Analytical Potential for HCP from Spectroscopic Data

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A potential function for HCP has been derived which reproduces the experimental vibrational energy levels, the geometry and dissociative energy of HCP. There is only a single minimum on this surface and the optimum energy and geometry of the linear structure HPC agrees well with calculated results.

Although HCP is an unstable molecule, several of its electronic states have been characterized spectroscopically.[1–3] Frost et al.[4] and King et al.[5] reported the photoelectronic spectrum of HCP and the emission spectrum of HCP$^+$, respectively. The microwave spectrum was studied by Tyler[6] and Johns et al.[7] The high resolution gas phase IR spectra of HCP and its common isotopically substituted species have been reported by Cabana et al.,[8–11] and most of the harmonic and second-order anharmonic force constants were deduced. In 1985, Kalasinsky et al.[12] published the gas-phase Raman spectrum of HCP. Detailed theoretical studies of the HCP bond lengths have been reported by Thompson and Ellam[13] and the theoretical determination of the HCP stretching potential in the linear geometry has been reported by Botshwina and Sebald.[14]

More recently, Lehmann et al.[15] published a detailed study of the bending potential of HCP by analysing its gas-phase vibrational spectra [($\tilde{A}$ $^1\Pi$)–($\tilde{X}$ $^1\Sigma^+$)] and by ab initio calculations. In this analysis, 94 vibrational energy levels have been deduced for the ground electronic state.[15]

An ab initio bending potential for HCP has been calculated at the MP4/6-31G* level using bond lengths optimized at the HF/6-31G* level for a given HCP bond angle. These calculations lead to the prediction that the linear structure HPC is ca. 3.7 eV higher in energy than HCP and is not a stable isomer. This is in sharp contrast to the HCN situation, a molecule with similar spectroscopic properties and electronic structure. Nguyen et al. reported a very similar ab initio result.[16] After that, a calculated geometry and vibrational frequencies of HCP were reported by Bloor et al.[17]

In 1982, Murrell and Carter[18] published a frequency-optimized potential-energy function of HCP which reproduced accurately the observed vibrational frequencies. However, it has an evident shortcoming, because there are two minima on this surface, one for HCP and the other for HPC (a linear molecule having bond lengths R_{HP} = 1.43 Å, R_{CP} = 1.56 Å and an energy of 3.8 eV above the HCP minimum). For this reason, a new examination of this surface is appropriate.

Calculation Methodology

Murrell and Carter's method has been adopted for our calculations. In a series of publications,[19–26] they developed a strategy for obtaining analytical potential-energy functions of triatomic molecules from a combination of spectroscopic, ab initio and thermodynamic data. The potential-energy function is based on a many-body expansion, as follows:

$$V(ABC) = V_{AB}^{(2)}(R_1) + V_{BC}^{(2)}(R_2) + V_{CA}^{(2)}(R_3)$$
$$+ V^{(3)}(R_1, R_2, R_3) \qquad (1)$$

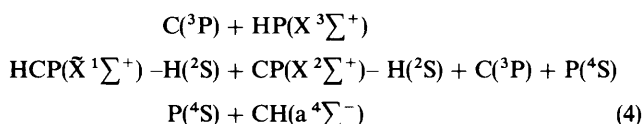where $V_{AB}^{(2)}$ etc. are the two-body potentials of the form,

$$V_{AB}^{(2)} = D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)$$
$$\times \exp(-a_1\rho); \qquad \rho = R - R^0 \qquad (2)$$

with parameters determined from spectroscopic or ab initio data on the diatomic species appropriate to the dissociation limit AB + C. $V^{(3)}(R_1, R_2, R_3)$ is a three-body term which becomes zero at the dissociation limits. This is ensured by choosing a function of the form:

$$V^{(3)} = P \prod (1 - \tanh \gamma_i\rho_i/2) \qquad (3)$$

where P is a polynomial in the interatomic displacement coordinates, $\rho_i = R_i - R_i^0$.

The ground-state surface has no cusps at any of the dissociation limits, the lowest energy electronic states of the fragment atoms plus diatoms being independent of the bond lengths of the diatoms. The dissociation channels for HCP are

$$C(^3P) + HP(X\,^3\Sigma^+)$$
$$HCP(\tilde{X}\,^1\Sigma^+) - H(^2S) + CP(X\,^2\Sigma^+) - H(^2S) + C(^3P) + P(^4S)$$
$$P(^4S) + CH(a\,^4\Sigma^-) \qquad (4)$$

so the full potential can be expressed as a single-valued function having these limits. Scheme 4 defines the one-body terms to be zero and two-body terms for HP and CP to be the ground-state diatomic potentials. Although the ground state of CH is $^2\Pi$, the required CH diatomic potential is that of CH ($^4\Sigma^-$); both the $^2\Pi$ and $^4\Sigma^-$ potentials are attractive and have the same dissociation limit [C(^3P) + H(^2S)].

Vibrational energy levels can be calculated for this potential function by the Whitehead–Handy variational procedure[27] in which the vibrational energy levels are obtained by diagonalizating the appropriate Hamiltonian matrix for a linear triatomic species. The first step in the Murrell–Carter method is to derive a potential from the energy, geometry and harmonic force constants, and to improve this by least-squares optimization of the variationally calculated vibrational frequencies to observed frequencies. A flow diagram for the computer program has been given in ref. 28.

Results and Discussion

The surface was first fitted to the bond lengths, energy and harmonic force constants of HCP and the bond lengths and energy of the optimum linear HPC structure. A 3.7 eV energy gap between HCP and HPC was adopted in our calculations. For selected values of γ_i, these data were sufficient to determine the coefficients up to second order in the polynomial.[20] As the potential surface has only one minimum it is physically most sensible to choose the equilibrium structure of the molecule for the reference geometry.

In order to obtain the best overall surface, a three-dimensional search in the parameters γ_i has been made. It was found that the overall shape of the surface was very sensitive to the values of γ_i. In particular, if γ_1 is large and γ_2 is small (where γ_1 is for the bond of HC and γ_2 for the bond of CP), a second minimum for linear HPC appears on the surface. This is absent, however, when $\gamma_1 < 0.5$ Å^{-1} and $\gamma_2 > 3.0$ Å^{-1}; surfaces with these parameters, have only a single minimum corresponding to the linear HCP structure. It appeared that the existence of one or two minima on the surface was less dependent on γ_3. The best potential function obtained from this analysis is given in Table 1. This function was then iterated to give agreement between the variationally calculated vibrational frequencies and the lowest 13 selected observed frequencies so that the coefficients up to all quartic terms of the polynomial were obtained; the parameters γ_i and R_i^0 were also optimized but it was found that their values changed very little.

The potential function, as fully specified by its parameters, is given in Table 2 and Table 3 summarizes some information about this potential function. A point to note is that a bent transition state with a geometry $R_{CP} = 1.521$ Å, $R_{CH} = 2.075$ Å and $\alpha = 88°$ [the angle between R_{CP} and $R_{CH}(H—C—P)$] was found on the surface, this being the transition state for the reaction $H + CP(X\,^2\Sigma^+)$–HCP. It has an energy only 2 kJ mol^{-1} higher than the reactants.

Fig. 1 shows contours for hydrogen moving around CP with fixed bond length of 1.539 Å which is the equilibrium bond length in HCP. It can be seen that there is a minimum at the HCP geometry and a saddle point for linear HPC. Contours go smoothly between these two structures. The optimum linear HPC structure was found by searching for zero first derivatives of the potential function; its energy is 4.8 eV below the separate atomic limits and its bond lengths are $R_{CP} = 1.576$, $R_{PH} = 1.385$. Thus, the geometry of HPC on our surface is very close to the calculated result.

Fig. 2 displays the potential energy as a function of the angle H—C—P, the CP bond and the HC bond being optimized. As expected, the bending potential decreases monotonically going from HPC to HCP, confirming that the linear HPC is a local energy maximum. The energy difference, 3.7 eV, between HCP and HPC calculated by Lehmann et al.,[15]

Table 2 Potential function of HCP

ijkl	$C_{ijkl}/\text{Å}^{-n}$	ijkl	$C_{ijkl}/\text{Å}^{-n}$
1	−16.32097	1233	−12.90673
2	−19.33951	1111	−4.53813
3	17.91460	2222	8.22374
12	17.58131	3333	6.85997
13	−4.17122		
23	1.93646		
11	5.39958	V^0/eV	−0.21207
22	5.01902		
33	−13.52119		
111	8.89728	$\gamma_1/\text{Å}^{-1}$	0.35870
222	−5.96115		
333	12.80709		
112	2.27361	$\gamma_2/\text{Å}^{-1}$	4.08146
122	−10.21362		
133	0.37210		
233	−3.30378	$\gamma_3/\text{Å}^{-1}$	0.71228
113	1.47703		
223	−3.81007		
123	−7.54640		
1112	−8.96254		
1222	1.03069	$R_1^0/\text{Å}$	0.68562
1113	−5.09879		
2223	8.51820		
1122	−7.84576		
1333	−10.16230	$R_2^0/\text{Å}$	1.67580
2333	1.07761		
1133	−7.23842		
2233	8.90712		
1123	−14.09706	$R_3^0/\text{Å}$	2.36136
1223	−1.80020		

$P(R_1, R_2, R_3) = V^0(1 + \Sigma C_{ijkl} \rho_i \rho_j \rho_k \rho_l)$.

at MP4SDQ/6-311G** level, is reproduced accurately by our potential.

Table 4 gives a comparison of observed and calculated vibrational wavenumbers (cm^{-1}) of HCP for $J = 0$. As can be seen, the agreement is excellent (better than ± 3 cm^{-1})

Table 1 Potential function of HCP fitted to energy, geometry and force constants

	two-body terms				
	D_e/eV	$R_e/\text{Å}$	$a_1/\text{Å}^{-1}$	$a_2/\text{Å}^{-2}$	$a_3/\text{Å}^{-3}$
C—H($a\,^4\Sigma^-$)	2.8521	1.0823	5.5297	8.7166	5.3082
C—P($X\,^2\Sigma^+$)	5.3568	1.5622	4.5794	5.9231	3.6189
H—P($X\,^3\Sigma^+$)	2.0559	1.4029	6.2947	12.9232	9.6841

	three-body term		
ijkl	$C_{ijkl}/\text{Å}^{-n}$		
1	−10.25440	V^0/eV	−0.22229
2	−8.55284	$\gamma_1/\text{Å}^{-1}$	0.50000
3	12.38931	$\gamma_2/\text{Å}^{-1}$	4.00000
12	−5.81570	$\gamma_3/\text{Å}^{-1}$	0.60000
13	−7.08543	$R_1^0/\text{Å}$	1.06000
23	9.24419	$R_2^0/\text{Å}$	1.56220
11	−0.54933	$R_3^0/\text{Å}$	2.60000
22	−24.98030		
33	2.96014		

$P(R_1, R_2, R_3) = V^0(1 + \Sigma C_{ijkl} \rho_i \rho_j \rho_k \rho_l)$.

Table 3 Stationary points

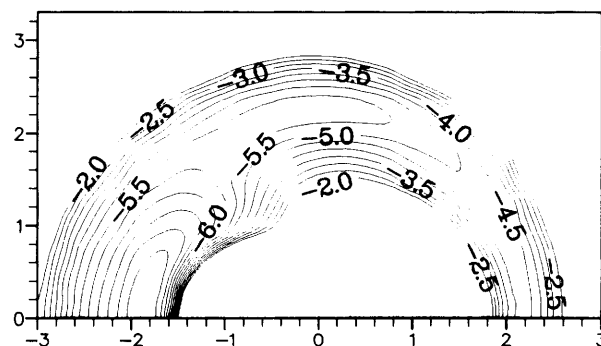| $R_{CP}/\text{Å}$	$R_{CH}/\text{Å}$	$R_{PH}/\text{Å}$	H—C—P/degrees	energies/eV	identity
1.562				−5.3568	H + CP
	1.0823			−2.8521	P + CH
		1.4029		−2.0559	C + HP
1.576		1.385	0.0	−4.7980	HPC
1.5398	1.0692		180.0	−8.500	HCP
1.5212	2.0753		88.0	−5.3357	transition state

Fig. 1 Potential contours of the HCP. H moves around the C—P bond (bond length = 1.54 Å, contour spacing = 0.5 eV, minimum contour = −8.5 eV)
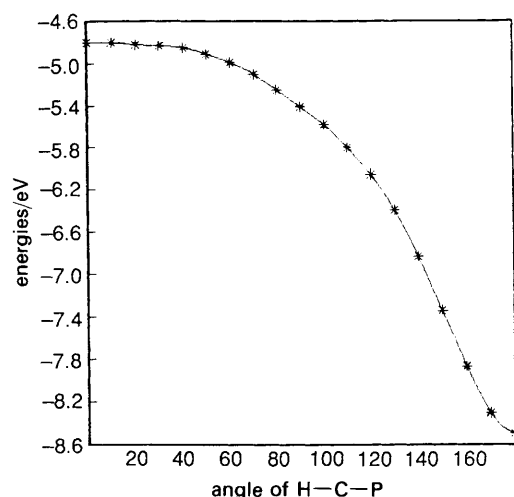
Fig. 2 Bending potential of HCP. H moves around the CP bond. The CP bond and the HC bond are optimized

Table 5 Unobserved vibrational frequencies of HCP

level	calc./cm^{-1}
110 + 101	4557
101 + 110	4619
111 + 102	5931
120 + 102	5973
120 + 111	5999
032 + 041	6433
112 + 121 + 103	7314
121	6086
130	5334

except for two states which are in strong Fermi resonance. In these calculations, the basis set consists of $\Sigma N_i \leqslant 5$ (56 states in all), with six integration points over all normal coordinates. The basis set to be used in the variational calculations should be as large as possible. In practice, however, a large basis set requests a large number of integration points and the computing is very time-consuming. The optimum size of basis set, a balance between accuracy and computing time, has been found in previous calculations to be that we have used. However, the eigenvalues arising from the basis functions with $\Sigma N_i = 5$ will not be accurate.

In addition to the bands associated with experimental observations we also calculated five other bands below 6322 cm^{-1}, as shown in Table 5. These are all strong Fermi resonances and being mixtures of overtone and combination bands would be weak in the spectrum. Other bands above 6322 cm^{-1} arising from states with $\Sigma N_i < 5$ are also shown in this table. There do not, at present, appear to be observed bands for comparison of these; most observed bands are for higher bending modes which are not given by our basis set.

It is well known that the bending potential of HCN has a minimum on the HNC side[29] and a double minimum potential-energy function has been obtained.[18] Although the

known spectroscopic properties of HCN are very similar to those of HCP, the striking difference between HCN and HCP has been noted before.[30-33] Recent theoretical studies of gas-phase proton affinities of molecules containing P—C multiple bonds show that HCN protonates at N to form the linear HCNH$^+$, whereas HCP protonates C to form the planar H$_2$CP$^+$. [30-33] The linear structure HCPH$^+$ was found to lie much higher in energy (185 kJ mol^{-1}) and also be unstable to the bending mode. The instability of HPC and HCPH$^+$ has been attributed to strong Σ (ground state)–Π (excited state) mixing through the bending mode.[15]

Table 4 Comparison of observed and calculated vibrational wavenumbers (cm^{-1}) of HCP for $J = 0$

level	calc.	obs.^{a}
010	674	675
001	1277	1279
020	1335	1336
011	1946	1947
030	2001	2002
002	2544	2545
021	2601	2598
040	2651	2652
012	3209	3208
100	3216	3216
031^b	3240	3260
003	3804	3804
022^b	3783	3853
013	4451	4453
004	5053	5055
200	6322	6322

^{a} Ref. 13. ^{b} Strong Fermi resonance cases.

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