Structure and Dynamics of the Methane-Propane van der Waals Complex

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Supporting Information

Structures and energies of the global and local minima comparing three levels of theory.

Figure S1.

Table S1.

Figure S2.

Two representative spectra of the A-state of CH_4-C_3H_8

Figure S3

Minimum R_{cm} and interaction energy for randomly chosen methane orientations.

Table S2.

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Figure S4.

Table S3.

Structures and energies of the global and local minima comparing three levels of theory.

        Optimized structures and their binding energies were compared in computations at the CCSD(T)-F12a, MP2, and CCSD(T) levels of theory, using the aug-cc-pVTZ basis set in all cases. The monomer geometries were held constant and were calculated at each respective level of theory (e.g., in the CCSD(T)-F12a calculations for the complex, the monomer geometries were taken from prior CCSD(T)-F12a calculations of the individual monomers). The goal of this comparison was to determine whether the MP2 results are sufficiently accurate— compared to the gold standard CCSD(T)-F12a results— to allow their use in scanning over large regions of the potential energy surface. MP2 calculations were typically 60 to 80 times faster per optimization step per processor (due partly to the speedup in single-point energies and, to a somewhat greater degree, to the speedup due to the use of analytic derivatives for MP2 but numerical derivatives for CCSD(T)-F12a in optimizations). MP2 also required about 25 times less memory and 25 times less disk space than CCSD(T)-F12a. The CCSD(T)-F12a was chosen instead of CCSD(T) as the benchmark level of theory because of its accelerated rate of convergence to the complete basis set limit.[1] The CCSD(T) results have been included here to allow a direct comparison to our results for the argon-propane complex, which were carried out at the CCSD(T)/aug-cc-pVTZ level of theory and published previously.[2]

        Structures of the global minimum (a) and local minima (b), (c), and (d) of the methane-propane complex are depicted in Figure S1. Shown below each structure is its value of ΔE, defined as the energy relative to the global minimum energy *at each level of theory*. Comparing values of ΔE between the different levels of theory is useful for assessing whether MP2 is suitable for quantitatively analyzing the internal motions of the complex.

        In addition, comparing the geometric coordinates of the global and local minima is important in validating the use of MP2. Thus, for each structure, the six intermolecular coordinates, R_{cm}, Θ, Φ, θ, ϕ, and χ as well as the counterpoise-corrected binding energy, E_{int}, and the relative energy, ΔE, are given in Table S1. Note that in structures (b) and (c), the methane is situated somewhat above the plane of the propane ($\Theta \approx 80°$; $\Theta = 90°$ would correspond to the methane being in the plane of the propane), while in structure (d), the methane is in the plane of the propane.

        As a further check on the validity of the MP2 calculations, a comparison of CCSD(T)-F12a and MP2 energies at geometries away from the minima was performed. In particular, energies at both levels of theory were calculated at selected points for rotation about methane's reference C-H bond. Figure S2 shows the interaction energy while methane is rotated about its figure axis— i.e., the angle χ is scanned. The scans are relaxed in the sense that for each value of χ, the position (Θ and Φ) of the methane is optimized. Note that the orientation of the figure axis is fixed at $\theta = 120°$, $\phi = -24°$, and the value of R_{cm} is fixed at three selected values. Each curve in Figure S2 represents a scan done at a particular value of R_{cm}. The value of $\phi = -24°$ was selected by minimizing the interaction energy when $\theta = 120°$ and $\chi = 0°$.

Figure S1. Structures and energies of the global and local minima; ΔE is the energy relative to the global minimum energy. The basis set in all cases is aug-cc-pVTZ.
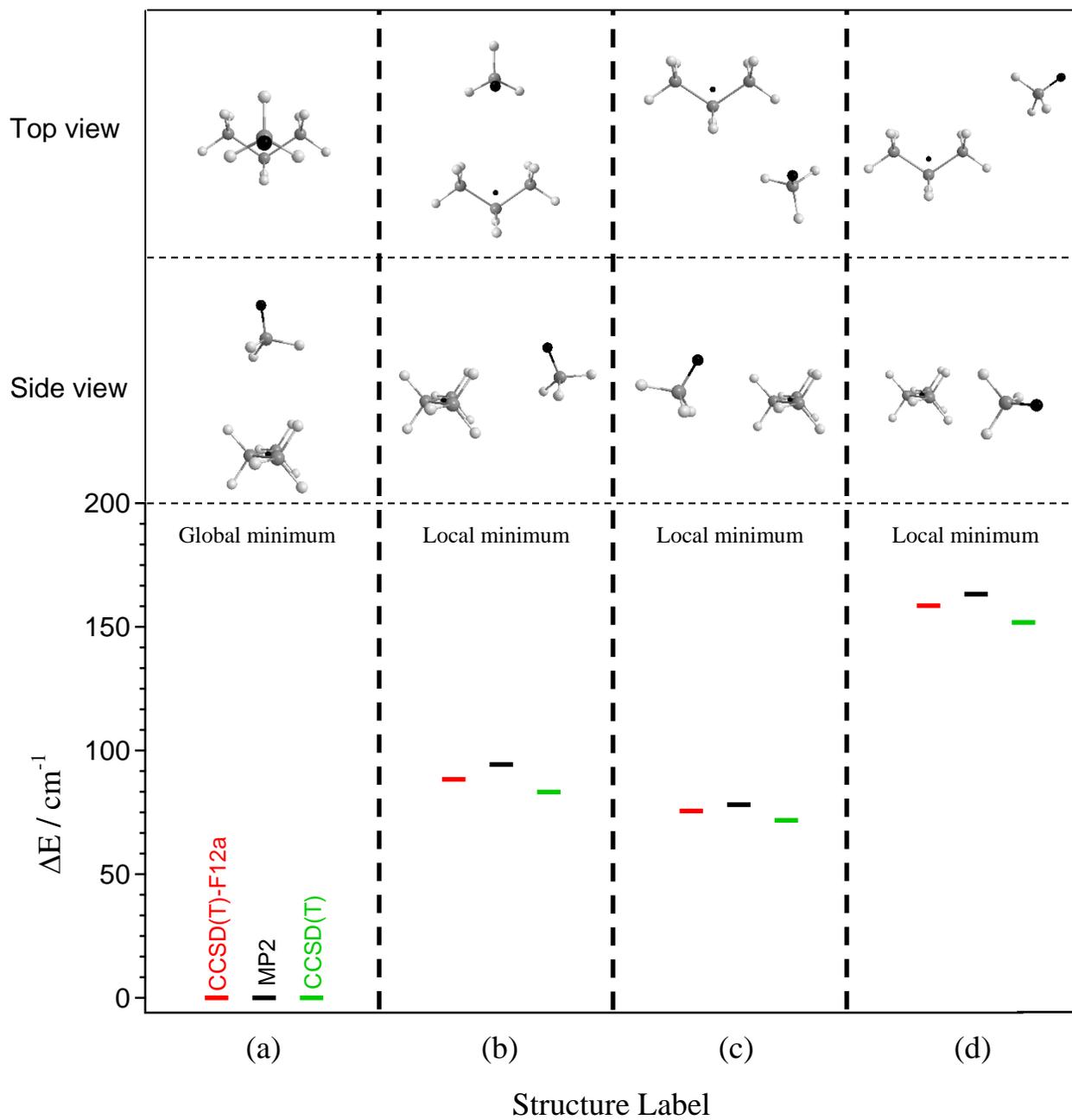
Table S1. Coordinates, binding energies (E_{int}), and energies (ΔE) relative to the global minimum energy at each level of theory, of the global and local minimum energy structures shown in Figure S1. The basis set in all cases is aug-cc-pVTZ. Definitions of the coordinates are given in Figure 1 of the main text of the article.

Structure	Level of theory	R_{cm}/Å	Θ/deg	Φ/deg	θ/deg	ϕ/deg	χ/deg	E_{int}/cm^{-1}	ΔE/cm^{-1}
(a)	MP2	3.74	2.6	0.0	5.3	180.0	0.0	-350.18	0
(a)	CCSD(T)	3.74	2.9	0.0	4.9	180.0	0.0	-361.57	0
(a)	CCSD(T)-F12a	3.71	3.0	0.0	4.6	180.0	0.0	-379.46	0
(b)	MP2	4.05	80.9	0.1	22.2	180.4	-0.2	-255.81	94.4
(b)	CCSD(T)	4.02	81.1	0.3	22.2	179.2	0.2	-278.34	83.2
(b)	CCSD(T)-F12a	4.00	81.1	0.3	22.2	179.6	-0.2	-291.13	88.3
(c)	MP2	4.28	80.3	140.3	35.0	109.4	108.5	-272.02	78.2
(c)	CCSD(T)	4.27	80.3	140.6	35.1	109.4	108.5	-289.79	71.8
(c)	CCSD(T)-F12a	4.25	80.6	140.8	35.3	109.7	108.0	-303.94	75.5
(d)	MP2	4.87	89.7	59.5	89.7	35.9	31.3	-186.92	163.3
(d)	CCSD(T)	4.85	89.6	59.5	89.8	35.9	30.7	-209.76	151.8
(d)	CCSD(T)-F12a	4.82	89.6	59.5	89.9	35.7	31.2	-220.86	158.6

Figure S2. Potential energy scans for rotation about methane's figure axis when it is oriented at $\theta = 120°$, $\phi = -24°$. MP2 data are connected by lines; CCSD(T)-F12a data are displayed as discrete points. The different colors represent data at different R_{cm} values. For MP2: red-R_{cm}=3.76Å, black-R_{cm}=3.80Å, green-R_{cm}=3.90Å. For CCSD(T)-F12a: red-R_{cm}=3.73Å, black-R_{cm}=3.77Å, green-R_{cm}=3.87Å. At each level of theory, the energy is relative to the χ=0° value for the lowest value of R_{cm}.
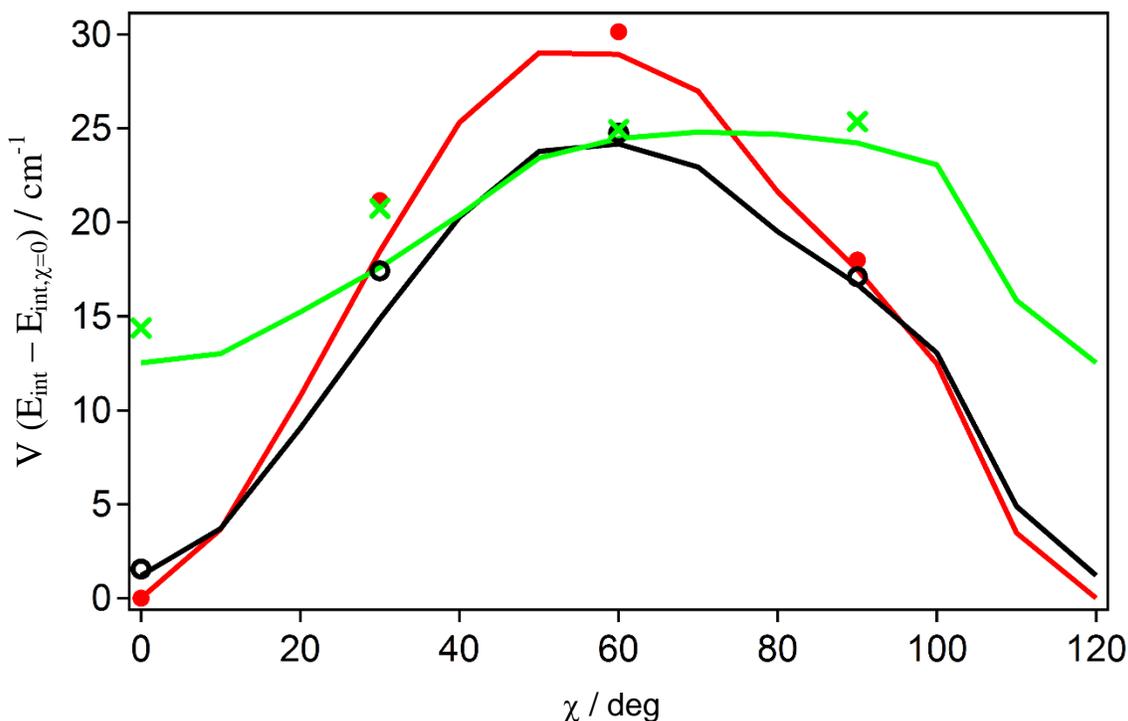
Figure S3. Two representative spectra of the A-state of CH_4-C_3H_8 demonstrating the difference in signal-to-noise for c- and a-type transitions: a) the $2_{11} - 1_{10}$ c-type transition, signal averaged with 128 pulses; b) the 3_{03}-2_{02} a-type transition signal-averaged with 1000 pulses. Both lines are Doppler doubled.
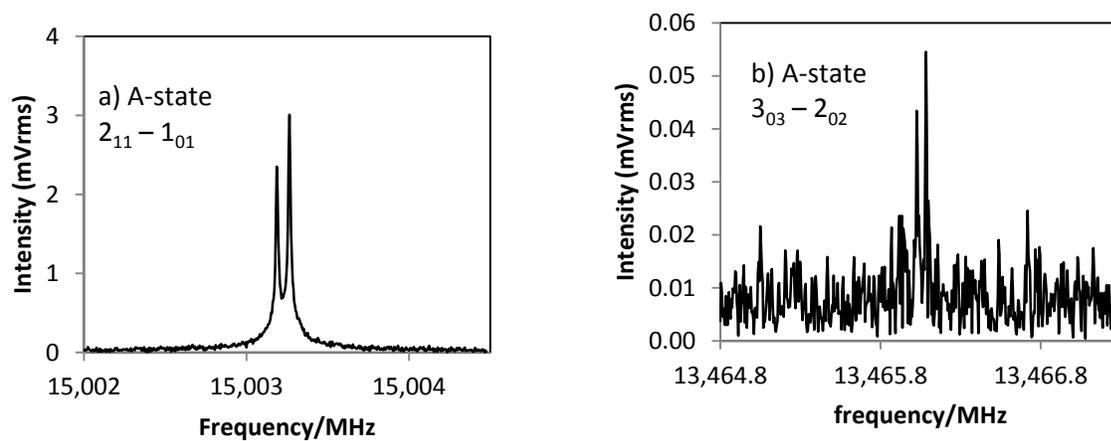
Table S2. Minimum R_{cm} and interaction energies optimized at the MP2/aug-cc-pVTZ level of theory for randomly chosen methane orientations. The position of the methane subunit is optimized for each value of θ, ϕ, and χ.

Run	ψ	ϕ	χ	R_{cm}/Å	E_{int}/cm^{-1}		Run	ψ	ϕ	χ	R_{cm}/Å	E_{int}/cm^{-1}
1	78	45	57	3.851	-317.71		36	115	78	1	3.752	-337.10
2	104	38	79	3.928	-296.29		37	179	-25	109	4.050	-271.00
3	78	67	19	3.996	-282.55		38	92	26	89	3.925	-296.01
4	150	11	51	3.940	-297.73		39	98	33	63	3.987	-285.65
5	57	-68	74	4.011	-281.64		40	98	39	53	3.988	-286.05
6	67	68	90	4.011	-278.91		41	83	-53	20	3.902	-303.58
7	172	70	51	4.045	-270.04		42	123	-57	61	3.832	-321.05
8	85	-6	56	4.018	-278.96		43	62	55	31	3.951	-287.55
9	91	-37	64	3.779	-329.58		44	75	-44	83	3.978	-281.76
10	55	88	72	3.877	-317.28		45	104	23	111	3.836	-316.45
11	95	-42	5	3.969	-283.68		46	31	-12	33	3.871	-315.79
12	95	5	83	3.927	-295.75		47	99	18	54	3.978	-289.16
13	110	79	36	3.875	-313.78		48	163	-65	16	4.015	-280.87
14	75	83	31	3.939	-298.98		49	88	83	102	3.977	-290.08
15	101	-86	85	3.878	-304.24		50	92	-2	77	3.863	-318.52
16	123	-9	71	3.789	-339.70		51	50	60	83	3.931	-303.09
17	147	-81	48	3.955	-295.30		52	118	1	25	3.809	-336.55
18	92	-71	93	3.930	-294.69		53	110	5	53	3.910	-305.95
19	99	-44	13	3.934	-288.91		54	81	-79	51	4.030	-272.45
20	98	59	114	3.808	-330.78		55	46	-49	65	3.975	-290.66
21	41	-66	88	3.910	-308.20		56	70	64	74	3.887	-314.79
22	95	9	61	3.987	-286.59		57	55	-63	44	4.010	-281.83
23	71	-46	118	3.832	-319.65		58	105	-84	58	3.830	-319.28
24	165	47	116	4.020	-274.23		59	23	18	3	3.895	-304.25
25	166	79	116	4.016	-274.48		60	50	49	15	3.984	-277.28
26	119	-23	115	3.852	-324.67		61	72	-5	84	3.991	-276.36
27	78	54	39	3.896	-305.53		62	153	89	36	3.977	-277.77
28	67	-63	91	3.947	-293.84		63	65	4	20	4.010	-272.94
29	65	-40	66	4.034	-274.17		64	123	-71	76	3.858	-315.60
30	24	-50	67	3.850	-322.93		65	38	24	54	3.872	-300.66
31	71	6	62	3.877	-307.50		66	31	62	26	3.850	-306.28
32	29	78	25	3.833	-314.98		67	64	19	78	3.939	-294.90
33	92	-38	20	3.939	-287.61		68	61	-85	65	4.042	-274.65
34	77	-13	65	4.035	-272.71		69	121	0	101	3.803	-334.77
35	54	47	4	4.016	-273.96		70	129	17	5	3.885	-306.02

Figure S4. Global minimum structure of the complex, with labels for the atoms involved in the internal motions that are listed in Table S3. The filled black circle in the C2-C3-C4 plane marks the center of mass of the propane.
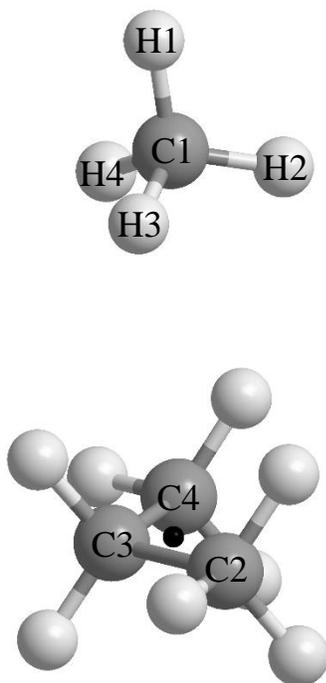
Table S3. Potential energy barriers for rotation of the methane subunit about each of its C-H bonds. Atom labels refer to those in Figure S4. Results are computed at the MP2/aug-cc-pVTZ level of theory. Each type of rotation corresponds to a scan of the angle χ about the specified C-H axis, while holding θ, ϕ, and R_{cm} constant but optimizing Θ and Φ; i.e. the orientation of methane was fixed, except for rotation about the specified C-H axis, and the position of methane was allowed to optimize, except for the center-of-mass distance, R_{cm}. At each value of R_{cm}, the initial position ($\chi=0°$) corresponds to the minimum energy structure, whose energy is E_{min}. The maximum energy in each scan is E_{bar}, and the barrier height is $V_b = E_{bar} - E_{min}$.

Motion	R_{cm} = 3.74 Å			R_{cm} = 3.80 Å			R_{cm} = 3.90 Å		
	E_{min}	E_{bar}	V_b	E_{min}	E_{bar}	V_b	E_{min}	E_{bar}	V_b
Rotation about C1-H1 bond	-350.17	-277.73	72.4	-347.34	-292.06	55.2	-333.91	-298.27	35.4
Rotation about C1-H2 bond	-350.17	-256.79	93.4	-347.34	-279.37	68.0	-333.91	-294.51	39.4
Rotation about C1-H3 or C1-H4 bond	-350.17	-296.56	53.6	-347.34	-308.75	38.6	-333.91	-312.02	21.9

REFERENCES

[1] Adler, T. B.; Knizia, G.; Werner, H.-J. A simple and efficient CCSD(T)-F12 approximation, *J. Chem. Phys.* **2007**, *127*, 221106.

[2] Peterson, K. I.; Pullman, D. P. Lin, W.; Minei, A. J.; Novick, S. E. Microwave spectra and ab initio studies of Ar-propane and Ne-propane complexes: Structure and dynamics, *J. Chem. Phys.* **2007**, *127*, 184306.