An ab initio Calculation of the Force Constants, Vibrational Frequencies, and Equilibrium Geometry of HCP

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All the harmonic, the diagonal cubic and quartic stretching and the semidiagonal cubic force constants of HCP have been calculated from Hartree-Fock wavefunctions by the force method of Pulay. The force constants are in good agreement with the experimental ones, except for F_{RR}, $F_{\alpha\alpha}$, F_{Rr}, $F_{R\alpha\alpha}$, and $F_{r\alpha\alpha}$ the latter two being rather uncertain from experiment. From the harmonic force constants, harmonic frequencies have been calculated by the method of Wilson and Eliashevich. The equilibrium geometry of HCP has been calculated by the force relaxation method of Pulay.

1. Introduction

The force field of methinophosphide (HCP) has been determined experimentally only very recently [1]. In calculating the force constants from the spectral data several constraints had to be imposed. On the other hand, Pulay and Meyer [2–8] have shown that force constants may be calculated from Hartree-Fock wavefunctions in good agreement with experimental values even with basis sets of medium size. Using a 7,3/3/1 basis set of Gaussian lobe functions deviations amount to 5 – 10% for the diagonal stretching force constants and about 20% for the diagonal bending ones. The off-diagonal or coupling force constants are accurate to about 0.1 mdynes/Å, mdynes/rad or mdynes·Å/rad², respectively. On the basis of these results, we thought it valuable to carry out ab initio calculations on the force field of HCP in order to test the validity of the constraints imposed on the experimental data.

2. Details of Calculations

The basis set built up from Gaussian lobe functions consisted of 12 s and 9 p functions for P, 9 s and 5 p functions for C and 4 s functions for H. These functional basis set has been contracted to a (7,5), (4,3) and (3) atomic basis set for P, C and H, respectively. The contraction coefficients for C and H have been taken from Dunning's work [9], whereas the contraction coefficients for P have been obtained from an uncontracted calculation on the Phosphorus atom. In Table 1 are listed the parameters of the basis set together with atomic energies.

Table 1. Parameters of the Gaussian lobe basis set (12,9/9,5/4) [a]. Results for the atoms.

Atom and atomic energy (a. u.)	Exponents and contraction coefficients [b]
P (⁴S) −340.7098327	s: 77718.0 (0.0003283), 11609.3 (0.0025534), 2644.29 (0.0131444), 753.328 (0.0519655), 248.525 (0.1580911), 91.0698, 36.1916 (0.40464), 15.2063 (0.17114), 4.71378, 1.78316, 0.343249, 0.125204
	p: 385.322 (0.0037292, 90.6269 (0.0287558), 28.7788 (0.122111), 10.6643 (0.303042), 4.24361 (0.433877), 1.73769, 0.595843, 0.228550, 0.083760
C (³P) −37.6844843	s: 4232.61 (0.002029), 634.882 (0.015535), 146.097 (0.075411), 42.4974 (0.257121), 14.1892 (0.596555), 1,9666 (0.242517), 5.1477, 0.4962, 0.1533
	p: 18.1557 (0.039196), 3.9864 (0.244144), 1.1429 (0.816775), 0.3594, 0.1146
H (²S) −0.4976992	s: 19.2406 (0.130844), 2.8992 (0.921539), 0.6534, 0.1776

[a] Parameters of the basis set are taken from [9–11].
[b] Contraction coefficients in brackets.

The 9,5/4 basis set in the (4,3/3) contraction has been used previously [12] to calculate the force fields of HCN and HNC. For HCN deviations from the best experimental values available [1] are as follows:

F_{rr} (harmonic CH stretch): + 0.33 mdynes/Å (+ 5%),

F_{RR} (harmonic CN stretch): + 1.17 mdynes/Å (+ 6%),

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$F_{\alpha\alpha}$ (harmonic bend): $+0.12$ mdynes·Å/rad^2 ($+46\%$),
F_{rR} (harmonic CH, CN coupling): -0.05 mdynes/Å (-26%),
F_{rrr} (cubic CH stretch): -0.13 mdynes/Å^2 (-2%),
F_{RRR} (cubic CN stretch): -0.05 mdynes/Å^2 (0%),
F_{rrrr} (quartic CH stretch): $+0.05$ mdynes/Å^3 ($+1\%$),
F_{RRRR} (quartic CN stretch): $+4.57$ mdynes/Å^3 ($+19\%$).

Following the suggestion of Schwendeman[13], the force constants have ben calculated around the experimental geometry for which the R_e structure of Strey and Mills has been taken[1]. The displacements of the coordinates from the experimental geometry amount to ±0.05 bohr for the stretching and to 3° for the bending coordinates. The diagonal cubic and quartic stretching force constants have been calculated from the energies (the cubic ones from the forces, too). A potential curve based on 5 points is reproduced by a polynomial of 4th degree, from which the anharmonic force constants are calculated at the experimental bond distances. The distortions from the experimental geometry amout to ±0.15, ±0.05 and 0 bohr. In calculating the anharmonic stretching force constants from the energies it is essential that the energy has converged to 10^{-6} to 10^{-7} a.u., otherwise numerical errors may alter the values considerably.

All the calculations have been performed with the program system MOLPRO III of Meyer and Pulay. The results (internal forces, total energies and dipole moments) are given in Table 2.

3. Force Constants

The force constants calculated from the values of Table 2 are listed in Table 3. Agreement between calculated and experimental force constants is quite good, except for four of them:

a) the diagonal harmonic CP stretching force constant (F_{RR}) is too large by 19%. We believe that this deviation is mainly due to an unsufficient description of the CP bonding region by the basis set used in our calculations (no d-functions or functions centered between the bond have been used), as in the case of HCN the 9,5/4 basis set gave only an error of $+6\%$,

b) the diagonal harmonic bending force constant $F_{\alpha\alpha}$ has an error of $+44\%$ which is of similar size as in the case of HCN. This error is probably due to non-dynamic correlation effects as is pointed out by Pulay[14],

c) the calculated coupling force constant R_{rR} agrees in sign, but not in magnitude with the experimental one. But this force constant is particularly hard to fix from experimental data and we believe that our calculated value is more reliable,

d) $F_{r\alpha\alpha}$ does not agree in sign. We believe that our calculations give the right sign for this force constant as we see no reason why this force constant should change in sign from HCN to HCP,

The cubic stretching/stretching constants F_{rRR} and F_{Rrr} have been calculated as -0.199 and $+0.171$ mdynes/Å^2, respectively.

Table 2. Internal forces, total energies and dipole moments for different nuclear configurations of HCP.

Geometry [a]	Internal forces [b] Force coordinate			Total energy +379.0 (a. u.)	Total dipole moment (a. u.)
	CP (R)	CH (r)	PCH bend (α)		
$R=+0.15$				-0.0799664	0.2772261
$R=+0.05$	-0.219782	-0.069385		-0.0854099	0.2672575
$R=-0.05$	0.352214	-0.081207		-0.0847556	0.2583742
$R=-0.15$				-0.0761830	0.2501541
$r=+0.15$				-0.0805799	0.2888796
$r=+0.05$	0.053358	-0.232346		-0.0850042	0.2712767
$r=-0.05$	0.041441	0.106107		-0.0858695	0.2538190
$r=-0.15$				-0.0819689	0.2366307
$\alpha=$ 3°	0.048289	-0.075119	0.019162	-0.0858339	0.2641744
exp.	0.047519	-0.075435		-0.0859496	0.2626240

[a] Displacements from the experimental equilibrium geometry[1], R(CP) = 2.9099 bohr (1.5398 Å) and r(CH) = 2.0205 bohr (1.0692 Å).

[b] Forces in mdynes and in mdynes·Å/rad for the stretching and bending coordinates, respectively.

Table 3. Force constants and four vibrational frequencies of $^1H^{12}C^{31}P$.

Force constant [a]	ab initio	experimental
F_{rr}	6.396	6.250
F_{RR}	10.809	9.100
F_{Rr}	−0.224	−0.060
F_{aa}	0.366	0.255
F_{rrr}	−5.918 (−5.864) [b]	−6.667
F_{RRR}	−8.927 (−8.903) [b]	−8.033
F_{raa}	−0.115	0.05
F_{Raa}	−0.281	−0.3
F_{rrrr}	7.469	7.938 [c]
F_{RRRR}	9.050	9.438 [c]
Frequencies (1/cm)	ab initio (harmonic)	experimental (anharmonic)
ν_1 (CH)	3449	3217
ν_2 (α)	823	675
ν_3 (CP)	1402	1278

[a] Force constants in mdynes/Å for the harmonic stretching, in mdynes·Å/rad² for the harmonic bending, in mdynes/Å² for the cubic stretching, in mdynes/Å³ for the quartic stretching and in mdynes/rad² for the cubic stretching/bending coupling force constants. Definition of force constants: $F_{ii}=\partial^2 V/\partial R_i^2$; $F_{ij}=\partial^2 V/\partial R_i\,\partial R_j$; $F_{iii}=1/6\,\partial^3 V/\partial R_i^3$; $F_{iiii}=1/24\,\partial^4 V/\partial R_i^4$ and $F_{ijj}=1/2\,\partial^3 V/\partial R_i\,\partial R_j^2$.

[b] Force constants calculated from the internal forces.

[c] Constrained values.

4. Harmonic Frequencies and First Derivatives of the Dipole Moment

From the harmonic force constants of Table 3, the harmonic frequencies have been calculated by the method of Wilson [15] and Eliashevich [16] with a program written by one of us (P. B.). In Table 3 these frequencies are listed together with the experimental anharmonic frequencies.

The first derivatives of the dipole moment with respect to the internal coordinates (R, r and α) have been calculated from the dipole moment values of Table 2 and amount to $\partial\mu/\partial R = 0.43$ D/Å, $\partial\mu/\partial r = 0.83$ D/Å and $\partial\mu/\partial\alpha = 1.83$ D/rad. No comparison with experimental data is possible at the moment, but we note that $\partial\mu/\partial R$ and $\partial\mu/\partial r$ are smaller than in the case of HCN indicating that the CP as well as the CH bond is less polar in HCP than in HCN.

5. Equilibrium Geometry

The equilibrium geometry of HCP has been calculated by the force relaxation method of Pulay [17]. We used an initial geometry which was calculated from the forces of Table 2 in linear approximation and the calculated harmonic force constant matrix of Table 3. Rapid convergency was achieved (to 10^{-4} bohr) in one iteration step. The final geometry is: $R_{CP} = 2.9179$ bohr (1.5441 Å) and $R_{CH} = 1.9991$ bohr (1.0579 Å). Deviations from the experimental R_e structure as given in [1] amount to $+0.0043$ Å (0.3%) for the CP, and to -0.0113 Å (1.1%) for the CH bond length.

Using a large basis set of Slater type orbitals (STO's) Thomson [18] obtained the following equilibrium geometry: $R_e(CP) = 2.85$ bohr (1.51 Å) and $R_e(CH) = 2.005$ bohr (1.061 Å). Thomson's CP bond length is shorter than the experimental one by 0.03 Å or 2% whereas our calculated bond length is only slightly larger than the experimental one. But we think that bond lengths are the only properties where an (sp) basis set could be better than basis sets including polarisation functions. E. g., our dipole moment at the experimental equilibrium geometry amounts to 0.67 D which is almost twice as large as the experimental μ_0 [19]. Thomson [18] obtained a dipole moment which is close (-9%) to the experimental one.

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