Change of molecular structure in the excited states : A (CNDO/2) hole-potential study on phosphine

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Abstract. Molecular structure of phosphine in a number of excited electronic states is studied using the method of hole-potential within the basic framework of CNDO/2 theory. Effects of including $3d$-functions of phosphorus in the basis set on computed molecular geometries, transition energies and inversion barriers in the excited states have been investigated. An attempt is made to rationalise qualitatively the structural changes in the excited state in terms of Walsh-type correlation diagram constructed with the eigenvalues of the Fock operator in the V_{N-1} potential model. A simple orbital model for predicting the nature of structural changes in the excited states is proposed.

Keywords. Excited states ; hole-potential ; molecular structure ; phosphine.

1. Introduction

Phosphine has a pyramidal geometry (C_{3v}) in the ground state. Though the inversion barrier does not seem to have been measured experimentally, several accurate *ab-initio* SCF (Petke and Whitten 1973) or even higher order (e.g. CEPA, PNO–CI) calculations (Veillard 1975) have predicted the existence of a rather high barrier (36–40 kcal/mol) to the molecular inversion process in the ground state. Surprisingly, however, very little information, either at theoretical or at experimental level is available regarding the structural features of PH_3 in different excited states. Experimental and theoretical evidence on ammonia suggest that PH_3 also should have a planar geometry (D_{3h}) in the $^{1,3}A_2''$ state. Extension of arguments based on Walsh-diagram (Walsh 1953) would lead us to an identical conclusion. But such a simple extrapolation is a bit too dangerous on several grounds. Thus participation of $3d$ orbitals of phosphorus in the bonding may vitiate the simple picture of electronic structure one assumes for PH_3 by analogy with ammonia. One may well question the reliability of " Walsh-type " arguments when $3d$ functions are involved.

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The present paper attempts to throw some light on these problems. The strategy adopted is simple. We employ the V_{N-1} potential method (Huzinaga and Arnau 1970, 1971) along with the standard CNDO/2 formulation (Pople *et al* 1965) of performing LCAO–MO–SCF calculation. The choice is motivated by the following considerations.

(i) The V_{N-1} potential model generates partially relaxed virtual manifold which should be more appropriate for " Walsh-type " diagrammatic analysis than the virtual orbitals generated by the Hartree-Fock (HF) operator directly.

(ii) The V_{N-1} potential method permits comparison of singlet and triplet species at an identical level of approximation.

(iii) The performance of CNDO/2 method is fairly satisfactory for molecular structure calculations in the ground state.

(iv) Our earlier calculations (Banerjee and Bhattacharyya 1979) on the excited states of thiocarbonyls using CNDO/2 + V_{N-1} potential method led to fairly satisfactory results.

2. Method

The theory of V_{N-1} potential is very simple. Let F be the HF operator for the ground state and P be the operator that projects into the ground state. Then,

$$P = \sum_{i=1}^{n} | \phi_i \rangle \langle \phi_i | \ (n = \text{number of occupied orbitals}).$$

Let an excited state be generated by the promotion of an electron from the orbital ϕ_i (occupied in the ground state) to any unoccupied (virtual) orbital. In the V_{N-1} potential method, one replaces the virtual orbitals generated by the ground state HF operator by a set of modified orbitals. For doing this, one replaces F by a modified operator F' such that,

$$F' = F + (I - P) v_i (I - P), \tag{1}$$

where

$$v_i = - J_i \text{ for describing the triplet state,}$$

and

$$v_i = - J_i + 2K_i \text{ for the corresponding singlet.}$$

The diagonalisation of F' leaves the first n eigenvalues (ϵ_i) coincident with those of F. The remaining eigenvalues are changed (we call these $\bar{\epsilon}_m$). Energy of the excited state arising from a transition $\phi_i \rightarrow \phi_m$ is given by

$$E_{i \rightarrow m} = E_0 + \bar{\epsilon}_m - \epsilon_i, \tag{2a}$$

where E_0 is the HF energy of the ground state.

3. Results and discussion

3.1. *A simple orbital model*

Our main interest will be to study the extent of pyramidality of phosphine in different electronic states of PH_3. As a measure of pyramidality we use either the angle (ϕ) made by a P–H link with the C_3-axis or the complimentary angle λ, $(\lambda = \frac{1}{2}\pi - \phi)$ which represents the angular elevation of the phosphorus atom from the plane of three hydrogen atoms. Having thus fixed the structural parameter of our interest, we prepare ourselves to develop some simple orbital model for predicting the qualitative features of molecular geometry in excited states.

In the V_{N-1} potential method, the energy of the excited state generated by the transition $(\phi_i \rightarrow \phi_j)$ is given by equation (2b), viz.

$$^{1,3}E_{ij} = E_0 + {}^{1,3}\bar{\epsilon}_j - \epsilon_i. \tag{2b}$$

Taking the present case of phosphine as an example, let λ_0 be the equilibrium pyramidality parameter of phosphorus atom in the ground state of PH_3.. From equation (2b) one can then easily write,

$$\left(\frac{dE_{ij}}{d\lambda}\right)_{\lambda=\lambda_0} = \left\{\frac{d}{d\lambda}({}^{1,3}\bar{\epsilon}_j)\right\}_{\lambda=\lambda_0} - \left\{\frac{d}{d\lambda}(\epsilon_i)\right\}_{\lambda=\lambda_0} = \bar{S}_{j\lambda_0} - S_{i\lambda_0}. \tag{3}$$

Thus the slope of the upper state energy curve at the ground state equilibrium geometry will be determined by the slopes of binding energies of the pair of orbitals involved in the transition. Thus a consideration of the right side of equation (3) alone would provide us with some information regarding the possible change in the equilibrium value of λ to be expected in the particular excited state being considered.

A number of different situations may arise. Few of these are relevant to our present example :

$$\text{(i)} \quad \bar{S}_{j\lambda_0} > 0, \qquad S_{i\lambda_0} < 0. \tag{4}$$

In this case the slope of the upper state curve at the ground state geometry will be positive. Immediately one would suggest that the equilibrium value of λ in the excited state has to be less than λ_0. This situation is exemplified in the present case by the excitation (2a) → (3a). As expected the corresponding $^{1,3}A_1$ states are planar.

$$\text{(ii)} \quad \bar{S}_{j\lambda_0} = 0, \qquad S_{i\lambda_0} < 0. \tag{5}$$

In this case also similar conclusions should be applicable. The only difference is that the slope of the upper state curve, though positive at the ground state geometry, is less steep so that the change in λ to be expected in the corresponding excited state should be much less.

$$\text{(iii)} \quad \bar{S}_{j\lambda_0} = 0, \quad S_{i\lambda_0} = 0 \quad \text{or} \quad \bar{S}_{j\lambda_0} = S_{i\lambda_0}. \tag{6}$$

In both these cases one would expect no change in λ on excitation.

If one assumes that partial relaxation effect (in the virtual manifold) included by the V_{N-1} potential method does not introduce any qualitative change in the nature of the orbital energy diagrams, similar conclusions should, in principle, be derivable from an analysis of the slopes of virtual orbital energies generated by the ground state HF operator. Let us now examine the orbital energy diagrams (Walsh type diagrams) constructed from the eigenvalues of the V_{N-1} model Hamiltonian with a view to testing the applicability of our simple orbital model for predicting the nature of structural changes in the excited states.

3.1a. " *Walsh-type* " *diagram for* PH_3 (Sp *basis*): In figure 1, the eigenvalues ($\bar{e}_i$) of the V_{N-1} model Hamiltonian corresponding to singlet excitation from the (2a) orbital of phosphine in different geometries are plotted against λ. It is clear from the figure that the slope of the 3a orbital energy curve at the equilibrium value of $\lambda (= \lambda_0)$ (i.e. $\bar{S}_{3a, \lambda_0}$) is positive while that of 2a orbital (i.e. S_{2a, λ_0}) is negative. The present case thus exemplifies the situation represented by equation (4). λ should thus decrease and one expects PH_3 to have much lesser pyramidality in the resulting $^1A_1$ state ($2a \rightarrow 3a$ excitation). In table 1 we have displayed the gradual variation of the extent of $3s$ (P) character in the 2a and 3a orbital pair involved in the transition. It is apparent that the $3s$ (P) participation in the 2a orbital increases and that in the 3a orbital decreases with increase in the pyramidal distortion. This is in conformity with the qualitative expectations from Walsh rules. On the other hand figure 1 clearly shows that $\bar{S}_{2e, \lambda_0} \approx 0$ so that
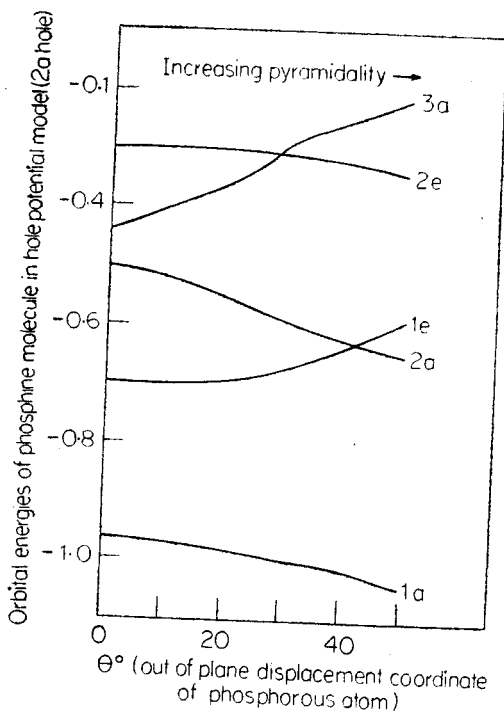

Figure 1. The orbital energies of phosphine computed by the CNDO/2-hole potential method ($3d$ functions of P excluded from the basis) shown as function of pyramidal distortion. The hole resides in 2a orbital.

Table 1. Variation of the squared amplitudes $(C_{\mu i}^2)$ of $3s$ and $3p$ basis elements of phosphorous in the $2a$, $3a$ and $2e$ orbitals of PH_3 in $^{1,3}A_1$ and $^{1,3}E$ excited states are shown as functions of the pyramidal angle.

Pyramidal angle $\left(\dfrac{\pi}{2} - \phi\right)^\dagger$	Basis functions (μ)	$C_{\mu i}^2$ in different molecular orbitals (i)				
		$2a*$	$3a\,(^1A_1)**$	$3a\,(^3A_1)$	$2e\,(^1E)$	$2e\,(^3E)$
0°	$3s$	0·0	0·3213	0·3213	0·0	0·0
	$3p$	1·0	0·0	0·0	0·5531	0·5531
10°	$3s$	0·0746	0·2299	0·2299	0·0	0·0
	$3p$	0·7933	0·2056	0·2055	0·5442	0·5442
20°	$3s$	0·1435	0·1681	0·1681	0·0	0·0
	$3p$	0·6563	0·3368	0·3368	0·5348	0·5348
30°	$3s$	0·2087	0·1337	0·1337	0·0	0·0
	$3p$	0·5706	0·4106	0·4106	0·5213	0·5213
40°	$3s$	0·2863	0·1114	0·1114	0·0	0·0
	$3p$	0·4927	0·4717	0·4717	0·4955	0·4955
45°	$3s$	0·3350	0·1025	0·1025	0·0	0·0
	$3p$	0·4488	0·5058	0·5058	0·4743	0·4743
50°	$3s$	0·3948	0·0942	0·0942	0·0	0·0
	$3p$	0·3973	0·5467	0·4447	0·4447	0·4447

$\dagger$ ϕ is the angle between the C_3-axis and the P–H link.

* $2a$ orbital remains frozen throughout the calculation.

** $^{1,3}A_1$ states correspond to $2a \rightarrow 3a$ transition and $^{1,3}E$ states to $2a \rightarrow 2e$ transition.

conditions of equation (5) are satisfied by the $2a \rightarrow 2e$ transition in PH_3. One, therefore, expects some lowering of pyramidality in the resulting ^1E state. The pyramidality in the ^1E state should, however, be higher than that in the $^1A_1$ state. In table 1 we find that an increase in pyramidal distortion somewhat decreases the $3p$ (P) character of the set of $2e$ orbitals, while $3s$ (P) character of the $2a$ orbital increases due to the same distortion. Pyramidality of PH_3 in ^1E state is thus expected also from "Walsh type" arguments. We have not shown in figure 1 the corresponding orbital energy diagrams for the triplet state, since there is no qualitative difference in the pattern from what is observed in the singlet counterparts. Identical conclusions therefore hold for the ^3A and ^3E states as well.

3.1b. *Walsh-type diagrams for PH_3 (SPD basis)*:

A glance at figure 2 reveals that there is no qualitative change in the Walsh-type orbital binding energy diagram of PH_3 when $3d$ orbitals of phosphorus are included in the basis set. Thus
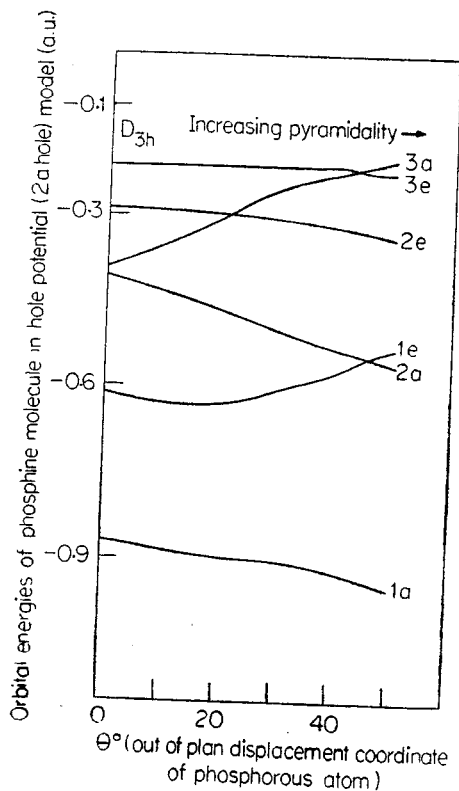
Figure 2. The orbital energies of phosphine computed by the CNDO/2-hole potential method ($3d$ functions of P included in the basis) shown as function of pyramidal distortion. The hole resides in $2a$ orbital.

$2a \rightarrow 3a$ excitation is expected to lead to much lower pyramidality of PH_3 in the resulting $^1A_1$ state while $2a \rightarrow 2e$ or $3e$ promotion would lead to ^1E excited states in which the pyramidality of PH_3 would be only slightly lower than that in the ground state. Identical conclusions also hold for the corresponding triplet states (triplet state orbital energy diagrams, however, have not been included in figure 2). In table 2 we have summarised the squared amplitudes of $3s$, $3p$ and $3d$ functions of phosphorus in the $2a$, $3a$ and $2e$ orbitals in the $^{1,3}A_1$ ($2a \rightarrow 3a$), $^{1,3}E$ ($2a \rightarrow 2e$) states of PH_3 as functions of λ. Once again we find that orbitals which have an increased degree of $3s$-participation as a result of an increase in the pyramidal distortion get stabilised by the distortion, while a decrease in $3s$ character has just the opposite effect. Participation of $3d$ functions has no major effect on this conclusion of the simple Walsh rule. If $3s$-participation is symmetry forbidden for a specific symmetry orbital, an increase in $3p$ (P) participation (relative to $3d$) stabilises the orbital as a result of the distortion. This explains the $2e$ and $3e$ orbital energy diagrams. Walsh-type diagrammatic analysis thus continues to be useful even when $3d$ functions are present in the basis set.

One would surely like to check the reliability of these predictions made on the basis of very simple orbital picture against predictions made from total energy considerations. This is taken up in § 3.2.

Table 2. Variation of the squared amplitudes ($C_{\mu i}^2$) of $3s$, $3p$ and $3d$ basis elements of phosphorus in the $2a$, $3a$ and $2e$ molecular orbitals of PH_3 in $^{1,3}A_1$ and $^{1,3}E$ excited states shown as functions of pyramidal angle.

Pyramidal angle $\left(\frac{\pi}{2} - \phi\right)^\dagger$	Basis functions (μ)	$C_{\mu i}^2$ in different molecular orbitals (i)				
		$2a^*$	$3a\,(^1A_1)$	$3a\,(^3A_1)$	$2e\,(^1E)$	$2e\,(^3E)$
0°	$3s$	0·0	0·3017	0·3017	0·0	0·0
	$3p$	1·0	0·0	0·0	0·4612	0·4612
	$3d$	0·0	0·2091	0·2091	0·4164	0·4164
10°	$3s$	0·1119	0·0149	0·1597	0·0	0·0
	$3p$	0·6546	0·3313	0·3386	0·4372	0·4372
	$3d$	0·0434	0·2183	0·1682	0·4575	0.3928
20°	$3s$	0·1555	0·1114	0·1265	0·0	0·0
	$3p$	0·6142	0·3284	0·3531	0·4646	0·5018
	$3d$	0·0188	0·2752	0·1846	0·4297	0·3644
30°	$3s$	0·2060	0·0826	0·1150	0·0	0·0
	$3p$	0·5730	0·2806	0·3707	0·4982	0·5316
	$3d$	0·0022	0·3698	0·1300	0·3015	0·3305
40°	$3s$	0·2790	0·0337	0·0792	0·0	0·0
	$3p$	0·5007	0·1672	0·3544	0·5195	0·5487
	$3d$	0·0016	0·6838	0·2778	0·3568	0·2996
45°	$3s$	0·3292	0·0355	0·0568	0·0	0·0
	$3p$	0·4502	0·2370	0·3421	0·5195	0·5461
	$3d$	0·0062	0·6128	0·4040	0·3437	0·2879
50°	$3s$	0·3925	0·0348	0·0476	0·0	0·0
	$3p$	0·3900	0·3081	0·3832	0·5079	0·5314
	$3d$	0·0123	0·5508	0·4136	0·3347	0·2802

† ϕ is the angle between the C_s-axis and the P–H link.
* $2a$ orbital remains frozen throughout the calculation.

3.2. Geometry of PH_3 in the excited state

Figures 3 (a) and (b) represent the variation of the net energy of the singlet and triplet excited states respectively arising from the $2a \rightarrow 3a$ transition with changes in the out-of-plane angle of phosphorous atom as computed by the V_{N-1} potential method with $3d$ orbitals of phosphorus included in the basis set. In each case a planar structure is predicted confirming the qualitative predictions of Walsh-type diagrammatic analysis and our simple orbital model. Figures 3 (c) and (d) represent similar plots for the singlet and triplet E states ($2a \rightarrow 2e$ transition). The molecule is seen to have pyramidal structure in these states in conformity with the expectations from Walsh rules or our simple orbital model. Figures 4 (a)
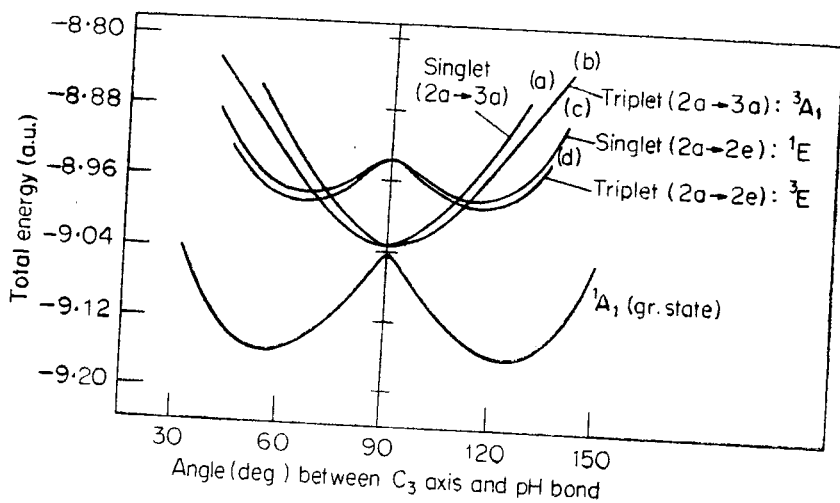
Figure 3. Variation in the net energies of the lowest $^{1,3}A$ (a and b) and $^{1,3}E$ states (c and d) of phosphine with pyramidal distortion as computed by the CNDO/2-hole potential method including $3d$ orbitals of P in the basis set.
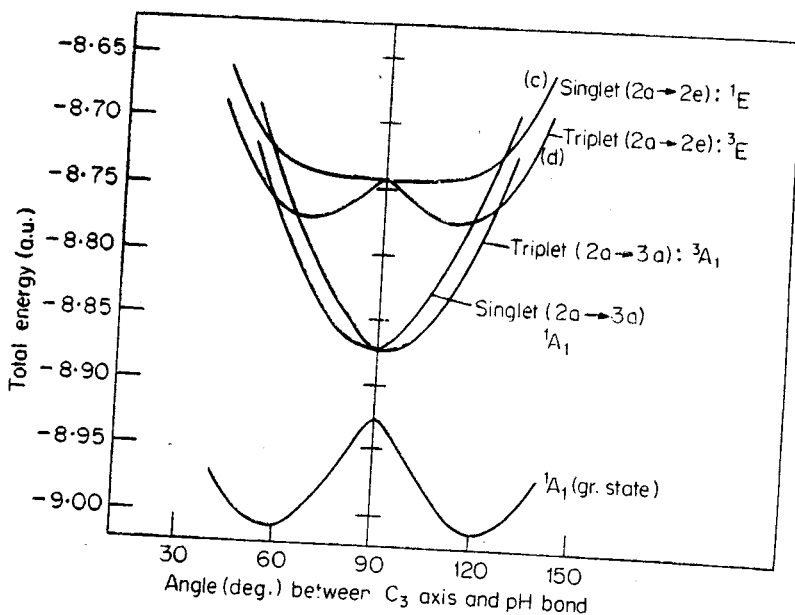

Figure 4. Variation in the net energies of the lowest $^{1,3}A$ (a and b) and $^{1,3}E$ states (c and d) of phosphine with pyramidal distortion as computed by the CNDO/2-hole potential method without $3d$ orbitals of P in the basis set.

and (b) exhibit the profile of variation of net energy along the bending coordinate (ϕ) in the singlet and triplet A states ($2a \rightarrow 3a$ transition) when V_{N-1} potential model is applied with a minimal basis set for phosphorus atom. The corresponding plots for the $^{1,3}E$ states ($2a \rightarrow 2e$ transition) are shown in figures 4 (c) and 4 (d) respectively. It is clear that inclusion or exclusion of $3d$ functions has no drastic

effect on the computed equilibrium geometries of the excited states $^{1,3}A_1$ and ^3E. For the ^1E state, however, the minimal basis set CNDO/2 + V_{N-1} potential calculation predicts planar structure, whereas the valence basis calculation leads to pyramidal geometry.

3.2a. *Inversion barriers in the excited E states* : As seen from figures 4 (a), (b), (c) and (d), the $^{1,3}E$ states are each characterised by the existence of double minimum potential along the bending coordinate (λ). It is thus of interest to compare the barrier heights in the ground and excited states. It can be seen from table 3 that the barriers to inversion in the excited (E) states are much smaller than the ground ($^1A_1$) state inversion barriers. No experimental data, however, are available to confirm this. The inclusion of $3d$ functions of phosphorus is seen to cause an increase of the computed barriers in the excited states as well as in the ground state. Particularly in ^1E ($2a \rightarrow 2e$) state, the barrier is predicted to be ≈ 0, if the $3d$ functions on phosphorus are removed from the basis. This is, however, expected since $3d$ type of basis functions on phosphorus lowers the SCF total energy more heavily in the pyramidal states than in the planar state. The effect could be offset to a large extent by the inclusion of p-type polarisation functions on hydrogen, which is missing in the CNDO/2 basis set. Still, the relative magnitudes of the barriers in different states are expected to be approximately correct.

3.2b. *Transition energies* : In table 4 we have displaced $^1A_1 \rightarrow {}^{1,3}A_1$ and $^1A_1 \rightarrow {}^{1,3}E$ transition energies as computed by the V_{N-1} potential method within the framework of CNDO/2 parametrisation both with and without the inclusion of $3d$ function of phosphorus in the basis set of expansion. Vertical and adiabatic transition energies are separately given along with the available experimental or *ab initio* results. It is evident that the inclusion of $3d$ functions lowers the computed transition energies in each case while the computed singlet-triplet splittings are not much affected. It is interesting to note that the MS $-$ X$_\alpha$ calculation of Norman (1974) on phosphine also led to the result that the inclusion of d-type spherical harmonics on P lowers the computed transition energies

Table 3. Inversion barriers in the ground and some excited states of phosphine as computed by the CNDO/2 + V_{N-1} potential model.

Type of transition	Excited state symmetry	Computed barrier height (eV)		Experimental/ *ab initio* data (eV)
		with d-basis on P	Without d-basis on P	
Ground state ($^1A_1$)		3·0475	2·778	1·74[a]
$2a \rightarrow 2e$	^1E	1·1784	0·0	
	^3E	1·3961	0·8767	

[a] Reference : Veillard 1975.

Table 4. Transition energies (transition from the ground state $^1A_1$) and singlet-triplet splitting in the electronic spectrum of phosphine as computed by CNDO/2 $+ V_{N-1}$ potential model.

Excited state symmetry	Vertical transition energies (eV)			Adiabatic transition energies (eV)			
	With d-basis on P	Without d-basis on P	Assumed geometry of final state	With d-basis on P	Computed geometry of final state	Without d-basis on P	Computed geometry of final state
$2\ ^1A_1$	6·65 (7·0)[a]	7·02	Pyramidal	3·30	Planar	3·78	Planar
$^3A_1$	6·07	6·21	Pyramidal	3·30	Planar	3·78	Planar
^1E	4·92	7·62	Pyramidal	4·92	Pyramidal	7·36	Planar
^3E	4·67	6·66	Pyramidal	4·67	Pyramidal	6·51	Pyramidal

[a] Reference : Humphries *et al* (1963).

$(^1A_1 \rightarrow {}^{1,3}A_1)$. Norman, however, considered only the adiabatic transition and computed the weighted average of singlet and triplet transition energies. Our results agree well with those of Norman as well as with the experimental transition energy.

One interesting feature in our computed electronic spectra of PH_3 is the large separation between the vertical and adiabatic $(2a \rightarrow 3a)$ transition energies. Further, the inclusion of $3d$ orbitals of phosphorus in the basis set leads to the result that in the vertical spectrum the $2a \rightarrow 2e$ transition occurs at lower energy (lowest energy band) than the $2a \rightarrow 3a$ transition, while the situation is reversed in adiabatic spectrum. However, the computed $2a \rightarrow 3a$ transition energy (singlet) lie around 7 eV region, as found experimentally. It may be that the low intensity of $2a \rightarrow 2e$ band makes it difficult to be noted in experimental spectra. In view of the lack of sufficient experimental data more rigorous theoretical work is necessary to examine these interesting features.

4. Conclusions

It seems that in spite of its limitations the CNDO/2-hole potential model can provide significant information regarding the structural features of molecules in the excited states. This is particularly important in view of the rather sparse availability of theoretical or experimental data on molecular properties in the excited states which chemists need for formulating trustworthy and useful generalisations. We hope to publish a host of such data in the near future.

Acknowledgement

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