The ScPH+ Cation

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We have obtained by ab initio calculations the energetics and the geometries of the X'Σ+, a1Π, and A'1Π 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+.

To do this, certain properties of the ScP' and PH fragments are needed. In a previous paper, 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 σ2(P) orbital (z is the molecular axis) while the latter has a single electron in a π2(P) orbital. Some conclusions for the phosphinidine radical, PH, are also arrived at here, which compare well with previous results.

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 (core183d14s1) and the first 3F state (core183d2) of Sc+, which differ by 0.596 eV (average over J values), and the ground 3Σ− state of PH (1σ22σ23σ4σ1τ15σ22τ12τ2).

Let us imagine ScPH+ as being formed either by an H atom approaching from infinity to ScP+(~Σ+) 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 'A' 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 and 3, one anticipates a strengthening and shortening of the Sc+-PH and ScP+–H bonds for the 1Σ+ state relative to the ScP'+(Σ+) and PH(3Σ−) fragments. (c) From Schemes 4 and 5, and in contrast to the ScP'+(Σ+) 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 0 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.
or \( \text{Sc}^{(2D)} + \text{P} - \text{H}^{(3\Sigma^-)} \rightarrow \text{Sc} \cdot \text{Sc} - \text{H}^{(1\Pi \text{or } 3\Pi)} \)

SCHEME 5

or \( \text{Sc} \cdot \text{P}^{\dagger}(3\Pi) + \cdot \text{H}^{(2S)} \rightarrow \text{Sc} \cdot \text{P} - \text{H}^{(1\Pi \text{or } 3\Pi)} \)

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-Cl 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 \(\mu\)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 \(C_2\), symmetry and for bent geometries under \(C_2\) symmetry.

For the Sc atom the 11s9p5d basis set of Wachters\(^10\) was employed, contracted to 8s4p2d.\(^11\) This was augmented with two \(p\) functions\(^13\) 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–Chandler\(^14\) 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, \(8\text{s}6\text{p}3\text{d}/6\text{s}5\text{p}3\text{d}/3\text{s}1\text{p}\).

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 method\(^17\) 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,\(^3\)\,\,4\,\,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 \(\Sigma^+\) section of the \(^1A'\) surface was done at a Sc–P internuclear distance of 2.209 \(\text{Å}\) (ScP\(^+\)–H channel) and at a P–H internuclear distance of 1.384 \(\text{Å}\) (Sc\(^+\)–PH channel), which are the equilibrium bond distances of ScPH\(^+\)(\(X^3\Sigma^+\)).

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>
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<tr>
<td>6</td>
<td>13490.7</td>
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</table>

\(^a\) Reference 3. \(^b\) Reference 4. With respect to the bottom of the well. \(^d\) Using \(G_v = \omega_v (v + 1/2) - \omega_{0v} (v + 1/2)^2\).

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 \(^1\text{II}\) section of the surface was done at a Sc–P internuclear separation of 2.406 \(\text{Å}\) (ScP\(^+\)–H channel) and at a P–H internuclear separation of 1.397 \(\text{Å}\) (Sc\(^+\)–PH channel), which are the equilibrium bond distances of ScPH\(^+\)(\(\Sigma^+\)). 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 \(\Sigma^+\) 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, \(D_v\), of the \(X^3\Sigma^-\) state of ScPH\(^+\), with respect to the ScP\(^+\)(\(\Sigma^+\)) + H(2S) channel is 85.2 kcal/mol, 17.5 kcal/mol higher than that of PH(\(X^3\Sigma^-\)). This increase
indicates a highly stabilizing effect of $\text{Sc}^+$ 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 $\text{Sc}^+(\Phi) + \text{PH}(\Sigma^+)$ channel, the well depth (intrinsic bond strength) of $\text{Sc}^+(\Sigma^+) + \text{H}(\Sigma^+)$ is 65.1 kcal/mol with a corresponding $D_e$ of 46.1 kcal/mol, referring to the ground $\text{Sc}^+(\Phi)$ state. This value is 19.7 kcal/mol higher than that of the free $\text{Sc}^+(\Sigma^+)$ ion. Yet, the Sc–P bond distance in $\text{ScP}^+$ has not appreciably changed relative to the free $\text{Sc}^+$.  

This almost symmetrical strengthening of the P–H and Sc–P bonds in the $\text{ScP}^+(\Sigma^+)$ state relative to the above mentioned free fragments is due to an enhanced mixing of the $\phi_3$ (lone pair) with the $\phi_3p$ orbitals of P upon complexation of $\text{Sc}^+(\Sigma^+)$ with H, Scheme 1, or the complexation of $\text{Sc}^+(\Phi)$ with $\text{PH}(\Sigma^+)$, Scheme 3. An analogous synergistic effect was observed in the isovalent species $\text{ScNH}^+$ and $\text{ScN}^+\text{H}$ bonds relative to the bonds of the free fragments $\text{ScN}^+(\Sigma^+)$ and $\text{NH}(\Sigma^+)$, respectively.

Further calculations have shown that $\text{ScPH}^+$ is linear but 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 $\Pi$ states of $\text{ScPH}^+$. From Table 3 we observe that the $\pi$ and $\Pi$ states are 26.9 and 28.7 kcal/mol, respectively, above the ground $\Sigma^+$ state. From Schemes 4 and 5, it is obvious that these $\Pi$ states have a single $\pi$ $\text{Sc}^+\text{–PH}$ bond. This is reflected in the very low dissociation energies of the $\text{Sc}^+(\Phi) + \text{H}(\Sigma^+)$ channels (19.2 (triplet) and 17.4 (singlet) kcal/mol). Also, the corresponding $\text{Sc}^+\text{–PH}$ bond lengths increase by 0.16 Å (a$\Pi$) and 0.20 Å (A$\Pi$) relative to the $\text{Sc}^+\text{–PH}$ $\Sigma^+$ bond distance. In either of the two $\Pi$ states, the P–H bond distance decreases only slightly (less than 0.03 Å) relative to the free PH($\Sigma^+$) species.
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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 \( \Delta E \) of the positive charge of Sc+ with the dipole \( (\mu) \), quadrupole \( (\theta) \) and octapole \( (\Omega) \) moment tensors along the internuclear axis of the PH(\( X^1\Sigma^- \)) molecule as well as of its polarizability \( (\alpha) \). 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 \( \Sigma^+ \) 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 \( \sigma(P) \) and the single electron of the oncoming H atom. Naturally, this barrier does not appear on the left side of the \( \Sigma^+ \) 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 \( \Sigma^+ \) symmetry with a \( \Pi^+ \) and a \( \Pi^+ \) state higher by 26.9 and 28.7 kcal/mol, respectively. In the \( \Sigma^+ \) 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+(\( \Pi^+ \)) and PH(\( X^1\Sigma^- \)) molecules. On the other hand, the Sc+−PH bond lengths of the \( \Sigma^+ \) and \( \Pi^+ \) 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

(3) Huber, K. P.; Herzberg, G. Constants of Diatomic Molecules; Van Nostrand Reinhold Co.: New York, 1979. The \( D_0 \) of 69.6 kcal/mol given here is the “recommended” ab initio value from ref 5.
(11) Wachters, A. J. H. IBM Technical Report RJ584, 1969 (contraction no. 3 of ref 8). We are indebted to M. Dupuis for securing a copy of this IBM report for us.