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Thermochemistry of the Reactions $F^+(^3P, ^1D) + PH_3$ in the Gas Phase

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High-level ab initio calculations in the framework of the G2 theory have been performed for the $[H_3, P, F]^+$ singlet- and triplet-state cations. The bonding characteristics of singlet- and triplet-state cations are rather different. The latter are weakly bound species involving electrostatic and/or polarization interactions, while the former present covalent bonds. As a consequence, while in the $F^+(^3P) + PH_3(^1A_1)$ reactions in the gas phase the charge-transfer process competes with the formation of $HF(^1\Sigma^+) + PH_2^+(^3B_1)$, the main products when the reaction involves the F^+ cation in its ^1D first excited state are $HF(^1\Sigma^+) + PH_2^+(^1A_1)$. In both cases, the reactions are extremely exothermic, and therefore, the products are anticipated to be vibrationally excited. The $[H_3, P, F]^+$ triplet-state cations are good examples of molecular planetary systems, in which a neutral fluorine atom or a neutral HF molecule orbits around a PH_3^+ or a PH_2^+ moiety, respectively. Although the singlet PES lies systematically below the triplet PES, there are regions where both surfaces approach each other significantly. The spin−orbit coupling between them, evaluated at the corresponding minimum energy crossing point, indicates that a fast transition between both PESs should take place, implying the possibility of having “spin-forbidden” reactions. From our calculations, the heat of formation for FPH_2 was estimated to be -58.2 ± 2.5 kcal/mol.

Introduction

Most of the processes which take place in interstellar space involve open-shell molecular ions which are elusive to experimental observation under normal laboratory conditions.[1] This has been one of the most serious limitations when attempting to establish the mechanisms associated with the formation of interstellar species. This also explains the important role that is played by the calculations which are carried out in the framework of molecular orbital theory in the development of astrochemistry. In fact, although more than 100 molecular species have been detected[2−5] in the interstellar medium by means of spectroscopic techniques,[5] relevant information on the structure of chemical species of interest in interstellar or atmospheric chemistry was obtained through the use of ab initio calculations.[6] On the other hand, a rationalization of the mechanisms involved in the astrochemical processes requires a detailed description of the potential energy surface (PES), which nowadays can be obtained only from quantum chemical calculations, because it implies an accurate knowledge of the energetics and the structures of the very short-lived transient species connecting the different local minima. Even when the energetics of ion−molecule reactions can be measured by means of experimental techniques such as the Fourier transform ion cyclotron resonance techniques (FT-ICR), the information obtained in ab initio calculations is of great relevance in two senses. On one hand, they normally provide unambiguous information on the active site of the neutral. On the other hand, through the calculation of harmonic vibrational frequencies of the system, they allow estimates of the entropy along the reactive process, which is needed to convert the measured free energies into reaction enthalpies.

The availability of high-level ab initio theoretical techniques,[7] which yield results within experimental chemical accuracy, that is, with errors of the order of 1 kcal/mol, is a very important factor in this development.

In the past few years our research group has focused its attention on the subset of reactive processes which involve open-shell monocations.[8] Along this line, a particular interest was concentrated on reactions involving the halogen cations,[8e−g] because these are characterized by quite-large recombination energies which strongly favor charge-transfer processes,[8e−g] and because they usually yield weakly bound species when reacting in the ground state. In contrast, when the reaction takes place in the first singlet excited state, covalently bound species are formed. One of the consequences is that, in general, the singlet potential PES lies below the triplet one, even though the corresponding entrance channel for the reaction lies higher in energy, opening the possibility of having “spin-forbidden” reactions.

One of the aims of our paper is to investigate if this possibility is open in $F^+ + PH_3$ reactions by analyzing, through the use of the molecular orbital theory, the PESs associated with the reactions between F^+, both in its triplet ground state and in its singlet first excited state, with PH_3. Although the ^1D state of F^+ must be considered as a metastable state, it is conveniently produced in electron-impact ionization processes and subsequently detected by collision with different neutrals by means of translational-energy spectroscopy.[9] Nevertheless, to the best of our knowledge there is a complete lack of information regarding reactions between F^+ and PH_3. Hence, one of the

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objectives of our work was to establish which are the main products of both the $F^+(^3P) + PH_3$ and the $F^+(^1D) + PH_3$ reactions.

The theoretical treatment of species containing halogen atoms is a challenge for the theory[10] in the sense that electron correlation effects are difficult to handle for halogen-containing species, and therefore, adequate description of the bonding in these species unavoidably requires the use of high-level ab initio techniques.

Computational Details

Standard ab initio calculations were performed using the Gaussian-94 series of programs.[11] Correlation effects are important when describing structural features, but they are usually dramatic for open-shell species. Hence, the geometries of the systems investigated were initially optimized at the MP2(full)/6-31G(d) level. The harmonic vibrational frequencies were evaluated at the same level in order to classify the stationary points found as either minima or transition states.

As we shall discuss in forthcoming sections, the $[H_3, P, F]^+$ triplet-state cations are weakly bound complexes where electron-correlation effects might be of special relevance. Therefore, we have considered it of interest to investigate whether the optimized geometries are sensitive to the inclusion of higher-order correlation corrections in the theoretical treatment. For this purpose the geometries of all the stationary points of the triplet PES were refined at the QCISD/6-311+G(d, p) level. It must be noted that we also included diffuse components in the basis set, which can be important when describing weakly bound species, which present anomalously large bond distances. For the different minima, these geometries were further refined at the QCISD/6-311+G(2d, p) level, because a larger number of high-angular-momentum basis may be necessary to account for electron-correlation effects in open-shell systems. More angular-correlation effects will probably be garnered by also including a set of *f*-type functions. However, for similar systems, we have found[12] that the effects on the optimized geometries are negligible.

The final energies of the species under investigation were obtained in the framework of the G2 theory.[7a] This composite procedure yields final energies of an effectively QCISD(T)/6-311+G(3df, 2p) quality and provides thermodynamic properties as heats of formation, protonation energies, ionization potentials, etc., within chemical accuracy. It must be noted that, although the geometries used in the standard G2 procedure are optimized at the MP2(full)/6-31G(d) level and the ZPE corrections are evaluated at the HF/6-31G(d) level, in the present case, both the MP2/6-31G(d)- and the QCISD/6-311+G(d, p)-optimized geometries have been used. The results so obtained will be denoted hereafter as G2//MP2 and G2//QCI, respectively. In all cases, the ZPEs employed were those calculated at the MP2(full)/6-31G(d) level and scaled by the empirical factor 0.9646.[13]

The minimum-energy-crossing point (MECP) between the singlet and triplet PESs was located by using the approach of Bearpark et al.,[14] as implemented in Gaussian-98. For this purpose we have employed a CASSCF method using a 6-31G* basis set and an active space of 6 electrons in five orbitals (6,5). The final energy of the MECP was obtained at the G2 level using the aforementioned optimized geometry. The spin−orbit coupling (SOC) at this point was evaluated[15] at the CASSCF(8,6)/6-31G* level.

The charge distribution of the different species studied was analyzed by means of the natural bond orbital (NBO) analysis of Weinhold et al.[16]

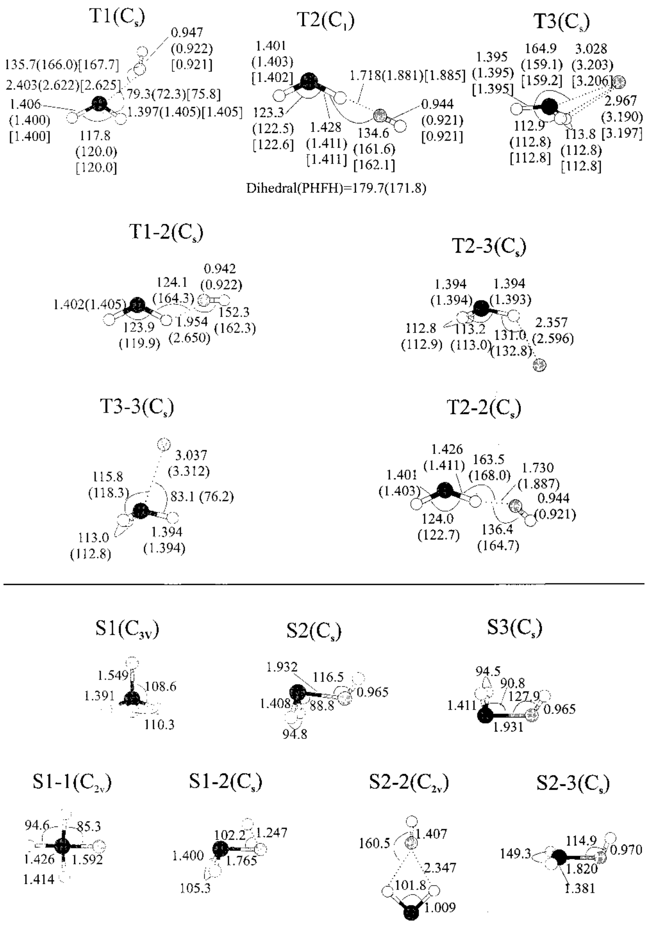

Figure 1. MP2(full)/6-31G(d)-optimized geometries for singlet and triplet $[H_3, P, F]^+$ cations. Bond lengths are in Å, and bond angles are in degrees. For triplet-state cations, the QCISD/6-311+G(d, p)- and the CCSD/6−311+G(d, p)-optimized parameters are given within parentheses and within brackets, respectively.

Results and Discussion

Structure and Bonding. The optimized structures of the stationary points of both $[H_3, P, F]^+$ singlet and triplet PESs have been schematized in Figure 1. The different local minima of the singlet PES are designated by S followed by a number which indicates its relative stability, so that **S1** names the global minimum. The transition structures are identified by adding two numbers which correspond to the two local minima they connect. For the triplets the nomenclature adopted was analogous, replacing S by T.

The first conspicuous feature of Figure 1 is the noticeable differences in the bonding between singlet- and triplet-state cations. This is apparent if one compares, for instance, the structures of the local minima **S1** and **T3**. In the former, a normal P−F covalent bond is formed, while in the latter, the P−F bond distance indicates that the interaction between the F and the PH_3 subunits is rather weak. Similar situations have been described before in the literature[8c−g] for reactions of F^+ or Cl^+ with different neutrals. Furthermore, an NBO analysis of the charge distribution of **T3** indicates that the positive charge is located at the PH_3 moiety, while the F atom is essentially neutral. In fact, the interactions between F^+ either in its triplet ground state or in its singlet first excited state are dominated by the enormous recombination energy of this cation. Accordingly, in both cases the first step in the $F^+−PH_3$ interaction is an electron transfer from the PH_3 molecule to the monocation. According to our estimates, these charge-transfer processes are

TABLE 1: Total G2 Energies and Relative Energies (Δ*E*) with Respect to the Most Stable Conformer (S1) Calculated by Using the MP2/6-31G(d,p) Geometries and Frequencies (G2//MP2) and Using QCISD/6-311+G(d,p) Geometries and MP2/6-31G(d,p) Frequencies (G2//QCI)[a]

	G2//MP2		G2//QCI	
compound	total energy (au)	Δ*E* (kcal/mol)	total energy (au)	Δ*E* (kcal/mol)
S1	−442.14635	0.0		
S2	−442.08412	39.1		
S3	−442.08285	39.8		
S1-1	−441.99805	93.1		
S1-2	−442.02936	73.4		
S2-2	−442.05527	57.2		
S2-3	−441.98693	100.0		
T1	−442.02580	75.7 (0.0)	−442.02628	75.3 (0.0)
T2	−442.02471	76.3 (0.7)	−442.02527	76.0 (0.6)
T3	−441.95162	122.2 (46.6)	−441.95143	122.3 (47.0)
T1-2	−442.02487	76.2 (0.6)[b]	−442.02758	74.5 (−0.8)[b]
T2-2	−442.02489	76.2 (0.6)[b]	−442.02544	75.9 (0.5)[b]
T1-3	−441.95107	122.5 (46.9)	−441.94756	124.7 (49.4)
T3-3	−441.95137	122.4 (46.7)	−441.95131	122.4 (47.1)
$F^+(^1D) + PH_3(^1A_1)$	−441.57378	359.3		
$FPH_2(^1A') + H^+$	−441.85706	181.5		
$FH_2^+(^1A_1) + PH(^3\Sigma^-)$	−441.92202	140.8		
$FH(^1\Sigma^+) + PH_2^+(^1A_1)$	−442.04198	65.5		
$FH^+(^2\Pi) + PH_2(^2B_1)$	−441.80724	212.8 (137.2)		
$F(^2P) + PH_3^+(^2A_1)$	−441.94908	123.8 (48.1)		
$FPH_2+(^2A') + H(^2S)$	−441.98669	100.2 (24.5)		
$F^+(^3P) + PH_3(^1A_1)$	−441.67264	297.3 (221.6)		
$FH(^1\Sigma^+) + PH_2^+(^3B_1)$	−442.00959	85.8 (10.2)		

[a] Values in parentheses correspond to the relative energies with respect to the most stable triplet conformer (**T1**).

[b] For some transition states the G2 energy is lower than the one corresponding to one (or both) of the minima it connects. This is due to an effect of the ZPE, i.e., the TS is above the minima in the PES, but when the ZPE correction is included the TS is below the minima.

exothermic by 173.5 kcal/mol for triplets and by 235.5 kcal/mol for singlets. Once the $F(^2P)$ and $PH_3^+(^2A_1)$ species are formed, their interactions are rather different, depending on the overall multiplicity of the system. While for singlets the unpaired electrons of both subunits are engaged in the formation of a normal covalent bond, which stabilizes the system by 123.8 kcal/mol, this is not possible for triplets, which must keep two unpaired electrons. In other words, the formation of a covalent bond between $F(^2P)$ and $PH_3^+(^2A_1)$, maintaining an overall triplet multiplicity, would require either promoting a valence electron of the F atom from the occupied 2p to the empty 3s orbital or promoting a valence electron of the PH_3^+ moiety from its highest occupied molecular orbital to the first unoccupied orbital of the appropriate symmetry. Both promotions require much more energy than the energy that can be released if a P−F covalent bond is formed, and accordingly, **T3** corresponds to a weakly bound complex between both doublet-state subunits, with an interaction energy of only 1.5 kcal/mol. It is worth noting that the geometry of this complex is consistent with the nature of the interaction between both subunits. In fact, as expected, species **S1** exhibits a C_{3v} symmetry where the fluorine atom lies along the C_3 axis of the PH_3 subunit. Conversely, species **T3** exhibits a C_s symmetry, where the F atom interacts simultaneously with two hydrogen atoms of the PH_3^+ moiety, that is, **T3** can be viewed as a hydrogen-bonded complex between a fluorine atom and a $PH_3^+(^2A_1)$ cation.

It can also be observed that the optimized geometries for the triplet-state cations are very sensitive to the method by which electron correlation is treated. In particular, the distance between the two moieties which interact in each weakly bound complex changes dramatically on going from MP2- to QCISD-optimized geometries (see Figure 1). To confirm that the geometries so obtained could be considered practically converged, we have refined them at the CCSD level using the same basis-set expansion. As shown in Figure 1, the changes in the optimized geometrical parameters are negligible. This confirms previous findings,[8h] at least in the sense that a QCISD procedure is required to adequately describe the geometries of these weakly bound complexes.

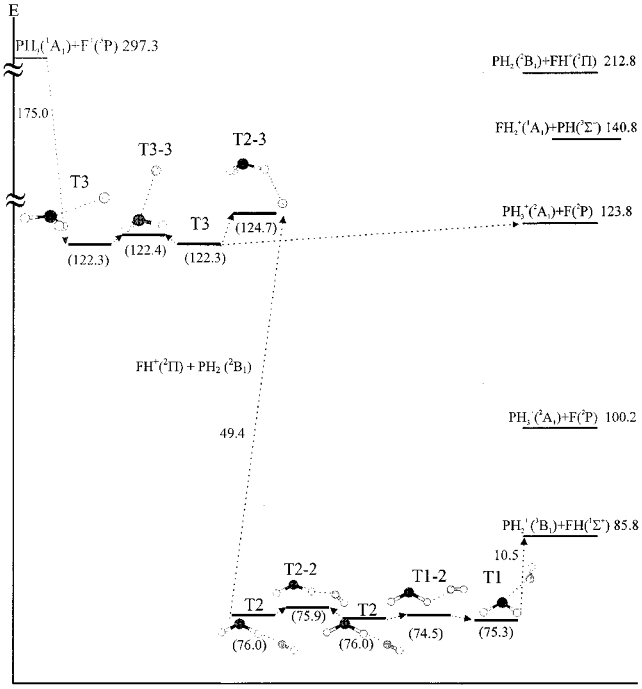

Figure 2. Energetic profile of the $[H_3, P, F]^+$ triplet PES. All values are in kcal/mol and have been evaluated at G2//QCI (stationary points) and G2//MP2 (dissociation limits) levels.

Relative Stability. Total and relative energies for the species under investigation are given in Table 1. The significant bonding differences between singlet- and triplet-state cations are reflected in differences between their relative stabilities. These differences will be of special relevance as far as their gas-phase reactivities are concerned. The most important finding is that although the entrance channel for the reaction $F^+(^3P) + PH_3(^1A_1)$ lies about 60 kcal/mol below that of the entrance channel for the $F^+(^1D) + PH_3\ (^1A_1)$ reaction, all of the local minima of the singlet PES lie lower in energy than all of the local minima of the triplet PES. In particular, the most stable singlet-state cation, **S1**, is estimated to be 75.3 kcal/mol below the most stable triplet-state cation, **T1**.

The enhanced stability of the singlet-state cations might favor a possible spin-forbidden process. In other words, the possibility of producing a singlet-state cation in reactions between $F^+(^3P)$ and $PH_3(^1A_1)$ cannot be discarded. We shall return to this point when discussing the characteristics of both PESs.

Triplet PES. The PES associated with $[H_3, P, F]^+$ triplet-state cations has been schematized in Figure 2. As mentioned above, the first step of the reaction between $PH_3(^1A_1)$ and $F^+(^3P)$ is a charge-transfer process. The subsequent association between the resulting subunits would yield the weakly bound complex **T3**, which can eventually dissociate into $F(^2P) + PH_3^+(^2A_1)$. Alternatively, this local minimum may evolve through a hydrogen transfer which involves the transient species **T2-3** toward the local minimum **T2**, which lies more than 40 kcal/mol lower in energy. This structure is stabilized by an ionic hydrogen bond between the PH_2^+ and the HF subunits. The local minimum **T2** presents another slightly more stable

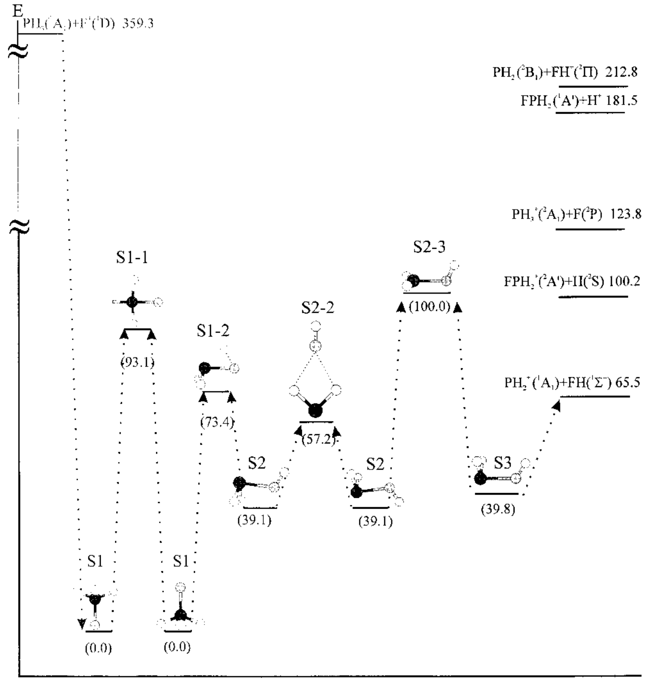

Figure 3. Energetic profile of the $[H_3, P, F]^+$ singlet PES. All values are in kcal/mol and have been evaluated at G2//MP2.

conformer, **T1**, in which an ion−dipole interaction holds together both subunits. Obviously, both minima can eventually dissociate to yield $FH(^1\Sigma^+) + PH_2^+(^3B_1)$.

In summary, our results indicate that charge transfer is a very favorable reaction channel in $F^+(^3P) + PH_3(^1A_1)$ gas-phase reactions. Also importantly, the exothermicity of this reaction, estimated from our calculations (−173.5 kcal/mol), is in very good agreement with the value obtained (−174.2 kcal/mol) when the corresponding experimental heats of formation are used. Similarly, the energies estimated for the other exit channels which lead to $FH^+(^2\Pi) + PH_2(^2B_1)$ or $FH(^1\Sigma^+) + PH_2^+(^3B_1)$, −84.5 and −231.8 kcal/mol, respectively, are also in fairly good agreement with the experimental estimates, −88.4 and −234.7 kcal/mol, respectively, obtained from the corresponding heats of formation.

It must be taken into account, however, that according to our calculations for the $F^+(^3P) + PH_3(^1A_1)$ reaction, the charge-transfer process competes with the formation of $FH(^1\Sigma^+) + PH_2^+(^3B_1)$. In fact, as illustrated in Figure 2, the activation barrier to go from complex **T3** toward the lower minimum **T2** is only slightly higher in energy than the $F(^2P) + PH_3^+(^2A_1)$ dissociation limit. It is also important to emphasize again that both processes are extremely exothermic, so that, very likely, the molecules or the molecular ions formed will be vibrationally excited.

It is worth noting that the displacement of the fluorine atom around the PH_3^+ molecular ion (see Figure 2) requires a very small amount of energy (essentially a few tenths of a kcal/mol). Hence, we may safely conclude that the complex **T3** is a suitable example of a "planetary system",[17] in which the fluorine atom may orbit freely around the PH_3^+ moiety at room temperature. Similarly, the activation energy which permits the interconversion of **T1** to **T2** and vice versa is also negligible. This implies that both structures are also good prototypes of planetary systems, in which the FH moiety orbits almost freely around the PH_2^+ molecular ion.

Singlet PES. The PES associated with $[H_3, P, F]^+$ single-state cations has been schematized in Figure 3. The attachment of the F^+ monocation to the phosphorus atom of the neutral yields the global minimum, **S1**. The interconversion between the two equivalent forms of this species implies a completely planar FPH_3^+ transient species, with a quite-high activation barrier. However, the most important feature is that the activation barrier corresponding to the 1,2-H shift connecting species **S1** and **S2** lies much lower in energy than the dissociation limit of the global minimum **S1** into $F(^2P) + PH_3^+(^2A_1)$. It is important to note that this hydrogen shift implies a substantial weakening of the F−P bond, which is reflected in a destabilization by 39 kcal/mol.

This can be understood if one takes into account that both structures can be viewed as the result of the protonation of the FPH_2 molecule, either at the phosphorus atom to yield species **S1** or at the fluorine atom to yield species **S2**. In the second case, the protonation takes place at the more electronegative atom of the bond, and following the arguments of Alcamí et al.,[18] the linkage must become weaker, because the basic center (in this case, the fluorine atom) recovers part of the charge transferred to the incoming proton by depopulating the F−P linkage. On the contrary, as discussed in ref 18, protonation at the less electronegative atom (phosphorus) results in a reinforcement of the bond. This is indeed reflected in the F−P bond lengths, as well as in the charge distributions of the systems. On going from FPH_2 to the phosphorus-protonated species **S1**, the F−P bond becomes 0.077 Å shorter and the F−P stretching frequency undergoes a significant blue shift (153 cm^{-1}). Consistent with our previous arguments, on going from FPH_2 to the fluorine-protonated species $FHPH_2^+$ (**S2**), the F−P bond lengthens substantially (0.306 Å), and the F−P stretching frequency appears red-shifted by 411 cm^{-1}.

In conclusion, species **S2** can be viewed as a tightly bound complex between $HF(^1\Sigma^+)$ and $PH_2^+(^1A_1)$. Nevertheless, this linkage has still a nonnegligible covalent character, reflected in a quite-large interaction energy (ca. 26 kcal/mol) between both moieties.

It can be also observed that an inversion of the PH_2 group, through the transition state **S2-3**, leads to the cis isomer, **S3**, where the hydrogen atom of the HF moiety and the hydrogen atoms of the PH_2^+ subunit lie on the same side with respect to the F−P axis. The connection between the two equivalent forms of **S2** involves an internal rotation of the PH_2 with respect to the HF subunit, which implies an activation energy of 18.1 kcal/mol.

In summary, contrary to what is expected for the $F^+ + PH_3$ reactions when the cation is in its triplet ground state, the charge-transfer process for the reactions in the first singlet excited state is not likely to be observed, because the dissociation of the global minimum **S1** into the corresponding products $F + PH_3^+$ demands more energy than its evolution toward the **S2** local minimum. As in the case of the triplets, the formation of $HF + PH_2^+$ is an extremely exothermic process, and therefore, the products are expected to be vibrationally excited. It is worth noting that this behavior is rather similar to that which has been described before in the literature[8f] for $F^+ + SH_2$ reactions, where also the charge transfer and the formation of $HF + SH^+$ are the dominant products. There are, however, some quantitative differences in the sense that in $F^+(^3P) + SH_2$ reactions, the charge-transfer process clearly dominates with respect to the formation of $HF + SH^+$ products, because the energy gap between the $F + SH_2^+$ dissociation products and the barrier for the isomerization of $F{-}SH_2^+$ into $HF{-}SH^+$ is much larger than the corresponding barrier found in $F^+(^3P) + PH_3$ reactions.

Finally, it should be observed that two stationary points of both PESs, namely **S1-2** and **T2** (or **T1**), are quite close in energy. In other words, although the whole triplet PES lies above the singlet PES, they approach each other at this point. It is also worth noting that both stationary points exhibit similar connectivity, the main difference being the P−F distances. We might, hence, assume that an interaction between both PESs in this region can be possible, so that a spin-coupling mechanism would permit going from the triplet to the singlet hypersurface and, therefore, observing a spin-forbidden reaction in which the entrance channel corresponds to an overall-triplet multiplicity, while the products exhibit an overall-singlet multiplicity.

To investigate this point from a more quantitative point of view we located the MECP in this region. The structure of this transient species is quite similar to that of the minimum **T2**, and we found, consistent with our previous discussion, that at the G2 level, the transient species lies only 0.58 kcal/mol above the minimum **T2**. More importantly, the SOC between both hypersurfaces at this point was estimated to be 131 cm^{-1}. This value is large enough[19] to ensure a fast transition from the triplet to the singlet surface. Hence, we may conclude that a mechanism which connects species **T2** with species **S2** is highly probable and that $F^+ + PH_3$ reactions are a good example of spin-forbidden processes. It must be mentioned that crossover between potential energy surfaces of different spins is not unusual,[20] and they play an important role in many chemical systems.

FPH_2 Heat of Formation. We mentioned above that some of the species involved in the $[H_3, P, F]^+$ singlet PES can be associated with the protonation of the FPH_2 molecule. This compound has received a great deal of attention in the past few years, because it was identified as a product of the reaction of $F_2 + PH_3$ in an Ar matrix.[21] Actually, FPH_2 has been quite well-characterized spectroscopically,[22] but there is a complete lack of information about its thermodynamic properties. Hence, we have considered it of interest to use our calculations to estimate its heat of formation, its ionization potential, and its proton affinity. The latter is estimated to be 181.5 kcal/mol, the basic center being the phosphorus atom. As shown in Figure 3, the protonation at the fluorine atom is 39.1 kcal/mol less-favorable. Its ionization potential is estimated to be 10.08 eV.

To estimate its heat of formation, we considered the following isogyric processes:

$$F^+(^1D) + PH_3(^1A_1) \rightarrow FPH_2(^1A') + H^+ \tag{1}$$

$$FH(^1\Sigma^+) + PH_3(^1A_1) \rightarrow FPH_2(^1A') + H_2 \tag{2}$$

$$FH(^1\Sigma^+) + PH_2(^2B_1) \rightarrow FPH_2(^1A') + H(^2S) \tag{3}$$

For the sake of completeness, we have also included the following reactions, which are not isogyric processes:

$$F(^2P) + PH_3^{\ +}(^2A_1) \rightarrow FPH_2(^1A') + H^+ \tag{4}$$

$$F(^2P) + PH_2(^2B_1) \rightarrow FPH_2(^1A') \tag{5}$$

$$FH(^1\Sigma^+) + PH(^3\Sigma^-) \rightarrow FPH_2(^1A') \tag{6}$$

As in the usual procedure, the enthalpies of these reactions, estimated from our G2 calculations, were combined with the experimental heats of formation of the species involved[23−25] to obtain the heat of formation of FPH_2. The results obtained have been summarized in Table 2. It can be observed that two values are quoted for reactions 3 and 5. The first one is obtained using the experimental heat of formation of PH_2 reported in ref 23, and the second value was obtained using the value reported in ref 24, which is 3.3 kcal/mol lower than the previous one. When the PH_2 heat of formation reported in the recent compilation of Chase[24] is used, the estimated values for the heat of formation of FPH_2 obtained using reactions 3 and 5 deviate significantly from the values estimated using the other processes. Hence, we must conclude that, very likely, the heat of formation of PH_2 should be closer to 33.3 kcal/mol, as reported in ref 23, than to 30.1 kcal/mol, as reported in ref 24.

TABLE 2: Evaluated Formation Enthalpy for $FPH_2(^1A')$[a]

reaction	$\Delta H_f[FPH_2(^1A')]$
$F^+(^1D) + PH_3(^1A_1) \rightarrow FPH_2(^1A') + H^+$	−57.5
$FH(^1\Sigma^+) + PH_3(^1A_1) \rightarrow FPH_2(^1A') + H_2$	−56.1
$FH(^1\Sigma^+) + PH_2(^2B_1) \rightarrow FPH_2(^1A') + H(^2S)$	−58.0 (−61.2)
$F(^2P) + PH_3^{\ +}(^2A_1) \rightarrow FPH_2(^1A') + H^+$	−55.9
$F(^2P) + PH_2(^2B_1) \rightarrow FPH_2(^1A')$	−59.1 (−62.3)
$FH(^1\Sigma^+) + PH(^3\Sigma^-) \rightarrow FPH_2(^1A')$	−55.5

[a] Using G2//MP2 reaction enthalpies and the following experimental values[24−26] of ΔH_f (kcal/mol): $F^+(^1D) = 480.44$, $PH_3(^1A_1) = 5.46989$, $H^+ = 365.7$, $FH(^1\Sigma^+) = -65.1401$, $PH_2(^2B_1) = 33.3 \pm 0.6$, $H(^2S) = 52.1$, $F(^2P) = 18.97469$, $PH_3^{\ +}(^2A_1) = 233.05 \pm 0.23$, $PH(^3\Sigma^-) = 60.6000$. The values in parentheses correspond to the ones obtained by using the formation enthalpy for $PH_2(^2B_1)$ reported in ref 25 (30.0999 kcal/mol).

From the values given in Table 2, we can reasonably estimate the heat of formation of FPH_2 to be -58.2 ± 2.5 kcal/mol. The error of this estimated value was obtained by adding the standard deviation of the eight estimates to the average experimental error on the heats of formation used in reactions 1−6.

Conclusions

From our high-level ab initio calculations, we can conclude that for $F^+(^3P) + PH_3(^1A_1)$ reactions in the gas phase, charge transfer competes with formation of $HF(^1\Sigma^+) + PH_2^{\ +}(^3B_1)$. In contrast, $HF(^1\Sigma^+) + PH_2^{\ +}(^1A_1)$ should be the main products when the reaction involves the F^+ cation in its ^1D first excited state. In both cases the reactions are extremely exothermic, and therefore, the products might be vibrationally excited.

In general, the $[H_3, P, F]^+$ triplet-state cations are weakly bound species in which a neutral fluorine atom or a neutral HF molecule interacts with a $PH_3^{\ +}(^2A_1)$ or a $PH_2^{\ +}(^1A_1)$ moiety, respectively. These complexes present several conformers separated by very low activation barriers, so that they can be considered as planetary systems in which the neutral subunit orbits almost freely around the $PH_3^{\ +}$ or the $PH_2^{\ +}$ molecular ions. Similar planetary systems, such as the $HF\cdots CH_4$ and $HF\cdots NH_4^{\ +}$ complexes,[26] have been reported before in the literature.

Although according to our results, the singlet PES lies systematically below the triplet PES, there are regions where a crossover between potential energy surfaces takes place. In this respect we have found that a transition from species **T2** to species **S2** through the corresponding MECP should be very favorable. This would imply the possibility of having spin-forbidden reactions in which the entrance channel would exhibit an overall triplet multiplicity, while the products would correspond to an overall singlet multiplicity.

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