Calculated Properties of PS_2^+ and PS_3^-

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The linear $S=P=S^+$ form of the recently studied PS_2^+ ion lies below the triangular one in energy; the calculated frequencies for the trithiometaphosphate anion, $PS_3^-(D_{3h})$ support its experimental identification in high-temperature melts and in $(AsPh_4)PS_3$.

New, simple A≡B, A=B=C or AB_3 (D_{3h}) inorganic ions can still be found. An example is the PBP^{3-} ion, predicted[1] and prepared[2] independently. To study them, normal HF *ab initio* calculations on the free ion were shown to be meaningful, both for the bond lengths and for the vibrational frequencies, down to trivalent anions.[3]

In addition to the 3rd-row ions with either P[1] or S[4] we here consider the mixed ions PS_n, among which the species PS_2^+ and PS_3^- are of recent experimental interest. The well characterized PS^+ [5,6] and PS_4^{3-} [7,8] are included as checks. PS_2^+ has just been studied by mass spectroscopy[9,10] but its structure and vibrational properties are unknown. PS_3^- has

Table 1. Calculated geometries (pm) and vibrational frequencies (cm^{-1}).[a]

Species ABC	Method	$d/$(A–B)	$d/$(B–C)	ν_1	ν_2	ν_3	ν_4	Ref.
PS^+	HF	179.2		984				b
	MP2	186.1		787				b
	MP3	182.8		—				b
	CI	187.2		873.9				6
	Exp.	—		844.6				5
SPS^+	HF	181.9		619	118	1028		b
	MP2	186.9		548	79	1018		b
SSP^+	HF	215.6	198.4[c]	439	462	759		b
	MP2	226.0	200.0[d]	—	—	—		b
PS_3^-	HF	194.9		516	300	749	259	b
	HF	196		—	—	—	—	12
	MP2	196.0		—	—	—	—	b
	Exp.	—		476	540	695	242	11
	Exp.	—		486	614	670	242	12
PS_4^{3-}	HF	210.0		406	186	567	274	b
	Exp.	205		416	215	548	270	7,8

[a] $D_{\infty h}$: $\nu_1(\sigma_g)$, $\nu_2(\pi)$, $\nu_3(\sigma_u)$. D_{3h}: $\nu_1(a_1')$, $\nu_2(a_2'')$, $\nu_3(e')$, $\nu_4(e')$. T_d: $\nu_1(a_1)$, $\nu_2(e)$, $\nu_3(t_2)$, $\nu_4(t_2)$. [b] This work. [c] S–S–P = 57.11°. [d] S–S–P = 55.59°.

been tentatively identified in high-temperature melts by Raman spectroscopy.[11] The compound $(AsPh_4)PS_3$ has been made.[12] Experimental IR frequencies but no P–S distance and a theoretical, *ab initio* distance but no frequencies were reported. The PS_3^- ion was found to rotate. Thus the present calculated frequencies provide support for the experimental identification of PS_3^- in both the melts and the tetraphenylarsonium salt.

The Hartree–Fock- or Møller–Plesset-level 6-31G* calculations were performed using Gaussian 88. As seen from Table 1, the HF and MP2 results bracket the experimental ν_e for PS^+. The HF values for thiophosphate also are close to experiment, as usual. The semiempirical calculations on PS_2^+ gave much shorter bond lengths for $SP5^+$ and SSP^+.[13] The linear SSP^+ bends spontaneously to a triangular geometry, lying −0.092 and 0.436 eV above the linear symmetric ion in HF and MP2, respectively. For the isoelectronic PPS,[14] the triangular form was slightly more stable than the linear one. The analogous $O{=}P{=}O^+$ [1] is still experimentally unknown.

Three of the four frequencies of PS_3^- agree with the calculated ones. The exception is the $\nu_2(a_2'')$, calculated to be at 300 cm^{-1} and experimentally assigned to the weak, broad line at 540 or 614 cm^{-1}.[11,12] Otherwise this calculation supports the experimental evidence for PS_3^- in molten $Tl_2P_2S_6$, its solution in alkali bromide melts,[11] and in the tetraphenylarsonium salt.[12] These are the only observations of trithiometaphosphate.

The calculations were carried out on a Cray X-MP EA/432 computer at the Centre for Scientific Computing at Espoo, Finland. Mr. Raimo Uusvuori helped to sort out a convergence difficulty.

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