCSD(T*)-F12a. Basis set: (VTZ-F12, AV (Q+d)Z).

Table S4. Intramolecular harmonic vibrational wavenumbers and shifts (in cm^{-1}) for C_s and C_{2v} structures of $H_2C_3H^+ \cdot Ar$[a]

No. of vibration[b]	C_s Min 1[c]	C_s Min 2[c]	C_{2v} [c]
1 ($1a_1$)	3362.5 (+4.9)	3363.7 (+6.1)	3314.2 (-43.4)
2 ($1b_2$)	3231.5 (+6.4)	3225.7 (+0.6)	3225.5 (+0.4)
3 ($2a_1$)	3121.3 (+6.0)	3116.3 (+1.0)	3116.3 (+1.0)
4 ($3a_1$)	2121.6 (+0.7)	2117.3 (-3.6)	2116.4 (-4.5)
5 ($4a_1$)	1479.0 (+0.1)	1478.8 (-0.1)	1479.8 (+0.9)
6 ($5a_1$)	1129.7 (-2.7)	1134.8 (+2.4)	1134.0 (+1.6)
7 ($1b_1$)	1114.5 (-2.5)	1111.9 (-5.1)	1115.8 (+1.2)
8 ($2b_2$)	1036.8 (+0.4)	1036.0 (-0.4)	1037.4 (+1.0)
9 ($2b_1$)	871.0 (-5.2)	872.8 (-3.4)	897.8 (+21.6)
10 ($3b_2$)	627.6 (+3.1)	622.9 (-1.6)	658.7 (+34.2)
11 ($4b_2$)	290.9 (+3.7)	288.8 (+1.6)	289.2 (+2.0)
12 ($3b_1$)	270.6 (+16.6)	269.1 (+15.1)	258.5 (+4.5)

[a] CCSD(T*)-F12a. Basis: VTZ-F12/AV(Q+d)Z.

[b] Vibrations are ordered according to decreasing wavenumber. Symmetry classification for free $H_2C_3H^+$ is given in parentheses.

[c] Shifts with respect to free $H_2C_3H^+$ are given in parentheses.

Table S5. Recommended equilibrium structures and equilibrium rotational constants for cations of type $H_2C_nH^+$ (n = 4-8).

	$H_2C_4H^+$	$H_2C_5H^+$	$H_2C_6H^+$	$H_2C_7H^+$	$H_2C_8H^+$
r_{1e} (Å)	1.0886	1.0848	1.0862	1.0841	1.0851
α_e(°)	119.54	119.08	119.43	118.96	119.36
R_{1e} (Å)	1.2838	1.3333	1.2936	1.3286	1.2986
R_{2e} (Å)	1.3188	1.2444	1.3014	1.2515	1.2940
R_{3e} (Å)	1.2239	1.3298	1.2422	1.3126	1.2508
R_{4e} (Å)		1.2199	1.3324	1.2367	1.3144
R_{5e} (Å)			1.2182	1.3378	1.2344
R_{6e} (Å)				1.2165	1.3408
R_{7e} (Å)					1.2152
r_{2e} (Å)	1.0715	1.0694	1.0687	1.0675	1.0671
A_e (GHz)	283.39	286.75	285.00	287.48	285.77
B_e (MHz)	4226.9	2193.4	1293.4	821.86	556.83
C_e (MHz)	4164.8	2176.8	1287.5	819.52	555.75