

Theoretical study of the dipole-bound anion (HPPH₃)⁻

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The possibility of electron binding to the HPPH₃ and H₂PPH₂ tautomers of diphosphine was studied at the coupled cluster level of theory with single, double, and noniterative triple excitations. The HPPH₃ tautomer, with a dipole moment of 3.7 D, binds an electron by 333 cm⁻¹, whereas the H₂PPH₂ tautomer forms neither a dipole- nor valence-bound anionic state. It is suggested that the HPPH₃ tautomer, which is kinetically stable but thermodynamically unstable relative to H₂PPH₂, may be formed by photodetachment from the P₂H₄⁻ species examined in this work. An unusual aspect of the (HPPH₃)⁻ anion is that electron correlation contributes 82% to the electronic stability and effects beyond the fourth order of the Møller–Plesset perturbation theory contribute 55%.
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I. INTRODUCTION

A. Diphosphine and its tautomer

Diphosphine (P₂H₄), known since 1844, is one of the simplest phosphorus compounds^{1,2} as reported in the early literature.³ Although some of its properties have been determined experimentally,^{1–13} and theoretically,^{14–24} the tautomer HPPH₃ (see Fig. 1) has been neither reported experimentally nor studied theoretically up to the mid 1990s, when Rak *et al.*²⁵ undertook theoretical studies on the structure, stability, and reactivity of P₂H₄. In the course of that study, the HPPH₃ tautomer was discovered and predicted to be thermodynamically less stable by 23.6 kcal/mol than the H₂PPH₂ tautomer. However, a high kinetic barrier exceeding 60.6 kcal/mol separates the H₂PPH₂ and HPPH₃ tautomers.

The H₂PPH₂ tautomer was predicted to adopt the gauche conformation in the gaseous, liquid, and solid phases as demonstrated in infrared (IR),¹¹ Raman,^{11,13} photoelectron,¹² and phosphorous nuclear magnetic resonance (³¹P-NMR)⁸ investigations. However, the x ray⁷ and certain IR and Raman studies⁹ on solid diphosphine do not rule out the existence of the staggered form.

It has been demonstrated in theoretical studies that the gauche conformer is the most stable H₂PPH₂ in the gas phase^{16–22} and its thermochemical properties, vibrational spectra, and its ability to undergo internal rearrangements and decompositions were addressed.^{21,23,24,25} Very recent investigations focused mainly on the thermochemic properties of H₂PPH₂ and its cation,^{26,27} and the gauche effect in this system.²⁸ However, the theoretical level of the calculations

was usually lower than that used in the earlier Ref. 25.

In the case of HPPH₃, the local minimum on the potential energy surface corresponds to a C_s symmetry structure,²⁵ with a dipole moment of 4.18 D, as determined at the restricted Hartree–Fock HRF/6-311++G(3df,3pd) level. This dipole moment is much larger than that of the gauche, (1.18 D) and staggered (0.0 D) conformers of H₂PPH₂. The orbital energy of the lowest unoccupied molecular orbital LUMO was found in that earlier work to be positive for the 6-311++G(3df,3pd) basis set for every isomer of diphosphine,²⁵ which suggested that anionic states may not be bound for these systems. However, in the case of HPPH₃, that finding is certainly an artifact of an incomplete basis set because the value of its dipole moment is sufficient to bind an electron.²⁹ These observations motivated us to take a closer look at the anticipated stable anion of HPPH₃.

B. Dipole-bound anions

Certain bound anionic states formed by polar molecules are classified as “dipole bound” when binding of the excess electron is due primarily to the electrostatic dipole potential of the underlying neutral system.³⁰ Indeed, it has been shown that such a potential with a dipole moment greater than 1.625 D possesses an infinite number of bound anionic states within the Born–Oppenheimer (BO) approximation.^{29–33} Jordan and Luken demonstrated that the loosely bound electron in a dipole-bound state occupies a diffuse orbital localized mainly on the positive side of the molecular dipole.³⁴ The role of non-BO coupling has been studied by Garrett, who concluded that such couplings are negligible for dipole-bound states with electron binding energies (E_{bind}) much larger than molecular rotational constants.³⁵

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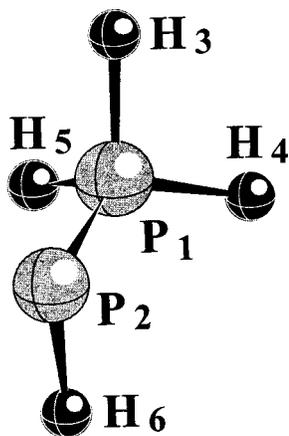


FIG. 1. The numbering of atoms for HPPH₃⁻.

The simplest theoretical approach to estimate E_{bind} of a dipole-bound anion is based on Koopmans' theorem (KT).³⁶ The KT binding energy ($E_{\text{bind}}^{\text{KT}}$) is the negative of the energy of the relevant unfilled orbital obtained from a Hartree-Fock self-consistent field (SCF) calculation on the neutral molecule. This is a static approximation which neglects both electron correlation and orbital relaxation effects. The latter effects have been found to be quite small for a variety of dipole-bound anionic states.³⁷⁻⁴⁶ On the other hand, the role of electron correlation has proven to be more significant, although early studies of polar diatomics^{47,48} and simple polar organic molecules³⁸ indicated that electron correlation played only a small role in electron binding to these species. However, in an early study, correlation effects were found to cause a significant *destabilization* of the dipole-bound anion of nitromethane.⁴⁹ In contrast, we have found that electron correlation leads to a sizable *stabilization* of the dipole-bound anions of HCN, CH₃CN, C₃H₂, C₄H₂, C₅H₂, uracil, (HF)_{*n*} (*n*=2,3), (H₂O)₂, and (HCN)₂,³⁹⁻⁴⁶ and more recent theoretical studies by others on the nitromethane,⁵⁰ water-trimer,⁵¹ and water-tetramer⁵² dipole-bound anions yielded a similar conclusion. Probably the most spectacular case in which correlation is important involves the weakly bound water-ammonia anion where we found that electron correlation contributes 77% to the electron binding energy of this system.⁴⁵ However, as will be shown below, the (HPPH₃)⁻ anion is even more strongly affected by electron correlation.

Based on the experience mentioned above, we concluded that the electron correlation contribution to E_{bind} encompasses: (i) a stabilizing dynamical correlation between the loosely bound electron and the electrons of the neutral molecule, and (ii) an improved description of the charge distribution (and hence the dipole moment) of the neutral. Furthermore, we found that effects beyond the second-order Møller-Plesset (MP2) level can contribute substantially to the stability of dipole-bound anionic states and solvated electrons.³⁹⁻⁴⁶

C. When is it proper to classify an anion as dipole bound?

When we say that an anion is dipole bound we mean that the existence of a bound anionic state is dictated by the long-

range dipole potential $\mu \cos \theta/r^2$. The simplest physical model of dipole-bound anions is based on a one-electron Schrödinger equation:

$$\left(-\frac{1}{2} \nabla^2 - \frac{\mu \cos \theta}{r^2} \right) \phi_{\text{lbe}} = \epsilon \phi_{\text{lbe}}, \quad (1)$$

where μ is the dipole moment of the neutral molecule, ϕ_{lbe} describes the loosely bound electron (lbe), and ϵ is the excess electron binding energy. The critical value of μ required to form a Σ anionic state was determined to be 1.625 D.²⁹ This model takes into account only the static Coulomb interaction between the extra electron and the dipole potential of the neutral molecule, but neglects many other interactions which decay faster with the electron-molecule distance than $1/r^2$. These interactions, although not responsible for the existence of a bound anionic state, may contribute significantly to the total electron binding energy. In consequence, the value of ϵ from Eq. (1) may be a poor approximation to E_{bind} for such a chemical system. It was early recognized by Jordan and Luken that this simple electrostatic model neglects orbital exclusion effects as a result of which the eigenvalue of Eq. (1) overestimates E_{bind} .³⁴ The value of E_{bind} determined at the Koopmans' theorem level was found to be more reliable because the constraints imposed on the orbital ϕ_{lbe} by the Pauli exclusion principle requirements are taken into account in this approach. More recent studies addressed the role of the relaxation of the orbitals of the underlying neutral as well as electron correlation in dipole-bound anions. In fact, the contribution to E_{bind} from electron correlation effects often proved to be at least as large as the value of $E_{\text{bind}}^{\text{KT}}$,³⁹⁻⁴⁵ which could call into question whether these systems are actually dipole bound. In our opinion the name "dipole bound" reflects the fact that a bound anionic state *exists* primarily due to the long-range $\mu \cos \theta/r^2$ potential and produces density of the excess electron localized primarily on the positive side of the molecular dipole. We acknowledge, however, that even in such cases where the state would not exist if the dipole potential were "turned off," the static Coulomb stabilization may not be the dominant component of E_{bind} . The system addressed in this study, HPPH₃⁻, is a startling example of the role of electron correlation effects in stabilization of weakly bound electrons.

II. METHODS TO DECOMPOSE E_{bind} INTO VARIOUS PHYSICAL COMPONENTS

In this work we present the results of highly correlated *ab initio* calculations for the anion of P₂H₄. We studied the potential energy surfaces of the neutral and anionic system at the MP2 level of theory and we calculated the values of E_{bind} using a supermolecular approach, (i.e., by subtracting the energies of the anion from those of the neutral). This approach requires the use of size-extensive methods, so we have employed Møller-Plesset perturbation theory up to fourth order as well as the coupled-cluster method with single, double, and noniterative triple excitations (CCSD(T)).⁵³ In addition, E_{bind} was analyzed within a perturbation framework designed for dipole-bound anions and solvated electrons.⁴³

In the perturbation scheme,⁴³ we consider a neutral molecule (N) and the extra electron as weakly interacting species and we follow an analogy with the theory of intermolecular interactions^{54,55} to analyze E_{bind} in terms of physically meaningful components. The total electronic Hamiltonian for the anion is partitioned into H^0 , which corresponds to the Hartree–Fock level of theory for N and the KT level of theory for the extra electron, and two perturbations, W^N and V^{lbe} :

$$H = H^0 + \lambda W^N + \eta V^{\text{lbe}}, \quad (2)$$

where the formal expansion parameters λ and η are introduced to define the perturbation theory orders and have physical values equal to unity. The zeroth-order Hamiltonian

$$H^0 = F^N + P^{\text{lbe}} \quad (3)$$

is the sum of Fock operators for all electrons in the anion, and every Fock operator is determined by the occupied orbitals of N . The fluctuation operator for the neutral molecule W^N results from Møller–Plesset partitioning of the electronic Hamiltonian of N and the fluctuation–interaction operator V^{lbe} has the form

$$V^{\text{lbe}} = \sum_{i \in N} \frac{1}{r_{\text{lbe},i}} - [J_N(\text{lbe}) - K_N(\text{lbe})], \quad (4)$$

where $r_{\text{lbe},i}$ is the distance between the i th electron of N and the extra electron, and J_N and K_N are, respectively, the Coulomb and exchange operators for N .

On applying the double-perturbation theory⁵⁴ to the Hamiltonian, Eq. (2), one obtains the perturbation expansion for the anion energy

$$E = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \epsilon^{(kl)}, \quad (5)$$

where $\epsilon^{(kl)}$ is of the k th order in W^N and the l th order in V^{lbe} . The sum of the three lowest-order terms reproduces the SCF energy of N and $E_{\text{bind}}^{\text{KT}}$:

$$\epsilon^{(00)} + \epsilon^{(10)} + \epsilon^{(01)} = E_N^{\text{SCF}} - E_{\text{bind}}^{\text{KT}}. \quad (6)$$

$E_{\text{bind}}^{\text{KT}}$ takes into account the Coulomb and exchange interaction between the extra electron and the SCF charge distribution of N . This is a static approximation which neglects both orbital relaxation and electron correlation effects.

The non-KT contributions to E_{bind} are given by other $\epsilon^{(kl)}$ terms with $l \geq 1$. The term $\epsilon^{(02)}$ separates into the induction and dispersion contributions^{54,55}

$$\epsilon^{(02)} = \epsilon_{\text{ind}}^{(02)} + \epsilon_{\text{disp}}^{(02)}, \quad (7)$$

with $\epsilon_{\text{ind}}^{(02)}$ describing polarization of N which, as an orbital relaxation effect, is reproduced when E_{bind} is obtained from the difference in the SCF energies of the neutral and anionic species

$$\Delta E_{\text{bind}}^{\text{SCF-ind}} = E_{\text{bind}}^{\text{SCF}} - E_{\text{bind}}^{\text{KT}} \approx -\epsilon_{\text{ind}}^{(02)}, \quad (8)$$

Here

$$E_{\text{bind}}^{\text{SCF}} = E_N^{\text{SCF}} - E_A^{\text{SCF}}, \quad (9)$$

where E_A^{SCF} stands for the SCF energy of the anion (A). In fact, the term $\Delta E_{\text{bind}}^{\text{SCF-ind}}$ includes not only the static polarization of N but also the secondary effect of back polarization.

The term $\epsilon_{\text{disp}}^{(02)}$ describes a dynamical correlation between the extra electron and the electrons of N . This stabilizing effect, brought by quantum mechanical charge fluctuations, can be very important for weakly bound anions in view of a significant polarizability of the extra electron's orbital. The term $\epsilon_{\text{disp}}^{(02)}$ is approximated here by $\Delta E_{\text{bind}}^{\text{MP2-disp}}$, which takes into account proper permutational symmetry for all electrons in the anion

$$\epsilon_{\text{disp}}^{(02)} \approx \sum_{a \in N} \sum_{r < s} \frac{|\langle \phi_a \phi_{\text{lbe}} | | \phi_r \phi_s \rangle|^2}{e_a + e_{\text{lbe}} - e_r - e_s} = -\Delta E_{\text{bind}}^{\text{MP2-disp}}, \quad (10)$$

where ϕ_a and ϕ_{lbe} are spin orbitals occupied in the zeroth-order wavefunction, ϕ_r and ϕ_s are unoccupied orbitals, and e_s are the corresponding orbital energies. Similar values of $\Delta E_{\text{bind}}^{\text{MP2-disp}}$ are obtained using the SCF orbitals of N or those of A , and the results reported in this work are obtained using the orbitals of the anion.

Higher order corrections to E_{bind} cannot be neglected. First, there are higher order corrections in V^{lbe} given by the $\epsilon^{(0l)}$ ($l > 2$) terms. Second, there are corrections $\epsilon^{(kl)}$ for $k, l \neq 0$ which contribute to E_{bind} not only through V^{lbe} but also through W^N . It is well established that electron correlation affects the static charge distribution of N and leads to a discrepancy between the SCF and correlated dipole moments of polar molecules. Therefore, the static Coulomb interaction between the extra electron and the SCF charge density of N , which is contained in $E_{\text{bind}}^{\text{KT}}$, has to be corrected for this charge density change. The lowest order correction of this type is contained in the MP2 electron binding energy.⁵⁵

The MP2 contribution to E_{bind} defined as

$$\Delta E_{\text{bind}}^{\text{MP2}} = E_{\text{bind}}^{\text{MP2}} - E_{\text{bind}}^{\text{SCF}} \quad (11)$$

is naturally split into the dispersion and nondispersion terms

$$\Delta E_{\text{bind}}^{\text{MP2}} = \Delta E_{\text{bind}}^{\text{MP2-disp}} + \Delta E_{\text{bind}}^{\text{MP2-no-disp}} \quad (12)$$

with the latter dominated by $\epsilon^{(21)}$.⁵⁵ The higher-order MP contributions to E_{bind} are defined as

$$\Delta E_{\text{bind}}^{\text{MP}n} = E_{\text{bind}}^{\text{MP}n} - E_{\text{bind}}^{\text{MP}(n-1)}, \quad n = 3, 4. \quad (13)$$

Finally, the contributions beyond the fourth order, are estimated by subtracting MP4 results from those obtained at the coupled-cluster (CC) level:

$$\Delta E_{\text{bind}}^{\text{CC}} = E_{\text{bind}}^{\text{CC}} - E_{\text{bind}}^{\text{MP4}}. \quad (14)$$

In particular, the DQ, SDQ, and SDTQ MP4 energies are subtracted from the D, SD, and SD(T) coupled cluster binding energies, respectively.⁵³

III. COMPUTATIONAL DETAILS

The diffuse character of the orbital describing the loosely bound electron (see Fig. 2) necessitates the use of extra diffuse basis functions having very low exponents.³⁴ In addition, the basis set chosen to describe the neutral molecular host should be flexible enough to: (i) accurately describe the static charge distribution of the neutral, and (ii) allow for

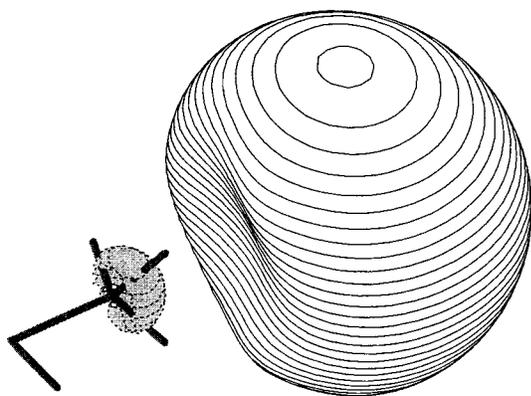


FIG. 2. Singly occupied molecular orbital (SOMOs) of the $(\text{HPPH}_3)^-$ (plotted with a 0.005 contour spacing).

polarization and dispersion stabilization of the anion upon electron attachment. The majority of our calculations were performed with aug-cc-pVDZ basis sets⁵⁶ supplemented with diffuse s , p , d , and sometimes f functions centered on the atom labeled P_1 in Fig. 1 (since this is the centroid of the positive end of the dipole). The extra diffuse s , p , and d functions do not share exponent values, but the exponents of the f functions were the same as those used for the d functions. The results presented below justify our basis set selection.

We explored the dependence of E_{bind} on the choice of the extra diffuse functions. These tests were performed with the aug-cc-pVDZ core basis set with only the extra diffuse functions being varied. We used even-tempered eight-term s , eight-term p , and five-term d basis sets. The geometric progression ratio was equal to 3.2,⁵⁷ and for every symmetry we started to build up the exponents of the extra diffuse functions from the lowest exponent of the same symmetry included in the aug-cc-pVDZ basis set designed for phosphorus. As a consequence, we achieved the lowest exponents of 3.7926(-6), 3.1196(-6), and 3.3677(-4) for the s , p , and d symmetries, respectively.

Next, we determined that the MP2 electron binding energy increases by only 0.7 cm^{-1} after inclusion of a five term set of diffuse f functions and that the sp -only diffuse basis recovers more than 95% of E_{bind} at the MP2 level. Moreover, the equilibrium structure of the neutral system was determined to be practically the same with the sp and spd diffuse bases. Therefore, the diffuse d functions were omitted from the basis set when carrying out the MP2 geometry optimizations and frequency calculations.

We also explored the dependence of E_{bind} on the *core* basis set chosen to describe the neutral molecular host. The MP2 value of E_{bind} obtained with Dunning's aug-cc-pVTZ basis set,⁵⁶ with the eight-term s , eight-term p , and five-term d diffuse set fixed, differs by less than 3 cm^{-1} from the results obtained using the aug-cc-pVDZ basis instead. We therefore believe that our MP2 electron binding energies obtained with the aug-cc-pVDZ basis set supplemented with the eight-term diffuse s and p , and five-term diffuse d functions are underestimated by less than 5% due to basis set incompleteness.

Therefore, our final basis set was selected to be the aug-cc-pVDZ basis supplemented with the $8sp$ diffuse set for the optimization of geometries and for calculating frequencies, and the aug-cc-pVDZ basis supplemented with the $8sp5d$ diffuse set for evaluating the electron binding energies.

In computing correlation energies, all orbitals except the $1s$, $2s$, and $2p$ orbitals of phosphorus were included, and all results reported in this study were obtained with the GAUSSIAN 94 program.⁵⁸ Finally, to avoid erroneous results caused by using the GAUSSIAN 94's (default) direct SCF module with the large s , p , d , and f sets of diffuse functions, we performed conventional SCF calculations, moreover, the two-electron integrals were evaluated (without prescreening) to a tolerance of 10^{-20} a.u. in the single point calculations.

IV. RESULTS

In the case of the *gauche* and staggered conformations of H_2PPH_2 we found neither valence- nor dipole-bound anionic states to exist. This is not surprising given that the dipole moment of the *gauche* structure falls below the 1.625 D critical value. Therefore, we present detailed results for the HPPH_3 tautomer only. The relevant rotational energy level spacings for this tautomer are much smaller than the calculated values of E_{bind} . Hence, non-BO coupling between the electronic and rotational degrees of freedom is expected to be of secondary importance for this anion and is not considered in this study.

A. MP2 geometries and harmonic frequencies

The C_s symmetry local minima on the MP2 potential energy surface of the neutral and anionic molecule are characterized in Table I. We studied the dependence of the dipole moment of the neutral molecule on geometrical displacements induced by electron attachment. In Table I we report the values of the neutral's dipole moment calculated using the SCF, MP2, MP3, MP4(SDQ) and QCISD densities at the neutral and at the anion geometries.

Our calculations indicate that the geometries of the neutral and anion differ only slightly (see Table I). In particular, electron attachment leads to an elongation of the P-P bond length by 0.005 \AA , while the other bonds are even less affected (less than 0.0005 \AA) and the valence angles change by less than 0.3° . These small geometrical distortions cause an increase of the dipole moment μ of the neutral by 0.05 D both at the SCF and QCISD levels (QCISD is an approximation to the CCSD method⁵³). These changes are much smaller than for hydrogen bonded systems, which we have studied previously,⁴²⁻⁴⁵ and reflect the fact that the bonding in the neutral HPPH_3 is much more rigid.

The barrier to rotation around the P-P bond is 655 cm^{-1} for the neutral and 630 cm^{-1} for the anion. This former may be compared with the value of 719 cm^{-1} obtained at the SCF level with the 6-31G** basis set.²⁵ We verified that the anion remains electronically stable in the course of rotation around the P-P bond.

The vibrational normal modes are characterized in Table I, where the (unscaled) harmonic MP2 frequencies are also reported. The frequencies usually decrease upon electron attachment, and the largest shift of 10 cm^{-1} is for the fourth a'

TABLE I. Geometries and harmonic vibrational frequencies for the neutral and dipole-bound anionic state of HPPH₃ at the stationary points.^a Frequencies in cm⁻¹, distances in Å, angles in degrees, dipole moment μ of the neutral dimer in D, zero-point vibrational energies in kcal/mol.^b

System	Geometry	μ_{neutral}		Frequencies	E_0^{vib}
		SCF	QCISD		
HPPH ₃	$r(\text{P}_1\text{P}_2) = 2.114$ $r(\text{P}_1\text{H}_3) = 1.412$ $r(\text{P}_1\text{H}_4) = 1.424$ $r(\text{P}_2\text{H}_6) = 1.434$ $\alpha(\text{H}_3\text{P}_1\text{H}_2) = 109.72$ $\alpha(\text{H}_4\text{P}_1\text{P}_2) = 121.62$ $\alpha(\text{H}_3\text{P}_1\text{H}_4) = 100.83$ $\alpha(\text{P}_1\text{P}_2\text{H}_6) = 88.75$ $\delta(\text{H}_3\text{P}_1\text{H}_4\text{P}_2) = 121.42$	4.14	3.66 ^c	$\omega_1(a'') = 265^e$ $\omega_2(a') = 522^f$ $\omega_3(a') = 532^g$ $\omega_4(a'') = 628^h$ $\omega_5(a') = 863^i$ $\omega_6(a') = 1067^j$ $\omega_7(a'') = 1081^k$ $\omega_8(a') = 1173^l$ $\omega_9(a') = 2408^m$ $\omega_{10}(a'') = 2425^n$ $\omega_{11}(a') = 2448^o$ $\omega_{12}(a') = 2549^p$	22.818
HPPH ₃ ⁻	$r(\text{P}_1\text{P}_2) = 2.119$ $r(\text{P}_1\text{H}_3) = 1.412$ $r(\text{P}_1\text{H}_4) = 1.423$ $r(\text{P}_2\text{H}_6) = 1.434$ $\alpha(\text{H}_3\text{P}_1\text{P}_2) = 109.68$ $\alpha(\text{H}_4\text{P}_1\text{P}_2) = 121.25$ $\alpha(\text{H}_3\text{P}_1\text{H}_4) = 101.12$ $\alpha(\text{P}_1\text{P}_2\text{H}_6) = 88.88$ $\delta(\text{H}_3\text{P}_1\text{H}_4\text{P}_2) = 121.38$	4.19	3.71 ^d	$\omega_1(a'') = 259^{(a)}$ $\omega_2(a') = 515^{(b)}$ $\omega_3(a') = 532^{(c)}$ $\omega_4(a'') = 627^{(d)}$ $\omega_5(a') = 860^{(e)}$ $\omega_6(a') = 1057^{(f)}$ $\omega_7(a'') = 1081^{(g)}$ $\omega_8(a') = 1165^{(h)}$ $\omega_9(a') = 2405^{(i)}$ $\omega_{10}(a'') = 2436^{(j)}$ $\omega_{11}(a') = 2451^{(k)}$ $\omega_{12}(a') = 2549^{(l)}$	22.784

^aFor the numbering of atoms see Fig. 1.

^bMP2 results obtained with the aug-cc-pVDZ basis set supplemented with the *8sp* diffuse set.

^cMP2, MP3, and MP4(SDQ) values of dipole moment are: 3.69, 3.69, and 3.68 D, respectively.

^dMP2, MP3, and MP4(SDQ) values of dipole moment are: 3.73, 3.74, and 3.72 D, respectively.

^eH₆P₂-P₁H_{3,4,5} torsion mode.

^fP₁-P₂ stretching.

^gH₆P₂-P₁H_{3,4,5} wagging (out-of-phase) mode.

^hH₄P₁H₅ twisting mode.

ⁱH₆P₂-P₁H_{3,4,5} wagging (in-phase) mode.

^jP₁ umbrella inversion mode.

^kH₃H₄ and H₃H₅ scissors.

^lH₄H₅ scissors.

^mP₂-H₆ stretching.

ⁿP₂-H₄ stretching and P₂-H₅ stretching (out-of-phase).

^oP₂-H₄ stretching and P₂-H₅ stretching (in-phase).

^pP₂-H₃ stretching.

mode (the PH₃ umbrella mode). The frequencies of the stiff stretching modes are nearly unchanged, and the largest shift of 11 cm⁻¹ occurs for the fourth *a''* mode, which describes primarily the out-of-phase stretching of the P₂-H₄ and P₂-H₅ bonds. Due to a partial cancellation of the frequency shifts, the change of the total zero-point vibrational energy upon electron attachment is rather small and amounts to -12 cm⁻¹.

B. Electron binding energies

The electron binding energy was partitioned into *incremental* contributions calculated at "successive" levels of theory [KT, SCF, MP n ($n = 2, 3, 4$), and CCSD(T)] and the results for the optimal C_s structures of the neutral and the anion are presented in Table II. In the KT approximation, the electron binding energy results from the electrostatic and exchange interactions of the extra electron with the SCF charge distribution of the neutral molecule (primarily characterized by the dipole moment, but interactions with higher permanent multipoles and penetration effects are also included). The value of $E_{\text{bind}}^{\text{KT}}$ increases only by 3 cm⁻¹ upon geometry

relaxation from the neutral to the anionic structure, which is consistent with the small increase in dipole moment accompanying this geometry change (see Table I).

The SCF binding energies include orbital relaxation and thus take into account static polarization of the neutral molecule by the extra electron and the secondary effect of back

TABLE II. Incremental electron binding energies^a (in cm⁻¹) for the anionic state of HPPH₃.

Component	HPPH ₃ for the geometry of the neutral	HPPH ₃ ⁻ for the geometry of the anion
$E_{\text{bind}}^{\text{RT}}$	48.03	51.30
$\Delta E_{\text{bind}}^{\text{SCF-ind}}$	8.01	8.71
$\Delta E_{\text{bind}}^{\text{MP2-disp}}$	107.59	113.70
$\Delta E_{\text{bind}}^{\text{MP2-no-disp}}$	-48.25	-50.47
$\Delta E_{\text{bind}}^{\text{MP3}}$	-2.40	-2.56
$\Delta E_{\text{bind}}^{\text{MP4}}$	26.72	28.01
$\Delta E_{\text{bind}}^{\text{CCSD(T)}}$	179.76	184.27
Sum	319.46	332.96

^aResults obtained with the aug-cc-pVDZ basis set supplemented with the *8sp5d* diffuse set.

TABLE III. Contributions of various classes of excitations to E_{bind} (cm^{-1}) at the neutral and anionic equilibrium geometries from Table I.

Method	HPPH ₃ for the geometry of the neutral		HPPH ₃ for the geometry of the anion	
	E_{bind}	ΔE_{bind}	E_{bind}	ΔE_{bind}
UMP4(DQ)	110.37	-2.61	117.90	-2.78
UMP4(SDQ)	132.44	19.46	140.95	20.27
UMP4(SDTQ)	139.70	26.72	148.69	28.01
CCD	109.15	-1.22	116.61	-1.29
CCSD	323.87	191.43	335.52	194.57
CCSD(T)	319.46	179.76	332.96	184.33
T4(CCSD)	...	151.98	...	151.30
T5(CCSD)	...	-156.39	...	-153.86

polarization. The 8–9 cm^{-1} values of the orbital relaxation correction to $E_{\text{bind}}^{\text{KT}}$, denoted $\Delta E_{\text{bind}}^{\text{SCF-ind}}$ in Table II, are modest and represent 2%–3% of the total E_{bind} .

The contribution denoted $\Delta E_{\text{bind}}^{\text{MP2-disp}}$ results from dynamical correlation between the extra electron and the electrons of the neutral molecule. This stabilizing effect, caused by quantum mechanical charge fluctuations, is more than two times larger than $E_{\text{bind}}^{\text{KT}}$ (see Table II). This finding is consistent with our earlier results for other weakly bound anions^{39–46} and has important implications for designing model potentials to describe dipole-bound anions and solvated electrons.^{59,60} The value of $\Delta E_{\text{bind}}^{\text{MP2-disp}}$ increases from 107.6 cm^{-1} at the optimal geometry of the neutral to 113.7 cm^{-1} at the optimal geometry of the anion.

In addition to the dispersion interaction, electron correlation also affects the charge distribution (and dipole moment) of the neutral molecule and then its electrostatic interaction with the extra electron. This effect first appears at the MP2 level and is denoted by $\Delta E_{\text{bind}}^{\text{MP2-no-disp}}$. The values of $\Delta E_{\text{bind}}^{\text{MP2-no-disp}}$ are strongly destabilizing which is consistent with the fact that electron correlation effects *reduce* the dipole moment of the neutral system by 0.48 D in comparison with the SCF value (see Table I). Interestingly, higher than the second-order corrections only marginally further reduce the dipole moment.

As Table II shows, the convergence of the MP series for the electron binding energy in HPPH₃⁻ is slow. The contribution from $\Delta E_{\text{bind}}^{\text{MP3}}$ is negligible, whereas that from $\Delta E_{\text{bind}}^{\text{MP4}}$ represents ~8% of E_{bind} , and higher-order electron correlation effects, approximated here by $\Delta E_{\text{bind}}^{\text{CCSD(T)}}$ [the difference in the CCSD(T) and MP4 binding energies] are very significant, stabilizing, and responsible for ~55% of the net electron binding energy and produce our final prediction for $E_{\text{bind}} = 333 \text{ cm}^{-1}$. This significant increase of E_{bind} cannot be related to the high-order electron correlation correction to the static Coulomb stabilization because the value of the dipole moment of N decreases slightly from the MP2 level onward. For these reasons, one must be careful to stress that even at the highest level of theory presented here, our estimation of E_{bind} may be inadequate.

The contributions to $\Delta E_{\text{bind}}^{\text{MP4}}$ and $\Delta E_{\text{bind}}^{\text{CCSD(T)}}$ from various classes of excitations are collected in Table III and will now be discussed for the anionic geometry. The MP4 contribution from double and quadruple excitations, $\Delta E_{\text{bind}}^{\text{MP4(DQ)}}$, is destabi-

lizing and amounts to -2.8 cm^{-1} . The contributions from single excitations, given by the difference between $\Delta E_{\text{bind}}^{\text{MP4(SDQ)}}$ and $\Delta E_{\text{bind}}^{\text{MP4(DQ)}}$, is stabilizing and equal to 23.1 cm^{-1} , whereas that from triple excitations, given by the difference between $\Delta E_{\text{bind}}^{\text{MP4(SDTQ)}}$ and $\Delta E_{\text{bind}}^{\text{MP4(SDQ)}}$, is also stabilizing and equal to 7.9 cm^{-1} . The final fourth-order contribution $\Delta E_{\text{bind}}^{\text{MP4(SDTQ)}}$ amounts to 28.0 cm^{-1} .

The effect of single excitations is an order of magnitude more important when evaluated in the framework of CC theory where its contribution, calculated as the difference between $E_{\text{bind}}^{\text{CCSD}}$ and $E_{\text{bind}}^{\text{CCD}}$, amounts to 218.9 cm^{-1} . The contribution from noniterative triple excitations, calculated as the difference between $E_{\text{bind}}^{\text{CCSD(T)}}$ and $E_{\text{bind}}^{\text{CCSD}}$, contains the fourth-order contribution with the CCSD amplitudes and a fifth-order term,⁵³ which are labeled T4 (CCSD) and T5 (CCSD), respectively, in Table III. The fourth-order contribution with the CCSD amplitudes is highly stabilizing and amounts to 151.3 cm^{-1} . However, the fifth-order contribution is highly destabilizing and amounts to -153.9 cm^{-1} . Hence, the total contribution from triple excitations of -2.6 cm^{-1} is very small because of cancellation of the T4 (CCSD) and T5 (CCSD) terms.

Higher-than-fourth-order electron correlation contributions to E_{bind} may also be extracted from the data collected in Table III. The difference between $E_{\text{bind}}^{\text{CCD}}$ and $E_{\text{bind}}^{\text{MP4(DQ)}}$ is very small and amounts to -1.3 cm^{-1} . However, when single excitations are included the situation is quite different; indeed the difference between $E_{\text{bind}}^{\text{CCSD}}$ and $E_{\text{bind}}^{\text{MP4(SDQ)}}$ amounts to 194.6 cm^{-1} . These results support our earlier conclusions that the MP4 treatment of electron correlation effects is not sufficient for weakly bound anions.^{44,45} The role of single excitations is extremely important and may be related to the fact that the charge distribution of the extra electron is seriously modified when the neutral molecular core is modified by electron correlation effects. This interpretation is supported by the fact that the largest CCSD amplitudes correspond to single excitations from the orbital occupied by the extra electron. It may well be that the physical interpretation of E_{bind} calculated in the CC framework would benefit if Brueckner CCSD orbitals⁵³ were used to construct the reference wave functions of the anion and the neutral.

The contribution from triple excitations proved to be very sensitive to the form of amplitudes of the single and double excitations. For this weakly bound anion it may be necessary to adopt methods such as CCSDT-1 or CCSDT, which treat high-order correlation effects more accurately than does the CCSD(T) method.⁵³

V. CONCLUSIONS

Our results indicate that the HPPH₃ tautomer of P₂H₄ can bind an electron by 333 cm^{-1} , whereas the H₂PBH₂ tautomer cannot. This suggests a practical route to formation of the HPPH₃ tautomer through photodetachment of the excess electron from P₂H₄⁻. The HPPH₃ tautomer is predicted to be kinetically stable with respect to tautomerization (having a barrier of 60.6 kcal/mol) although thermodynamically unstable²⁵ by 23.6 kcal/mol.

The excess electron in (HPPH₃)⁻ is already bound due

to the dipole potential of the neutral as obtained at the KT level of theory, but electron correlation effects contribute 82% to the total value of the electron binding energy at the highest CCSD(T) level of theory employed here. Interestingly, the dipole moment of the neutral is decreased by 13% when electron correlation effects are included.

The second-order dispersion stabilization was found to be very important for the stabilization of the excess electron, but more important are higher-than-fourth-order corrections which are responsible for 55% of the total electron binding energy. The contributions to E_{bind} from single and triple excitations proved to be more significant in the CCSD(T) than in the MP4 approach.

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