Normal Mode and Isomerization Bending States in HCP: Periodic Orbit Assignment and Spectroscopic Signature

Stavros C. Farantos*, Hans-Martin Keller, and Reinhard Schinke
Max-Planck-Institut für Strömungsforschung
D-37073 Göttingen, Germany,
Koichi Yamashita
Department of Applied Chemistry
Graduate School of Engineering
University of Tokyo
7-3-1 Hongo, Tokyo 113, Japan,
Keiji Morokuma
Cherry L. Emerson Center for Scientific Computation and
Department of Chemistry, Emory University
Atlanta, Georgia 30322, USA

*Permanent address: *Institute of Electronic Structure and Laser, Foundation for Research and Technology, Hellas, and Department of Chemistry, University of Crete, Iraklion 711 10, Crete, Greece.*

Abstract

We present exact quantum mechanical bound-state calculations for HCP using an *ab initio* potential energy surface. The main result is the existence of two distinct families of bending states: one with normal-mode type behavior and wavefunctions confined to small bending angles and the other one sampling the isomerization path all the way from H–CP to CP–H. The former start at low energies and persist to very high energies well above the isomerization plateau, whilst the latter occur abruptly at high energies. Stable periodic orbits provide a clear-cut assignment. The different types of bending motion lead to distinctly different moments of inertia and therefore to different rotational constants; possible relations to recent spectroscopic observations are discussed.

The development of new spectroscopic techniques such as Stimulated Emission Pumping (SEP) has greatly advanced our knowledge about the dynamics of highly excited small polyatomic molecules.[1] The list of molecules investigated by SEP has recently been increased by HCP in its ground electronic state.[2] Electronic, vibrational, and rotational spectra revealing the equilibrium geometries and the fundamental spectroscopic constants for the ground as well as the first excited electronic states[3–8] have shown—in accord with quantum chemistry calculations of Lehmann and coworkers[5]—that the equilibrium geometry of HCP($\tilde{X}$) is linear. However, the *ab initio* calculations have also revealed that, unlike the homologue HCN, HCP($\tilde{X}$) has no stable isomer. Instead, they predicted[5] that the linear CP–H configuration corresponds to a saddle point with the curvature of the potential energy along the bending coordinate changing near 90°.

In order to find—for the first time in a spectroscopic experiment–clues about how the unimolecular isomerization of a triatomic molecule, H–AB $\leftrightarrow$ AB–H, might be encoded in the rotation-vibration energy level structure, Field and coworkers have recorded the $\tilde{A}-\tilde{X}$ and $\tilde{C}-\tilde{X}$ SEP spectra for HCP.[2] The former band is believed to sample pure bending overtones $(0, v_2, 0)$ with v_2 ranging from 26 to 42. These levels span an energy regime up to *ca.* 3 eV above the vibrational ground state, which is sufficiently high to allow large-amplitude motion of H around CP, provided the molecule were to move along the minimum energy path. By fitting the spectra to a well known spectroscopic model for linear molecules it was established, however, that despite the opening of a whole new portion of the coordinate space the spectrum is surprisingly regular, as was also revealed by Lehmann *et al.*[5] some time ago.

Nevertheless, the MIT group made two quite surprising observations which might indicate that a structural change from mainly H–CP to CP–H motion is entangled: First, with $v_2 \geq 32$ perturbations of the pure bending overtones set in which were absent at lower excitations. Second, the vibrational fine structure

constants of the $(0, v_2, 0)$ levels change abruptly around $v_2 = 36$. For example, the rotational constant B_0 (shown in Fig. 3 below) rises suddenly by about 8% from $v_2 = 34$ to $v_2 = 42$. One possible explanation for such a relatively large increase is a substantial change of the molecular structure. The authors conjectured, on the basis of our *ab initio* potential energy surface (PES), that the change in the character of H–CP stretch from dominantly H–C to P–H motion should cause a large change in the vibrational level structure and therefore lead to the sudden turning on of perturbations as well as the abrupt changes in the fine structure constants.[2]

In order to shed some light on these rather surprising findings we have carried out three-dimensional quantum mechanical bound-state calculations employing an *ab initio* PES. In addition, the dynamics of the system is studied by exploring the classical phase space by means of periodic orbits and bifurcation/continuation diagrams. Details of the *ab initio* calculations, which cover an extended region of the nuclear configuration space, together with the fit expression will be described in a forthcoming publication.[9] In what follows energy will be normalized so that $E = 0$ corresponds to H+CP(r_e); with this normalization the bottom of the well has an energy of $-5.236\,\mathrm{eV}$ and the energy of the vibrational ground state is $-4.866\,\mathrm{eV}$. Both the classical and the quantum calculations are performed using Jacobi coordinates r, the bond length of CP, R, the distance of the hydrogen atom from the center of mass of CP, and ϑ, the angle between the vectors $\mathbf{r}$ and $\mathbf{R}$; $\vartheta = 0$ corresponds to H–CP. Contour plots of the PES as functions of (R, ϑ) for fixed $r = 1.55\,\text{Å}$ and (r, ϑ) for fixed $R = 2.0\,\text{Å}$ are depicted in Figs. 1 and 2. There is no minimum for the CP–H configuration, but there is an abrupt change in the curvature along the minimum energy path from H–CP to CP–H at about $2.2\,\mathrm{eV}$ above the minimum ($\vartheta \approx 75°$, see upper panel of Fig. 1).

The exploration of the classical phase space has been done by means of periodic orbits (PO; see, for example, Refs. [10-12] and references therein).

Periodic orbits are exceedingly helpful in the analysis and characterization of quantum mechanical systems (Refs. [11-15] and references therein), especially if the system is highly energized. This is particularly true in the case of HCP, with *ca.* 700 bound states up to an energy of about 3 eV above the (0,0,0) level, *i.e.* the energy regime explored by the SEP experiment.

We first examined the principal families of periodic orbits which emerge, with increasing energy, from the bottom of the potential well; they correspond to the normal modes of the molecule and we denote them by [r], [R], and [B] because at very low energies they represent r-stretching, R-stretching, and bending motions, respectively. Since the equilibrium geometry of HCP is linear, the [r] and [R] periodic orbits are restricted to the (r, R) plane with no bending motion ($\vartheta = 0$). However, we have found that the principal family of [r] POs becomes singly unstable very early as the energy increases; merely 0.36 eV above the bottom of the well it shows a bifurcation by reflection[11] giving rise to a new family of periodic orbits which we denote by [r1A] (branch A of the 1st bifurcation). These periodic orbits have double periods compared to the main family [r] and they do extend to angles $\vartheta > 0$. In Fig. 1 we show projections of the [B]- and the [r1A]-type periodic orbits in the (R, ϑ) and (r, ϑ) planes; the projections of [r]- and [R]-type periodic orbits coincide with the r and R axis respectively, and therefore they are not seen in the figure.

Astonishingly, both the [B]-type and the [r1A]-type POs are constrained to angles below 40°, even at high excitation energies. This behavior, which is best seen in the lower part of Fig. 1, seems to be counterintuitive if one considers only the (R, ϑ) representation in the upper part of Fig. 1 which suggests that the bending motion should extend to larger and larger angles towards the CP–H plateau as the energy increases. However, this is not the case and the explanation for this remarkable behavior might be found in the lower part of the same figure: The trajectories follow the minimum energy path in the (r, ϑ) plane (for fixed value of R) and prefer to extend the CP stretch coordinate r with the angle

remaining relatively small rather than exploring large-amplitude bending motion. The strong force $-\partial V/\partial\vartheta$ around $\vartheta \approx 50°$ deflects the trajectories to larger and / or smaller values of r.

The first POs extending to angles larger than 40°, towards the CP–H hemisphere of the PES, occur *suddenly* at an energy of 2.08 eV above the bottom of the well. To be precise, they emerge from a *saddle-node* (SN) *bifurcation*[16] and therefore we will refer to them as [SN1]-type POs (the 1st saddle-node bifurcation). Examples are depicted in Fig. 1. These [SN1] POs follow the minimum energy path in the (R, ϑ) plane and seem to be unaffected by the minimum energy path in the (r, ϑ) plane, *i.e.* the CP stretch coordinate r remains almost constant. The differences to the [B]-type POs are clearly seen in the figure. With increasing energy more saddle-node bifurcations occur giving rise to more complicated POs ([SN2] etc.) that extend to ever larger angles ϑ.[9]

Next we demonstrate that the particular POs discussed above form the backbones of the quantum mechanical wavefunctions. The quantum calculations are carried out by representing the Hamiltonian (for total angular momentum $J = 0$) in a highly contracted / truncated 3D basis and diagonalizing the resulting matrix.[17] Details will be given in a future publication;[9] here we mention only that the basis consists of about 9000 functions and that the estimated convergence error is less than 1meV for levels up to 3 eV above the bottom of the well.

We have visually examined, both by 2D projections and 3D representations, more than 700 wavefunctions! As expected, the regularity of the classical phase space and the dominance of resonances (i.e. the approximately rational relationship between the different vibrational periods) results in mostly regular quantum wavefunctions which are clearly localized along the various classes of POs discussed above. In Fig. 2 we show representative eigenfunctions, together with the corresponding POs, projected on the (R, ϑ) and (r, ϑ) planes; the POs have roughly the same energies as the eigenstates. Overtones of states with pure excitation in R (not shown in Fig. 2) and the bending mode [B] consistently trace

the corresponding [R]- and [B]-type POs. Interestingly, the wavefunctions of the states with excitation in the CP stretch coordinate r follow the periodic orbits of [r1A] character.

The eigenfunctions in the lower and middle panels of Fig. 2 belong to the (0,36,0) state of the [B] mode and the (0,0,19) level of the [r1A] mode, respectively. The fundamental excitation energies for one quantum of the CP stretch ($1234\,\mathrm{cm}^{-1}$) and two quanta of the H-C-P bend ($1283\,\mathrm{cm}^{-1}$) are very similar (Fermi resonance) with the consequence that the [B] and the [r1A] POs as well as the corresponding quantum mechanical wavefunctions are strongly mixed. This mixing persists to high excitations and is clearly documented by the 'orthogonality' of the [r1A] and [B] type wavefunctions. In other words, the normal-mode type bending states and the CP stretch states are grouped into polyads $(0, P, 0)$, $(0, P-2, 1)$,..., $(0, 0, P/2)$.[2,8] The [B] type wavefunction in Fig. 2 is the highest member of the $P = 36$ polyad while the [r1A] state is the lowest level of the $P = 38$ polyad. In accordance with the underlying POs the wavefunctions of both the [B] and [r1A] modes are restricted to small bending angles and do not substantially extend beyond $\vartheta \approx 40°$, even for very high polyad quantum numbers. Both classes of wavefunctions 'climb' up the steep walls of the potential well in the (r, ϑ) plane (which explains the surprisingly harmonic behavior of these modes), but they do not sample the isomerization path!

The first wavefunction that shows large-angle motion and significantly extends beyond $\vartheta \approx 40°$ is found at an energy of 2.26 eV above the minimum, just slightly above the first saddle-node bifurcation in the classical phase space, which occurs at 2.08 eV. It appears rather suddenly (as a function of energy), is scarred by the saddle-node periodic orbit [SN1], and has 26 nodes along that orbit. As the energy rises the number of [SN]-type wavefunctions increases and the wavefunctions penetrate deeper and deeper into the (PC)-H region; an example with 50 nodes along the PO is shown in the upper part of Fig. 2. The [SN] type states form a new class of states and are completely independent of the

[B] or [r1A] states; for distinction we will assign them as $(0, v_2, 0)_{\mathrm{SN}}$, where v_2 counts the nodes along the [SN] type trajectory. The energy difference between the first two states of this progression, $(0, 26, 0)_{\mathrm{SN}}$ and $(0, 28, 0)_{\mathrm{SN}}$, is of the order of $850\,\mathrm{cm}^{-1}$ but rapidly decreases with v_2 because of strong anharmonic effects at larger angles.

In their recent SEP study Field and coworkers[2] found that the pure bending levels $(0, v_2, 0)$ are suddenly perturbed when $v_2 \geq 32$. This observation might be qualitatively accounted for by the abrupt appearance of the [SN]-type states. In the calculations the [SN] states appear at an energy which is comparable to the energy of the $(0, 26, 0)$ state of the [B] mode. Either the energy where the [SN] mode occurs, which is expected to depend very sensitively on the form of the PES, is significantly underestimated by theory or in reality the perturbations start earlier than $v_2 = 32$ but the experiment is sensitive to them only at higher excitations.

Explanation of the second startling observation in Ref. [2], the abrupt change of the rotational and other fine structure constants around the $v_2 = 36$ level of the pure bending mode, in principle requires calculations for $J > 0$. However, since the necessary basis size increases linearly with J and since the $J = 0$ calculations already use the entire memory of our workstation, such exact calculations are impossible for us at present time. For this reason we determined the rotational constants A, B, and C for each of the 700 vibrational levels by calculating the expectation value of the inverse of the moments of inertia with the $J = 0$ eigenfunctions. Of course, this is an approximation and especially effects due to Coriolis coupling are not taken into account. The rotational constant for rotation around an axis in the HCP plane and approximately perpendicular to the CP axis, B, is close to the spectroscopic B_0.

In Fig. 3 we plot the calculated B values for the vibrational levels of the [B] and the [SN] type and it is seen that they differ distinctly for the two families of bending states. After an initial increase the rotational constants for the [B]

states decrease continuously with the quantum number v_2 whereas the constant for the [SN] states stays more or less stable as function of v_2. The B values of the [r1A] states are qualitatively similar to those of the bending states, with the only exception that their variation with v_3 is not as smooth. The different behaviors can be qualitatively explained in terms of the quite different amplitudes of bending motion for the two sets of bending states. In the case of the small-amplitude angular motion of the [B] states, the hydrogen atom is always far away from the rotation axis; its contribution to the overall moment of inertia is small but, nevertheless, of the order of a few percent of the contribution that results from the CP rotation. On the other hand, in the case of the large-amplitude angular motion of the [SN] states the H atom spends most of the time close to the rotation axis ($\vartheta \approx 90°$) with the net result that its contribution to the moment of inertia is negligibly small. Since the rotational constant is proportional to the inverse of the moment of inertia, the [B] states have a rotational constant which is a few percent smaller than for the [SN] states. Moreover, the wavefunctions of the [B] family show a continuous increase of the expectation value $\langle r \rangle$ with the degree of excitation which explains the gradual decrease of B for these states. On the other hand, $\langle r \rangle$ remains approximately constant with v_2 for the [SN] states and so does the corresponding B value.

The calculated B values for the normal-mode type bending states agree quite well with the experimental values for $26 \leq v_2 \leq 34$ and even the very small increase from $v_2 = 0$ to 2 seems to be reproduced; the deviation of the order of only 0.015 cm^{-1} or 2% might be explained by a small inaccuracy of the CP equilibrium distance. All of the sudden, however, the measured B_0 constants increase abruptly from $v_2 = 34$ to 38 and, surprisingly, take on values which are close to the rotational constants calculated for the [SN] states. In the absence of more exact calculations for $J > 0$, however, this coincidence must be considered with cautiousness. Since the B values are calculated by means of $J = 0$ wavefunctions, effects due to ro-vibrational coupling are not included, which might

become important under certain resonance conditions.

Our classical and quantum mechanical calculations, using an *ab initio* PES, have shown: 1) The energy spectrum and the underlying wavefunctions are surprisingly regular; for example, the normal-mode type bending and CP stretching states, which form a 2:1 polyad, remain harmonic like to very high excitations, even at energies where anharmonic couplings due to the potential are prominent. 2) Both, the normal-mode like bending states and the CP stretching states are confined to the H–CP hemisphere, *i.e.* the (Jacobi) angle γ remains smaller than 40° or so, even if the energy is high enough for following the isomerization path. 3) A new class of bending states, following the isomerization path all the way to the CP–H side, suddenly comes into existence at a relatively high energy. 4) Classical periodic orbits quantitatively describe all the findings observed in the quantum calculations. In particular, the sudden appearance of the isomerization-type bending states is the consequence of a saddle node bifurcation; it might explain the abrupt onset of perturbations observed in the experimental SEP spectra. 5) The two classes of bending states have distinctly different moments of inertia reflecting the small- and large- amplitude bending motions.

The resulting rotational constants for rotation about an axis perpendicular to the CP axis, B, agree up to $v_2 = 34$ very well with the experimental values. The abrupt change of the vibrational fine structures in the range $v_2 = 34$–36 observed experimentally is either the consequence of ro-vibrational couplings not present for $J = 0$ or due to 'mixing' with the isomerization-type bending motion. In a future more complete publication we will analyze all calculated $J = 0$ vibrational states. However, calculations for non-zero total angular momentum are mandatory for a clarification of all the experimental details; they are in prospect.

Acknowledgments

SCF and RS are very grateful to Prof. Field for stimulating their interest in the spectroscopy of HCP, for sending a preprint of Ref. [2] prior to publication, and most importantly, for many invaluable discussions. SCF acknowledges financial support through the Sonderforschungsbereich 357 'Molekulare Mechanismen Unimolekularer Reaktionen' and the Max-Planck-Institut für Strömungsforschung.

References

[1] In *Molecular Dynamics and Spectroscopy by Stimulated Emission Pumping*, edited by Hai-Lung Dai, and Robert W. Field. World Scientific, (1995).

[2] H. Ishikawa, Y.-T. Chen, Y. Ohshima, B. Rajaram, J. Wang, and R. W. Field, J. Chem. Phys., **submitted** (1995).

[3] J. W. C. Johns, H. F. Shurvell, and J. K. Tyler, Can. J. Phys. **47**, 893 (1969).

[4] A. Cabaña, Y. Doucet, J.-M. Garneau, C. Pépin, and P. Puget, J. Mol. Spectrosc. **96**, 342 (1982).

[5] K. K. Lehmann, S. C. Ross, and L. L. Lohr, J. Chem. Phys. **82**, 4460 (1985).

[6] M. A. Mason, and K. K. Lehmann , J. Chem. Phys. **98**, 5184 (1993).

[7] Y.-T. Chen, D. M. Watt, R. W. Field, and K. K. Lehmann , J. Chem. Phys. **93**, 2149 (1990).

[8] M. Jung, M. Winnewisswer, and B. P. Winnewisser, J. Mol. Spectrosc., **submitted**

[9] S. C. Farantos, H.-M. Keller, R. Schinke, K. Yamashita, and K. Morokuma, **in preparation**.

[10] M. C. Gutzwiller. *Chaos in Classical and Quantum Mechanics.* Springer, New York, (1990).

[11] S. C. Farantos, Int. Rev. Phys. Chem., **in press** (1996).

[12] J. M. Gomez Llorente, and E. Pollak, Annu. Rev. Phys. Chem. **43**, 91 (1992).

[13] E. J. Heller, and S. Tomsovic, Physics Today **64**,No.7 (1993).

[14] R. Schinke. *Photodissociation Dynamics.* Cambridge University Press, Cambridge, (1993).

[15]H. S. Taylor. In *Molecular Dynamics and Spectroscopy by Stimulated Emission Pumping*, edited by H.-L. Dai and R. W. Field. (World Scientific, Singapore, 1995).

[16]S. Wiggins. *Introduction to Applied Nonlinear Dynamical Systems and Chaos.* Springer, New York, (1990).

[17]A. J. Dobbyn, M. Stumpf, H.-M. Keller, and R. Schinke, J. Chem. Phys. **103**, 9947 (1995).

Figure Legends

1. Projections of periodic orbits belonging to the three families [r1A], [B], and [SN1]; see the text for definitions. The energies of the orbits range from -3 eV to -2 eV. Contours of the potential energy surface are shown by the dashed lines; the energy spacing is 1 eV and the lowest contour corresponds to an energy of -4 eV [with $E = 0$ for H+CP(r_e)]. The full circle marks the equilibrium point of the upper electronic state used in the SEP experiments, $\tilde{A}$. Jacobi coordinates are employed with distances measured in Å and the angle given in degrees.

2. Representative examples of the three characteristic types of quantum mechanical wavefunctions corresponding to the [SN]-, [r1A]-, and [B]-families of periodic orbits; the energies are -2.0492 eV, -2.1622 eV, and -2.1618 eV, respectively. Plotted is the modulus square of the wavefunction multiplied with the volume element $rR\sin\vartheta$; the small-angle part of the [SN] wavefunction is hardly seen in this picture; better views are obtained in a 3D representation. The thick solid lines represent the scaring periodic orbits with approximately the same energy. Distances are measured in Å and the angle is given in degrees.

3. The calculated values of the rotational constant B (in cm^{-1}) for the [B]- (filled diamonds) and the [SN]-type (filled squares) quantum states as functions of the angular quantum number v_2. The open circles denote the experimental results quoted in Ref. [2].