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Structural Characterization of ScP^+

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We present the ab initio potential energy curves of the lowest $^2\Pi$ and $^2\Sigma^+$ valence states of the scandium phosphide cation, ScP^+. Within the resolving power of our calculations, the two states are practically degenerate, with a binding energy $D_e \approx 31.0$ kcal/mol and equilibrium geometries $r_e(^2\Pi) = 2.34$ Å and $r_e(^2\Sigma^+) = 2.20$ Å.

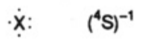
Introduction

Our interest is focused here on the structural characterization of the scandium phosphide cation, ScP^+, in the gas phase. To the best of our knowledge, there are no experimental data on ScP^+. We concentrate on the characteristics of both the ground and the first excited states: the method of binding, the dissociation energy (D_e and D_0), and the bond length. We do not explore possible higher states originating from selective spin decoupling of the various bonds.[1,2] The present study can be considered a continuation of work on the isovalent scandium nitride, ScN^+.[1,2]

Approach to the Problem

Only two states of Sc^+ and one state of P are relevant to our calculations since they correlate to the two lowest dissociation channels of ScP^+. For Sc^+, these are the ^3D ground state and the first ^3F state, which lies 0.596 eV (average over the *J* values) above the ground state. These two states originate from the $(core)^{18}(3d^1)(4s^1)$ and $(core)^{18}(3d^2)$ configurations, respectively.[3] For P, the relevant state is the ^4S ground state originating from a $(core)^{10}(3s^2)(3p^3)$ configuration. The combination of thse states gives the two lowest valence states of ScP^+: the $^2\Pi$ state correlating with $Sc^+(^3D) + P(^4S)$ and the $^2\Sigma^+$ state correlating with $Sc^+(^3F) + P(^4S)$. Excited states of P are not considered here because they correspond to dissociation channels of ScP^+ which are too high in energy.[3]

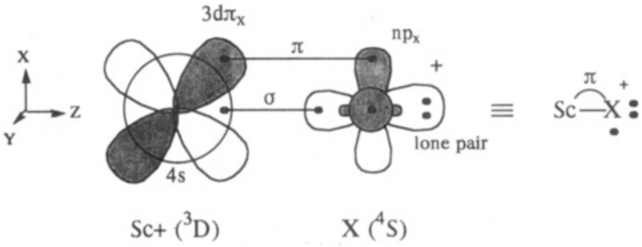
For an element X of the 15 (VA) column of the periodic table (N, P, or As) with a conventional Lewis structure


$$\cdot\dot{\underset{\cdot}{\mathrm{X}}}: \qquad (^4\mathrm{S})^{-1}$$

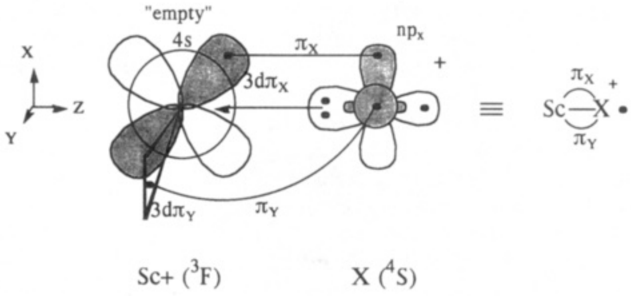
we can imagine two competing schemes of bonding with Sc^+, one being Scheme I (Sc^+ in its ground ^3D state).

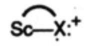
As X approaches from infinity, we can singlet couple the four out of five available valence electrons and form two formal bonds in an obvious way. The 4s electron on Sc^+ singlet couples with the np_z of X ($n = 2$, 3, or 4 depending on X) and gives rise to a σ bond, while the $3d\pi_x$ electron on Sc^+ singlet couples with the np_x of X and forms a π_x bond. The symmetry-defining, nonbonding (observer) electron of X (np_y at infinity) has its orbital angular momentum along the molecular axis, thus giving rise to a $^2\Pi$ molecular state ($^2B_2$ under C_{2v} symmetry). The resulting Kekulé (valence-bonded) structure will be

SCHEME I



SCHEME II




$$\overset{\frown}{\mathrm{Sc{-}}\underset{\cdot}{\mathrm{X}}}{:}^{+}$$

which stands for the $^2\Pi$ function:

$$|^2\Pi\rangle \sim [\sigma(4s)\sigma(np_z) + \sigma(np_z)\sigma(4s)][\pi(3d_{xz})\pi(np_x) + \pi(np_x)\pi(3d_{xz})]np_y(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)\alpha$$

Scheme II shows Sc^+ in the ^3F (d^2) excited state. Allocating the two uncoupled electrons of Sc^+ along the d_{xz} and d_{yz} distributions gives the molecular structure shown in Scheme II.

As in Scheme I the four out of five valence electrons are singlet coupled in forming two formal bonds. But in this case, two π bonds are formed by singlet coupling the $3d_{xz}$ and $3d_{yz}$ electrons on Sc^+ with the corresponding np_x and np_y electrons on X, while at the same time the lone pair of X can possibly find its way onto the 4s "empty" (atomic) orbital of Sc^+, thus forming a third "dative" bond. The nonbonding (observer), symmetry-defining electron projects its orbital angular momentum perpendicular to the molecular axis and gives rise to a $^2\Sigma^+$ state ($^2A_1$ under C_{2v} symmetry). The resulting Kekulé structure is

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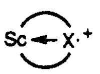

which stands for the $^2\Sigma^+$ function:

$$|^2\Sigma^+\rangle \sim [\pi(3d_{xz})\pi(np_x) + \pi(np_x)\pi(3d_{xz})][\pi(3d_{yz})\pi(np_y) + \pi(np_y)\pi(3d_{yz})]\sigma(ns)^2 np_z(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)\alpha\beta\alpha$$

Notice that a $(d_{xz})^1(d_{yz})^1$ electron allocation in the atom does not lead to a pure ^3F state, since this state originates from a $(d_{z^2})^1(d_{x^2-y^2})^1$ allocation. However, both the $(d_{xy})^1(d_{yz})^1$ and the pure ^3F distributions have practically the same energies at the asymptotic channels of the cation when calculated at the SCF+1+2 level,[1] and therefore we will not be concerned with this fine point here.

Which of the two schemes above leads to a ground molecular state depends on the excitation energy $\Delta E(^3F \leftarrow {}^3D)$ of Sc$^+$ vis-à-vis both the relative energetics of the σ versus π bonds and the possibility of formation of a dative bond. In the isovalent ScN$^+$ system,[1,2] it has been proven that Scheme II is the path leading to the ground $^2\Sigma^+$ state (*vide infra*). In the ScP$^+$ system, the $^2\Pi$ state (Scheme I) drops 4.6 kcal/mol below the $^2\Sigma^+$ state (Scheme II) and formally becomes the ground state (but see qualifying discussion).

To obtain the vibrational structure of both states, we integrated numerically the vibrational Schrödinger equation, using a modified Numerov method.[4] For this purpose, the ab initio points of both curves were fitted to two nine-segment cubic splines.

Computational Approach

We have employed the MRDCI series of codes.[5-7] 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 0.3 μH with 7–20 reference configurations, depending on the geometry, and this resulted in 5000–17000 selected configurations respectively for the diagonalization of the Hamiltonian matrix. All computations were done under C_{2v} symmetry.

For the Sc atom, the 11s9p5d basis set of Wachters[8] was employed, contracted to 8s4p2d.[9] This was augmented with two additional p functions[1] to represent the 4p orbital (exponents 0.089 75 and 0.031 03) and an extra d (exponent 0.0588) as recommended by Hay,[10] thus resulting in an 8s6p3d contracted basis set. The basis set on P atom is that of McLean and Chandler[11] 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),[12] thus resulting in 6s5p2d contracted basis set. Over all, our basis set consists of 77 contracted Cartesian Gaussian functions, [8s6p3d/6s5p3d].

Results and Discussion

Our most important numerical results are presented in Table I. About 30 ab initio points for each state have been calculated, and they are shown in Table II. The fitted curves, scaled to the minimum of the $^2\Pi$ state (−1100.3517 au), along with the first six vibrational levels are shown in Figure 1. Table III presents the calculated vibrational levels for the $^2\Pi$ and $^2\Sigma^+$ states, expressed in cm^{-1}, relative to the bottom of each well.

TABLE I: Total Energies E (hartrees), Bond Lengths r_e (Å), and Bond Energies D (kcal/mol) of the Valence $^2\Pi$ and $^2\Sigma^+$ States of ScP$^+$

state	E_{MRDCI}	$E_{\mathrm{MRDCI+D}}{}^a$	r_e	D_e	D_0
$^2\Pi$	−1100.3419	−1100.3517	2.34	31.0	30.5
$^2\Sigma^+$	−1100.3347	−1100.3443	2.20	26.4	25.9

[a] E_{MRDCI} + Davidson correction.

TABLE II: Computed Potential Energies (au) of ScP$^+$ as a Function of Internuclear Distance, Scaled to −1100.0000 au

R	$^2\Pi$	$^2\Sigma^+$	R	$^2\Pi$	$^2\Sigma^+$
3.2	–	−0.1947	4.9	−0.3459	−0.3232
3.3	–	−0.2334	5.0	−0.3443	−0.3204
3.4	−0.2183	−0.2632	5.2	−0.3406	−0.3106
3.5	−0.2513	−0.2867	5.4	−0.3368	–
3.6	−0.2780	−0.3051	5.5	–	−0.2991
3.7	−0.2988	−0.3189	5.6	−0.3333	–
3.8	−0.3154	−0.3296	6.0	−0.3271	−0.2872
3.9	−0.3277	−0.3371	6.5	−0.3209	−0.2817
4.0	−0.3372	−0.3420	7.0	−0.3159	−0.2787
4.1	−0.3436	−0.3441	8.0	−0.3083	−0.2758
4.2	−0.3485	−0.3443	9.0	−0.3052	−0.2740
4.3	−0.3512	−0.3430	10.0	−0.3037	−0.2731
4.4	−0.3517	−0.3411	12.0	−0.3027	−0.2725
4.5	−0.3512	−0.3385	14.0	−0.3025	−0.2724
4.6	−0.3507	−0.3350	16.0	−0.3024	−0.2723
4.7	−0.3494	−0.3319	18.0	−0.3024	−0.2723
4.8	−0.3480	−0.3273	20.0	−0.3023	−0.2723

As was mentioned previously, the magnitude of the energy separation between the ^3F and ^3D states of Sc$^+$ is crucial in determining the ground state of the ScP$^+$ system. At the MRDCI + Davidson correction level, we calculated a ^3F–^3D splitting of 18.8 kcal/mol as compared to the experimental value of 13.74 kcal/mol,[3] a difference of 5.1 kcal/mol. Exactly the same energy separation between the molecular states $^2\Pi$ and $^2\Sigma^+$ was obtained at the asymptotic region (20 bohrs) of the potential curves, as can be deduced from Table II. Now, from Table I it is seen that the binding energy of the $^2\Sigma^+$ state, with respect to the ground-state products Sc$^+$(^{3}D) + P(^{4}S), is D_e = 26.4 kcal/mol. Downshifting this value by 5.1 kcal/mol (i.e., using the experimental rather than the calculated $\Delta E(^3F \leftarrow {}^3D)$ of Sc$^+$) yields a binding energy of 31.5 kcal/mol, thus making the two states practically degenerate.

The intrinsic bond strength of the $^2\Sigma^+$ state, with respect to the Sc$^+$(^{3}F) + P(^{4}S) channel, is 45.2 kcal/mol. This is reflected in the shorter bond length of this state (2.20 Å) as compared to that of the $^2\pi$ state (2.34 Å).

In the isovalent ScN$^+$, the $^2\Pi$ state is 7.7 kcal/mol above the $^2\Sigma^+$ state, which therefore is definitely the ground state.[1,2] The binding energy of the ground state is D_e = 63.0 kcal/mol with respect to the products in their ground state, and its intrinsic bond strength with respect to the Sc$^+$(^{3}F) + N(^{4}S) channel is 76.7 kcal/mol. The bond length of the $^2\Sigma^+$ state (1.738 Å) is shorter than that of the $^2\Pi$ state (1.804 Å), just as in ScP$^+$. The twice as large binding energy of ScN$^+$ as compared to ScP$^+$ is attributed to the much larger electronegativity of N as compared to P ($\Delta\chi^P$ = 1 in the Pauling scale), as well as the larger size of P.

That the bonding in the $^2\Pi$ state can be described as a (σ,π) system while that of the $^2\Sigma^+$ state as a (π,π) system can be deduced from the asymptotic (r = 20 bohrs) electron distributions in combination with the distributions around equilibrium. For the $^2\Pi$ state, the most heavily contributing references in the multireference variational function have the following in *situ* valence atomic distributions (C is the coefficient of the respective reference):

for r = 2.34 Å (equilibrium)

$$\mathrm{Sc}^+\text{: } (4s)^2(3d_{xz})^2 \quad \mathrm{P}\text{: } (3s)^2(3p_y)^1 \quad (C^2 = 0.46)$$

$$\mathrm{Sc}^+\text{: } (4s)^2(3d_{xz})^1, \quad \mathrm{P}\text{: } (3s)^2(3p_x)^1(3p_y)^1 \quad (C^2 = 0.16)$$

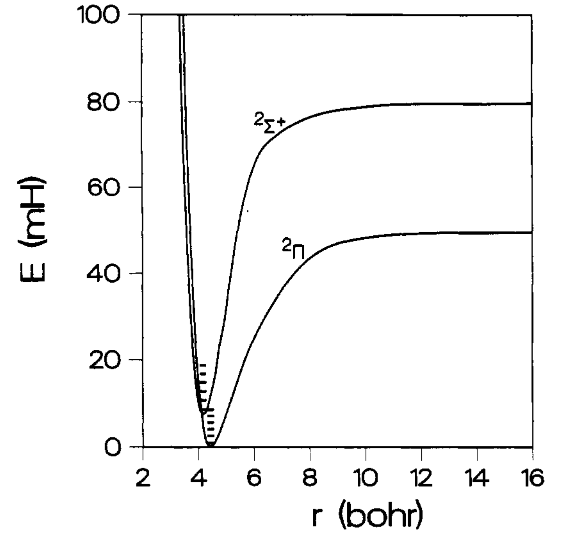

Figure 1. Potential energy curves of the valence $^2\Sigma^+$ and $^2\Pi$ states of ScP$^+$ along with their first six vibrational levels. The $^2\Pi$ state correlates with Sc$^+$(^{3}D) + P(^{4}S), and the $^2\Sigma^+$ state correlates with Sc$^+$(^{3}F) + P(^{4}S).

TABLE III: Vibrational Energy Levels ΔG_v (cm^{-1}) of the Valence Σ^+ and $^2\Pi$ States of ScP$^+$, Relative to the Bottom of Each Well

v	$\Delta G_v(^2\Pi)$	$\Delta G_v(^2\Sigma^+)$
0	180.0	190.9
1	529.8	643.1
2	869.1	1106
3	1205	1547
4	1535	1971
5	1850	2397
6	2151	2829

for r = 11 Å (asymptotic)

$$\text{Sc}^+\text{: } (4s)^1(3d_{xz})^1, \quad \text{P: } (3s)^2(3p_x)^1(3p_y)^1(3p_z)^1 \quad (C^2 = 0.96)$$

The first configuration of the equilibrium geometry indicates σ binding, while the second one indicates both σ and π binding. The corresponding distributions in the $^2\Sigma^+$ state are as follows:

for r_e = 2.20 Å (equilibrium)

$$\text{Sc}^+\text{: empty,} \quad \text{P: } (3s)^2(3p_x)^2(3p_y)^2(3p_z)^1 \quad (C^2 = 0.44)$$

$$\left.\begin{matrix}\text{Sc}^+\text{: } (3d_{xz})^1 \\ \text{P: } (3s)^2(3p_y)^2(3p_x)^1(3p_z)^1\end{matrix}\right\} + \left\{\begin{matrix}\text{Sc}^+\text{: } (3d_{yz})^1 \\ \text{P: } (3s)^2(3p_x)^2(3p_y)^1(3p_z)^1\end{matrix}\right. \quad (C^2 = 0.38)$$

for r = 11 Å (asymptotic)

$$\text{Sc}^+\text{: } (3d_{xz})^1(3d_{yz})^1, \quad \text{P: } (3s)^2(3p_x)^1(3p_y)^1(3p_z)^1 \quad (C^2 = 0.96)$$

The equilibrium configurations clearly indicate the formation of two π bonds.

Recent unpublished results of ab initio calculations on scandium phosphide, ScP (neutral), at the MCSCF+1+2 level[13] predict a ground state of $^1\Sigma^+$ ($^1A_1$) symmetry with a binding energy D_e = 35.6 kcal/mol with respect to the ground-state products. They also predict a bond length r_e = 2.277 Å and a Kekulé type structure with two π bonds and one σ bond. The ground state of ScP correlates with the first ^{4}F (4s3d^2) state of Sc, which is located 32.8 kcal/mol above its ground ^{2}D (4s^{2}3d) state[3] and is analogous to the $^2\Sigma^+$ state of ScP$^+$, which traces its lineage to the ^{3}F of Sc$^+$. Both species have comparable binding energies and bond lengths, with the bond length of the cation being shorter by about 0.08 Å.

Mutatis mutandis, the same situation prevails with the ScN (X$^1\Sigma^+$)[14] and ScN$^+$ (X$^2\Sigma^+$) species. The binding energy of the cation is higher by only 0.3 kcal/mol, and its bond length is shorter by 0.03 Å.

Summary

The most important properties of ScP$^+$ are summarized here: (a) The valence $^2\Pi$ and $^2\Sigma^+$ states are practically degenerate. (b) The dissociation energy for both states is ~31 kcal/mol, but the $^2\Sigma^+$ state has an intrinsic bond strength of ~45 kcal/mol with respect to its correlating fragments. (c) The $^2\Pi$ state has a σ and a π bond, while the $^2\Sigma^+$ state has two π bonds.

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Note Added in Proof. Please note that the largest components of the wave functions at the equilibrium position of each state are depicted here not by their electronic distributions at equilibrium, which we could not calculate, but by their electronic distributions at the asymptotic region. In that region, these components are very small for our low lying states and become appreciable only at highly excited states. Thus (for example), the component with an "empty" Sc$^+$ distribution (C^2 = 0.44) does *not* imply that at equilibrium Sc$^+$ loses one electron.

References and Notes

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