

The ScPH⁺ Cation

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Received: June 17, 1994[⊗]

We have obtained by *ab initio* calculations the energetics and the geometries of the X¹Σ⁺, a³Π, and A¹Π valence states of the ScPH⁺ cation, which we have found to be nonrigid in its ground state. We have also examined its bond energies and lengths *vis-a-vis* the same quantities of the free ScP⁺ and PH species and have generated potential curves for its Sc⁺ + PH and ScP⁺ + H asymptotic channels.

Introduction

The ScPH⁺ ion can be thought of as the result of either the ScP⁺ + H → ScPH⁺ or the Sc⁺ + PH → ScPH⁺ reaction. We plan to examine both of these paths and to calculate some experimentally verifiable properties of the ScPH⁺ system for which, to the best of our knowledge, neither theoretical nor experimental results are available. We also plan to ascertain the effect of the H atom on the ScP⁺ ion as well as the effect of the Sc⁺ ion on the PH radical and to contrast the results with the isovalent species ScNH⁺.¹

To do this, certain properties of the ScP⁺ and PH fragments are needed. In a previous paper,² we calculated the lowest ²Σ⁺ and ²Π states of the scandium phosphide ion, ScP⁺, and found them practically degenerate with a binding energy of 31 kcal/mol. The former state has a single electron in a σ_z(P) orbital (*z* is the molecular axis) while the latter has a single electron in a π_y(P) orbital. Some conclusions for the phosphinidene radical, PH, are also arrived at here, which compare well with previous results.^{3–5}

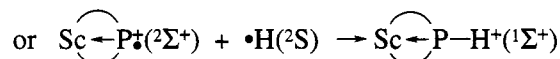
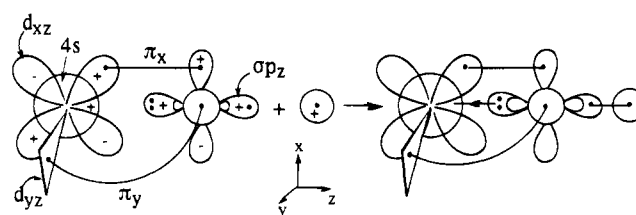
Analysis of the Problem

Only a few states of the fragments of the ScPH⁺ ion are relevant to our calculations. These are the ground ³D state (core¹⁸3d⁴4s¹) and the first ³F state (core¹⁸3d²) of Sc⁺, which differ by 0.596 eV (average over *J* values),⁶ and the ground ³Σ⁻ state of PH (1σ²2σ²3σ²4σ²1π⁴5σ²2π¹2π¹).

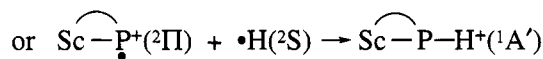
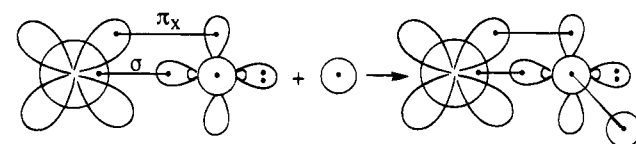
Let us imagine ScPH⁺ as being formed either by an H atom approaching from infinity to ScP⁺(²Σ⁺ or ²Π) or by a Sc⁺ ion approaching from infinity to PH(³Σ⁻), Schemes 1–5. Notice that in Scheme 2 the hydrogen atom approaches along the *y* axis (perpendicular to the bond). However, upon optimization, the resulting ¹A' state ends up in the linear (¹Σ⁺) state (see below).

Schemes 1–3 and 4 and 5 are equivalent as far as the end products are concerned, namely, ScPH⁺(¹Σ⁺) and ScPH⁺(¹Π or ³Π), respectively. The pictorial “wave functions” above, along with their Kekulé–Lewis representations, allow us to make the following qualitative predictions: (a) The ScPH⁺ system has a ground state of ¹Σ⁺ symmetry. However, its linearity is not evident from Scheme 2. (b) From Schemes 1

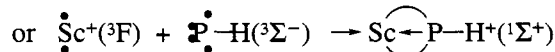
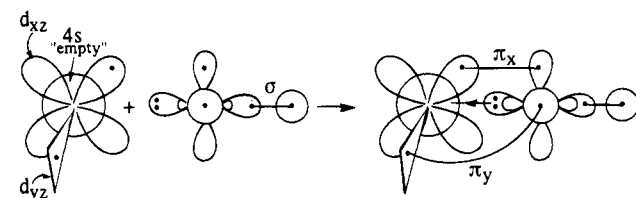
SCHEME 1



SCHEME 2



SCHEME 3

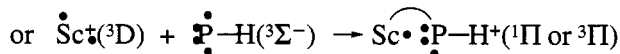
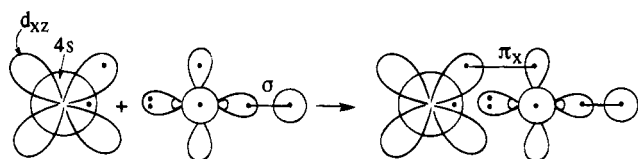


and 3, one anticipates a strengthening and shortening of the Sc⁺–PH and ScP⁺–H bonds for the ¹Σ⁺ state relative to the ScP⁺(²Σ⁺) and PH(³Σ⁻) fragments. (c) From Schemes 4 and 5, and in contrast to the ScP⁺(²Π) free ion, one anticipates a weakly bound state of ¹Π or ³Π symmetry with a long single Sc⁺–PH bond. The Scheme 5 potential curve should have a small barrier, owing to the Pauli repulsion between the σ lone pair on P and the 1s electron on the oncoming H.

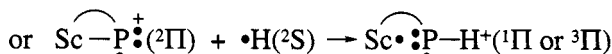
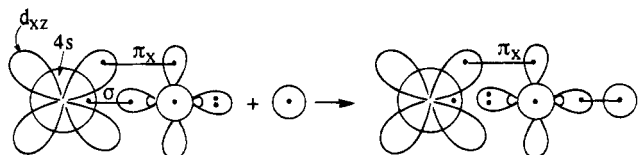
The results of the computed potential curves shown in Schemes 1–5 closely follow the expectations of the outline above.

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1994.

SCHEME 4



SCHEME 5



Details of the Calculation

We have employed the MRDCI series of codes.⁷⁻⁹ The procedure employs a multiconfiguration CI with a configuration selection and extrapolation technique which gives a near "singles and doubles" accuracy for the MRD-CI space, using explicitly only a fraction of the original space. Quadruple excitations are accounted for by the Davidson correction. In the present calculations we used an accuracy threshold of 1.0 μ hartree with 20-40 reference configurations, depending on the geometry, and this resulted in 10 000 to 20 000 selected configurations, respectively, for the diagonalization of the Hamiltonian matrix. All computations for linear geometries were done under C_{2v} symmetry and for bent geometries under C_s symmetry.

For the Sc atom the 11s9p5d basis set of Wachters¹⁰ was employed, contracted to 8s4p2d.¹¹ This was augmented with two p functions¹² to represent the 4p orbital (exponents 0.08975 and 0.03103) and a d function (exponent 0.0588) as recommended by Hay,¹³ thus resulting in an 8s6p3d contracted basis set. The basis set on the P atom is that of McLean-Chandler¹⁴ consisting of 12s9p functions, contracted to 6s4p. This was augmented with one diffuse p function (exponent 0.0838) and two d polarization functions (exponents 2.0 and 0.55),¹⁵ thus resulting in a 6s5p2d contracted basis set. For the H atom we used a set of 5s1p functions contracted to 3s1p.¹⁶ Overall, our basis set consists of 83 contracted Cartesian Gaussian functions, [8s6p3d/6s5p3d/3s1p].

Results and Discussion

First, we focused on the PH fragment. We calculated the potential energy curve of the PH($X^3\Sigma^-$) radical, and using a modified Numerov method¹⁷ in conjunction with a segmented spline fit we computed its seven lowest vibrational levels. The fitted curve, scaled to the minimum of the $X^3\Sigma^-$ state (-341.3970 hartrees), along with the first seven vibrational levels are shown in Figure 1. A comparison with reference data, both experimental and theoretical,³⁻⁵ is presented in Table 1 and shows a fair agreement.

Regarding the ScPH⁺ potential energy surfaces, sections corresponding to both the ScP⁺-H and Sc⁺-PH channels were computed. The $^1\Sigma^+$ section of the $^1A'$ surface was done at a Sc-P internuclear distance of 2.209 Å (ScP⁺-H channel) and at a P-H internuclear distance of 1.384 Å (Sc⁺-PH channel), which are the equilibrium bond distances of ScPH⁺($X^1\Sigma^+$).

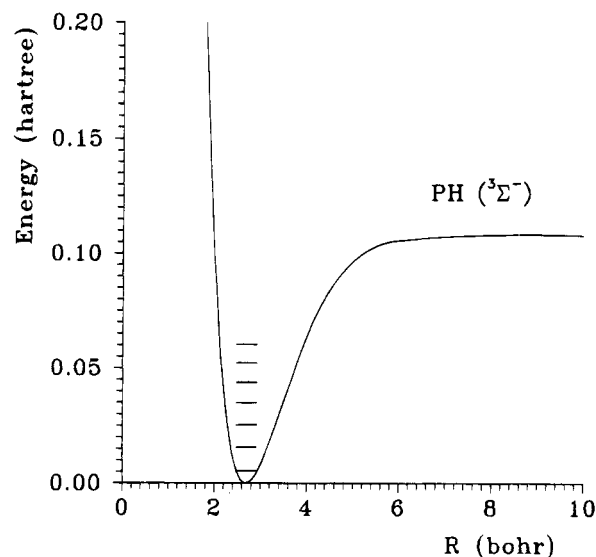


Figure 1. The potential energy curve of the $X^3\Sigma^-$ state of the PH radical, shifted by 341.3970 hartrees, along with its first seven vibrational levels.

TABLE 1: Comparison between Our Results and Reference Data on Bond Lengths r_e (Å), Bond Energies $D_{e,0}$ (kcal/mol), and Vibrational Levels ν for the $^3\Sigma^-$ Ground State of PH. The Energy at Equilibrium Is -341.3970 hartrees Including the Davidson Correction

	PH($X^3\Sigma^-$)		
	r_e	D_e	D_0
present work	1.423	67.7	64.3
experimental ^a	1.4223	69.6	
theory ^b	1.4226	69.9	66.4

vib level (ν)	G_ν^c (cm ⁻¹)	
	this work	ref 3 ^d
0	1174.47	1171.47
1	3468.66	3447.67
2	5681.32	5634.88
3	7781.11	7733.08
4	9777.80	9742.27
5	11681.8	11662.5
6	13490.7	13493.7

^a Reference 3. ^b Reference 4. ^c With respect to the bottom of the well. ^d Using $G_\nu = \omega_e(\nu + 1/2) - \omega_e x_e(\nu + 1/2)^2$.

Small departures from these distances have almost no effect on the energy, so we kept them fixed for all P-H and Sc-P separations, respectively. The results are shown in Table 2 and depicted in Figure 2.

Similarly, the $^1\Pi$ section of the surface was done at a Sc-P internuclear separation of 2.406 Å (ScP⁺-H channel) and at a P-H internuclear separation of 1.397 Å (Sc⁺-PH channel), which are the equilibrium bond distances of ScPH⁺($A^1\Pi$). For the same reasons as above, we were able to keep these distances fixed for all P-H and Sc-P separations, respectively. The same procedure was followed in computing the $a^3\Pi$ potential curve (Sc⁺-PH channel). The results are also shown in Table 2 and depicted in Figure 2.

From the results above, one can obtain dissociation energies and bond distances for the channels under consideration. These quantities are shown in Table 3. We should mention at this point that the equilibrium distances were obtained iteratively, with the help of three- to four-point interpolations.

The dissociation energy, D_e , of the $X^1\Sigma^+$ state of ScPH⁺, with respect to the ScP⁺($^2\Sigma^+$) + H(^2S) channel is 85.2 kcal/mol, 17.5 kcal/mol higher than that of PH($X^3\Sigma^-$). This increase

TABLE 2: A Selected Set of Potential Energies of ScPH⁺ Shifted by 1100 hartrees (*R* in bohr, Energies in hartrees)

<i>R</i>	ScP ⁺ -H channels		Sc ⁺ -PH channels		
	A ¹ Π	X ¹ Σ ⁺	A ¹ Π	a ³ Π	X ¹ Σ ⁺
30			-0.9084		-0.8781
20	-0.8528	-0.8461	-0.9089		-0.8785
10	-0.8524	-0.8462	-0.9118		-0.8814
8.0	-0.8524	-0.8470	-0.9149		-0.8851
7.0	-0.8524		-0.9171		-0.8903
6.0	-0.8506	-0.8512	-0.9208		-0.9016
5.6			-0.9226	-0.9226	-0.9160
5.4			-0.9238	-0.9238	
5.2			-0.9251	-0.9251	
5.0	-0.8479	-0.8659	-0.9277	-0.9283	-0.9474
4.8	-0.8473		-0.9329	-0.9342	-0.9596
4.6	-0.8464		-0.9359		-0.9698
4.547			-0.9361	-0.9389	
4.486				-0.9390	
4.4	-0.8469	-0.8850	-0.9339	-0.9387	-0.9775
4.2	-0.8476	-0.8947	-0.9277	-0.9338	
4.174					-0.9818
4.1		-0.8993	-0.9224	-0.9290	-0.9812
4.0	-0.8526	-0.9061			-0.9788
3.9		-0.9130			-0.9741
3.8	-0.8700	-0.9188			-0.9664
3.6	-0.8829	-0.9330			
3.4	-0.8971	-0.9463			
3.2	-0.9111	-0.9591			
3.0	-0.9237	-0.9722			
2.8	-0.9331	-0.9802			
2.640	-0.9361				
2.165		-0.9818			
2.5	-0.9335	-0.9792			
2.4	-0.9278	-0.9736			
2.2	-0.9021	-0.9476			

TABLE 3: Potential Energies *E* (hartrees), Bond Lengths *R* (Å), and Bond Energies *D_e* (kcal/mol) of the Valence X¹Σ⁺, A¹Π, and a³Π states of ScPH⁺

state	<i>E</i> _{MRDCI+D} ^a	<i>R</i> _{PH}	<i>R</i> _{ScP}	<i>D_e</i>	
				ScP ⁺ -H	Sc ⁺ -PH
X ¹ Σ ⁺	-1100.9818	1.384	2.209	85.2 ^b	46.1 ^d
A ¹ Π	-1100.9361	1.397	2.406	52.5 ^c	17.4 ^e
a ³ Π	-1100.9389	1.395	2.371	54.3 ^c	19.2 ^e

^a *E*_{MRDCI} + Davidson correction. ^b Corresponding asymptotic channel: ScP⁺(²Σ⁺) + H(²S). ^c Corresponding asymptotic channel: ScP⁺(²Π) + H(²S). ^d Corresponding asymptotic channel: Sc⁺(³F) + PH(³Σ⁻), but with respect to Sc⁺(³D) + PH(³Σ⁻). ^e Corresponding asymptotic channel: Sc⁺(³D) + PH(³Σ⁻).

indicates a highly stabilizing effect of Sc⁺ on the PH bond, and it is reflected in the shortening of the ScP-H bond length by 0.04 Å relative to the free PH radical (Tables 1 and 3).

With respect to the Sc⁺(³F) + PH(X³Σ⁻) channel, the well depth (intrinsic bond strength) of ScPH⁺(X¹Σ⁺) is 65.1 kcal/mol with a corresponding *D_e* of 46.1 kcal/mol, referring to the ground Sc⁺(³D) state. This value is 19.7 kcal/mol higher than that of the free ScP⁺(²Σ⁺) ion.² Yet, the Sc-P bond distance in ScPH⁺ has not appreciably changed relative to the free ScP⁺.²

This almost symmetrical strengthening of the P-H and Sc-P bonds in the ScPH⁺(X¹Σ⁺) state relative to the above mentioned free fragments is due to an enhanced mixing of the *σ*3s (lone pair) with the *σ*3p_z orbitals of P upon complexation of ScP⁺(²Σ⁺) with H, Scheme 1, or the complexation of Sc⁺(³F) with PH(X³Σ⁻), Scheme 3. An analogous synergistic effect was observed in the isovalent species ScNH⁺¹ where a symmetrical bond strengthening of 43 kcal/mol was found for the Sc⁺-NH and ScN⁺-H bonds relative to the bonds of the free fragments ScN⁺(²Σ⁺) and NH(X³Σ⁻), respectively.

Further calculations have shown that ScPH⁺ is linear but

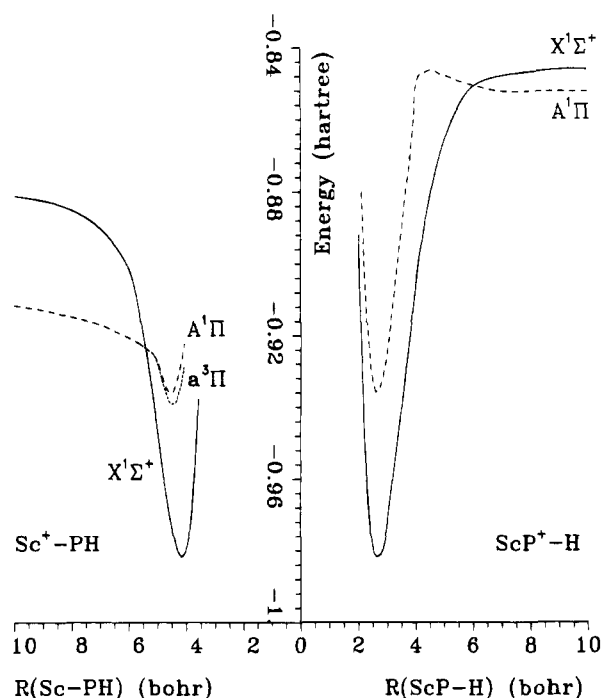


Figure 2. The potential energy curves of the valence X¹Σ⁺ (solid line), a³Π (dotted line), and A¹Π (dashed line) states of ScPH⁺ shifted by 1100 hartrees. On the right side, the asymptotic channels are ScP⁺(²Σ⁺) + H(²S) for the X¹Σ⁺ state (*R*_{Sc-P} = 2.209 Å) and ScP⁺(²Π) + H(²S) for the A¹Π state (*R*_{Sc-P} = 2.406 Å). On the left side, the asymptotic channels are Sc⁺(³F) + PH(³Σ⁻) for the X¹Σ⁺ state (*R*_{P-H} = 1.384 Å) and Sc⁺(³D) + PH(³Σ⁻) for both the a³Π state (*R*_{P-H} = 1.395 Å) and the A¹Π state (*R*_{P-H} = 1.397 Å).

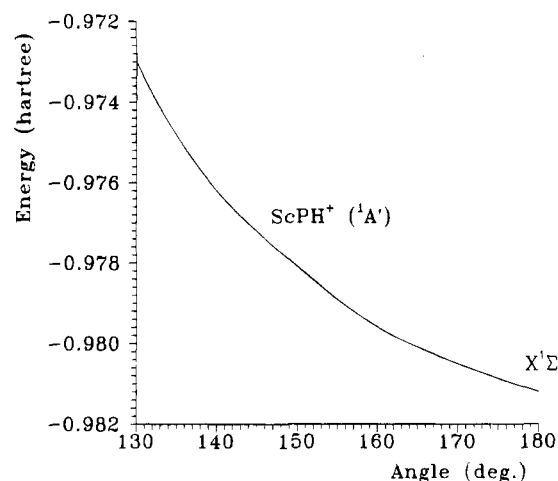


Figure 3. The potential curve of ScPH⁺(X¹A), shifted by 1100 hartrees, as a function of the bending angle. The internuclear separations are fixed at the equilibrium values of the linear X¹Σ⁺ state (Table 3). The nonrigidity of the linear equilibrium geometry is evident.

nonrigid. Its potential energy is a slowly varying function of the bending angle. This is shown in Figure 3.

We now turn to the singlet and triplet Π states of ScPH⁺. From Table 3 we observe that the a³Π and A¹Π states are 26.9 and 28.7 kcal/mol, respectively, above the ground ¹Σ⁺ state. From Schemes 4 and 5, it is obvious that these Π states have a single π Sc⁺-PH bond. This is reflected in the very low dissociation energies of the ScP⁺(²Π) + H(²S) channels (19.2 (triplet) and 17.4 (singlet) kcal/mol). Also, the corresponding Sc⁺-PH bond lengths increase by 0.16 Å (a³Π) and 0.20 Å (A¹Π) relative to the Sc⁺-PH (X¹Σ⁺) bond distance. In either of the two Π states, the P-H bond distance decreases only slightly (less than 0.03 Å) relative to the free PH(X³Σ⁻) species.

Let us now focus on the differences in the shapes between the left and right potential curves in Figure 2. The curves on the right half of the plot reach their asymptotic behavior practically around 10 bohr, the ones on the left around 30 bohr (Table 2). The very long tails of the left potential curves correspond to the Sc⁺ + PH asymptotic channels and are the result of the electrostatic interaction (ΔE) of the positive charge of Sc⁺ with the dipole (μ), quadrupole (θ) and octapole (Ω) moment tensors along the internuclear axis of the PH($X^3\Sigma^-$) molecule as well as of its polarizability (α): $\Delta E = -\mu/R^2 + \theta/R^3 - \Omega/R^4 - \alpha/(2R^4)$, where R is the distance between Sc⁺ and the center of mass of PH. The tails of the right potential curves correspond to the ScP⁺ + H asymptotic channels and are relatively short because of the negligible electrostatic interaction.

A hump appearing on the A¹Π potential curve at around 4 bohr on the right side of Figure 2 is assumed to be due to the Pauli repulsion between the electron pair of the σ (P) and the single electron of the oncoming H atom. Naturally, this barrier does not appear on the left side of the A¹Π potential curve, which corresponds to Scheme 4.

Summary

The most important findings of the *ab initio* study of the ScPH⁺ cation are summarized here: The ground state is of ¹Σ⁺ symmetry with a ³Π and a ¹Π state higher by 26.9 and 28.7 kcal/mol, respectively. In the X¹Σ⁺ state the bond dissociation energies of the Sc⁺-PH and ScP⁺-H channels are stabilized by 19.7 and 17.5 kcal/mol, respectively, relative to the free ScP⁺(²Π) and PH($X^3\Sigma^-$) molecules. On the other hand, the Sc⁺-PH bond lengths of the a³Π and A¹Π states increase by 0.16 and 0.20 Å, respectively, relative to the Sc⁺-PH($X^1\Sigma^+$)

bond distance owing to the breaking of one bond. Finally, in its ground state, the cation is a nonrigid molecule.

References and Notes

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