ChemPhysChem

Supporting Information

Low-Temperature Thermal Formation of the Cyclic Methylphosphonic Acid Trimer [*c*-$(CH_3PO_2)_3$]

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Error determination of computed ionization energies

As the identification of different isomers in our studies focuses on the ionization energy of each isomer, we also performed additional ionization energy computations at the CCSD(T)/CBS//B3LYP/cc−pVTZ level of theory for some nitrogen- and phosphorus-bearing molecules as benchmarks (Table S2). The adiabatic ionization energies (IEs) were computed by taking the zero-point vibrational energy corrected energy difference between the neutral and ionic species that correspond to similar isomers. Error bounds were determined by subtracting the calculated ionization energy from the error boundaries of the experimentally determined and hence known values for each molecule. Afterward, the average difference between the lower and upper boundary as well as their standard deviation was calculated. Finally, the standard deviation was subtracted from or added to the average difference for the lower and upper boundaries. This conservative analysis yielded errors of −0.08/+0.07 eV, which allows us to get their calculated determined ionization energy.

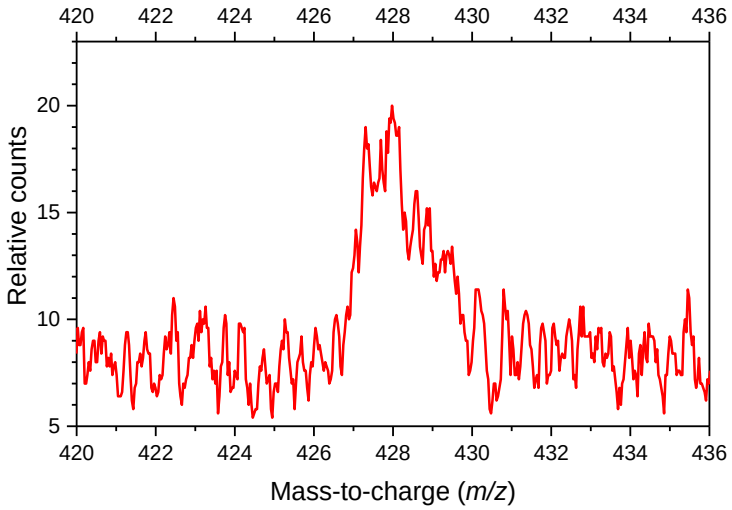


Figure S1 Integrated mass spectrum between mass-to-charge from 420 to 436 of methyphosphonic acid photoionized by photons of energy 10.35 eV. The signals at $m/z = 428$ are overlapped by the broad band from $m/z = 427–429$. If it is from $m/z = 427$ then it can be a molecular cluster composed of one HCMPAT and two methylphosphonic acid molecules.

Table S1 Parameters for the vacuum ultraviolet (VUV) light generation used in the present experiments.[a]

$2\omega_1 - \omega_2$	Photoionization energy (eV)	10.35	9.50
	Flux (10^{12} photons pulse^{-1})	1.2 ± 1	1.1 ± 1
	Wavelength (nm)	119.792	130.510
ω_1	Wavelength (nm)	202.316	202.316
Nd:YAG (YAG A)	Wavelength (nm)	532	532
Dye laser (DYE A)	Wavelength (nm)	606.948	606.948
Dye		Rhodamine 610 and 640	Rhodamine 610 and 640
ω_2	Wavelength (nm)	650.3	449.8
Nd:YAG (YAG B)	Wavelength (nm)	532	355
Dye laser (DYE B)	Wavelength (nm)	651	448
Dye		DCM (DMSO)	Coumarin 450
	Nonlinear medium	Kr	Kr

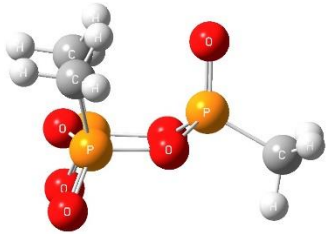
Note:

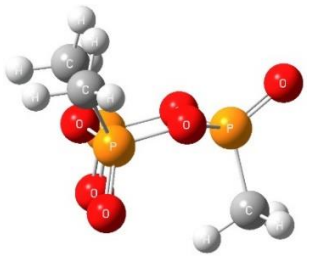
[a] The uncertainty for VUV photon energies is 0.001 nm.

Table S2 Computed adiabatic ionization energies (IEs) of distinct cyclic methyphosphonic acid trimer isomers **1–3** along with error limits and previous computational (CCSD(T)/CBS//B3LYP/cc–pVTZ + zero-point vibrational energy (ZPVE) corrections) and experimental benchmarks of some compounds. An offset of 0.03 eV was subtracted to correct for the electric field effect.

Compounds	Experimental IE (eV)	Experimental Error Limits (eV)	Computed IE (eV)	Computed IE– Experimental IE (max) (eV)	Computed IE– Experimental IE (min) (eV)	IE range after error analysis (eV)	Corrected IE with electric field effect (eV)
Ammonia NH_3	10.07 ± 0.02	10.05 – 10.09 [1]	10.15	+0.06	+0.10		
Phosphine PH_3	9.869 ± 0.002	9.867 – 9.871 [1]	9.82	–0.051	–0.047		
Hydrogen cyanide HCN	13.60 ± 0.01	13.59 – 13.61 [1]	13.57	–0.04	–0.02		
Methinophosphide HCP	10.79 ± 0.01	10.78 – 10.80 [2]	10.76	–0.04	–0.02		
Acetonitrile CH_3CN	12.20 ± 0.01	12.19 – 12.21 [3]	12.20	–0.01	+0.01		
Methyl Isocyanide CH_3NC	11.24 ± 0.01	11.23 – 11.25 [3]	11.25	+0.00	+0.02		
2H-Azirine c-H_2CCHN	10.05 ± 0.03	10.02 – 10.08 [3]	10.02	–0.06	+0.00		
1			10.36			10.28 – 10.43	10.25 – 10.40
2			10.39			10.31 – 10.46	10.28 – 10.43
3			10.19			10.11 – 10.26	10.08 – 10.23
				Average –0.04 ± 0.04	Average 0.02 ± 0.05		
				Error Limits –0.08 – +0.00	Error Limits –0.02 – +0.07		
				Combined Error Limits –0.08 – +0.07			

Table S3. Cartesian coordinates (distances in Å) and normal modes (vibrational frequencies in cm^{-1} and intensity in km mol^{-1}) of cyclic methyphosphonic acid trimer [*c*-$(CH_3PO_2)_3$].

Structure and energies in Hartrees	Cartesian coordinates			Normal modes								
		X	Y	Z	Symm.	Freq.	Intensity	Symm.	Freq.	Intensity	Symm.	Freq.	Intensity
1, Boat, C_s	P	0.00000000	0.00000000	0.00000000	A"	44	5	A'	533	20	A"	1347	0
CCSD(T)-F12b/cc-pVTZ-F12	O	0.51373700	0.34375800	1.50979500	A'	48	1	A'	608	2	A'	1351	91
Energy: -1593.690540067944	P	0.00000000	0.00000000	3.01959000	A'	69	14	A"	669	50	A'	1455	5
	O	-1.59962300	-0.24288900	2.76725500	A"	157	0	A'	676	99	A"	1456	7
	P	-2.48576800	0.28800300	1.50979500	A"	174	4	A"	767	17	A"	1456	2
	O	-1.59962300	-0.24288900	0.25233500	A'	179	0	A'	771	43	A'	1459	1
	O	-2.71798200	1.74304300	1.50979500	A"	190	1	A"	797	0	A"	1460	0
	C	-3.90881500	-0.79572300	1.50979500	A"	217	2	A'	806	26	A'	1463	8
	H	-3.59363100	-1.83624500	1.50979500	A'	227	0	A"	919	1	A"	3053	0
	H	-4.50307800	-0.58433100	2.39688100	A'	235	0	A'	921	21	A'	3053	0
	H	-4.50307800	-0.58433100	0.62270900	A'	246	0	A"	929	33	A'	3058	1
	O	0.64422500	-1.14318500	3.66873300	A"	250	1	A'	932	4	A"	3137	0
	C	0.11777400	1.58581700	3.85094800	A"	307	4	A'	939	2	A'	3137	0
	H	1.16559500	1.87706900	3.89798700	A'	314	10	A"	942	2	A"	3139	0
	H	-0.46225700	2.33838100	3.32076300	A"	353	1	A'	969	870	A"	3143	0
	H	-0.26349600	1.46821100	4.86370600	A'	381	56	A"	981	979	A'	3143	0
	O	0.64422500	-1.14318500	-0.64914300	A"	400	40	A'	1284	194	A'	3151	0
	C	0.11777400	1.58581700	-0.83135800	A'	404	3	A"	1312	204			
	H	1.16559500	1.87706900	-0.87839700	A"	442	42	A'	1326	221			
	H	-0.26349600	1.46821100	-1.84411600	A'	477	46	A'	1347	68			
	H	-0.46225700	2.33838100	-0.30117300									



2, Chair, C_s

CCSD(T)-F12b/cc-pVTZ-F12

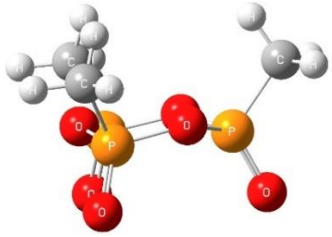
Energy: -1593.689549949898

	X	Y	Z
P	0.00000000	0.00000000	0.00000000
O	1.23946300	-1.05501200	-0.13486500
P	1.42545700	-2.56608000	0.44303700
O	-0.06262100	-3.19059800	0.18698300
P	-1.52586800	-2.51046500	0.44540200
O	-1.28188000	-1.00431100	-0.12331100
O	-2.00426300	-2.56613100	1.83144900
C	-2.55443600	-3.27010700	-0.81026800
H	-2.11380200	-3.15580600	-1.79748500
H	-3.53208800	-2.79231400	-0.78289400
H	-2.66862600	-4.32537000	-0.56890700
O	1.89987500	-2.63160300	1.83011200
C	2.42514300	-3.37156500	-0.80726100
H	2.49857700	-4.42904700	-0.55983900
H	1.98984800	-3.24609900	-1.79548500
H	3.42036700	-2.93144300	-0.78167700
O	0.01587900	1.01890100	-1.05164700
C	0.01859600	0.56197500	1.70346000
H	0.00682700	-0.28150400	2.39180100
H	0.91860300	1.15402400	1.85929200
H	-0.85770000	1.18635200	1.86799400

Symm.	Freq.	Intensity
A	31	8
A	61	11
A	66	3
A	159	0
A	161	0
A	166	0
A	183	4
A	208	0
A	232	0
A	241	0
A	246	0
A	258	2
A	288	14
A	322	7
A	355	5
A	374	19
A	379	38
A	433	24
A	436	34
A	482	67

Symm.	Freq.	Intensity
A	533	18
A	611	15
A	658	60
A	671	79
A	768	12
A	777	75
A	794	4
A	803	3
A	919	10
A	921	20
A	923	15
A	932	1
A	938	1
A	940	13
A	976	966
A	980	886
A	1297	119
A	1313	369
A	1321	129
A	1347	7

Symm.	Freq.	Intensity
A	1349	120
A	1356	8
A	1450	11
A	1455	4
A	1457	0
A	1457	4
A	1458	2
A	1458	6
A	3052	1
A	3057	1
A	3058	0
A	3138	0
A	3138	0
A	3139	0
A	3139	0
A	3149	0
A	3149	1



3, Circle, C_{3v}

CCSD(T)-F12b/cc-pVTZ-F12

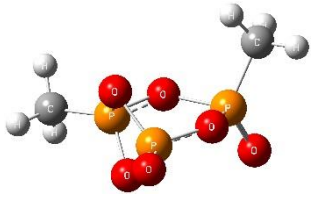
Energy: -1593.680731913442

	X	Y	Z
P	-0.000000	1.720273	0.138017
O	1.259574	0.727249	-0.165901
P	1.489800	-0.860136	0.138017
O	0.000030	-1.454447	-0.165901
P	-1.489800	-0.860136	0.138017
O	-1.259603	0.727198	-0.165901
O	-2.043754	-1.180033	1.454379
C	-2.439098	-1.408213	-1.284272
H	-1.955796	-1.129177	-2.217339
H	-3.428080	-0.956984	-1.227554
H	-2.542832	-2.490311	-1.227551
O	2.043815	-1.179926	1.454379
C	2.439098	-1.408214	-1.284272
H	2.542812	-2.490312	-1.227554
H	1.955794	-1.129180	-2.217339
H	3.428089	-0.957002	-1.227551
O	-0.000061	2.359959	1.454379
C	0.000000	2.816428	-1.284272
H	0.000001	2.258357	-2.217339
H	-0.885256	3.447313	-1.227551
H	0.885268	3.447296	-1.227554

Symm.	Freq.	Intensity
E	43	0
E	43	0
A	62	0
E	163	0
E	163	0
A	166	0
A	186	0
E	214	1
E	214	1
E	244	0
E	244	0
A	245	1
E	303	12
E	303	12
A	357	0
E	379	60
E	379	60
E	435	13
E	435	13
A	484	62

Symm.	Freq.	Intensity
A	522	0
A	606	9
E	653	69
E	653	69
E	763	17
E	763	17
A	788	0
A	810	66
E	919	37
E	919	37
A	921	0
A	926	1
E	937	7
E	937	7
E	980	972
E	980	972
E	1312	165
E	1312	165
A	1331	121
E	1347	0

Symm.	Freq.	Intensity
E	1347	0
A	1353	304
A	1455	0
E	1458	8
E	1458	8
E	1459	3
E	1459	3
A	1461	1
E	3056	1
E	3056	1
A	3056	1
A	3137	0
E	3137	0
E	3137	0
E	3145	0
E	3145	0
A	3146	5



CMPAT-CH$_3$, C_1

CCSD(T)-F12b/cc-pVTZ-F12

Energy: -1553.493471899912

	X	Y	Z
P	1.029238	-0.972210	0.035099
O	1.205336	0.148355	-1.110381
P	0.822923	1.351157	0.018933
O	-0.765232	1.230754	0.057542
P	-1.704617	-0.134906	-0.182741
O	-0.486270	-1.356642	0.071256
O	-2.266568	-0.245191	-1.517713
C	-2.710458	-0.246352	1.282206
H	-2.106578	-0.180441	2.184331
H	-3.424743	0.577066	1.247026
H	-3.252403	-1.190919	1.247165
O	1.459263	2.643774	0.014301
O	1.250565	0.163311	1.157329
C	2.114092	-2.359839	0.021300
H	3.141806	-1.995870	0.009970
H	1.926756	-2.957856	0.914846
H	1.903433	-2.950353	-0.872420

Symm.	Freq.	Intensity
A	65	5
A	130	2
A	139	6
A	161	0
A	180	2
A	209	0
A	232	2
A	241	5
A	284	5
A	324	2
A	336	7
A	364	8
A	391	25
A	397	35
A	475	54

Symm.	Freq.	Intensity
A	500	23
A	535	8
A	563	17
A	584	61
A	650	5
A	744	313
A	779	55
A	805	24
A	851	30
A	871	89
A	914	8
A	926	87
A	947	174
A	975	133
A	989	221

Symm.	Freq.	Intensity
A	1047	681
A	1342	21
A	1343	38
A	1368	153
A	1426	11
A	1426	12
A	1428	197
A	1442	12
A	1444	7
A	3035	54
A	3049	20
A	3121	23
A	3130	10
A	3133	23
A	3151	4

Supplementary References

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[2] D. C. Frost, S. T. Lee, C. A. McDowell, *Chem. Phys. Lett.* **1973**, *23*, 472−475.

[3] A. M. Turner, S. Chandra, R. C. Fortenberry, R. I. Kaiser, *ChemPhysChem*. **2021**, *22*, 985−994.