Highly excited vibrational states of HCP and their analysis in terms of periodic orbits: The genesis of saddle-node states and their spectroscopic signature

Max-Planck-Institut für Strömungsforschung, D-37073 Göttingen, Germany

Stavros C. Farantos
Institute of Electronic Structure and Laser Foundation for Research and Technology—Hellas, Greece, and Department of Chemistry, University of Crete, Iraklion 711 10, Crete, Greece

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

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We present quantum mechanical bound-state calculations for HCP($\tilde{X}$) using an ab initio potential energy surface. The wave functions of the first 700 states, corresponding to energies roughly 23 000 cm$^{-1}$ above the ground vibrational state, are visually inspected and it is found that the majority can be uniquely assigned by three quantum numbers. The energy spectrum is governed, from the lowest excited states up to very high states, by a pronounced Fermi resonance between the CP stretching and the HCP bending mode leading to a clear polyad structure. At an energy of about 15 000 cm$^{-1}$ above the origin, the states at the lower end of the polyads rather suddenly change their bending character. While all states below this critical energy avoid the isomerization pathway, the states with the new behaviour develop nodes along the minimum energy path and show large-amplitude motion with H swinging from the C- to the P-end of the diatomic entity. How this structural change can be understood in terms of periodic classical orbits and saddle-node bifurcations and how this transition evolves with increasing energy is the focal point of this article. The two different types of bending motion are clearly reflected by the rotational constants. The relationship of our results with recent spectroscopic experiments is discussed. © 1997 American Institute of Physics.

I. INTRODUCTION

Spectroscopy is an extremely powerful tool for determining the structure of molecules.$^1$ Usually one starts at low excitation energies, deep inside the potential well, and develops a simple Hamiltonian which is able to reproduce the measured spectrum. With increasing energy it becomes necessary to gradually extend the Hamiltonian model in order to take into account higher order effects such as anharmonicities or couplings between the different modes. However, although this rather general approach has been applied very successfully in the past, it is uncertain how far it can be extended. If the energy approaches the dissociation threshold, the mixing between states normally becomes so strong that simple models are bound to fail. Likewise, if the energy comes close to an isomerization barrier, some new dynamical behaviors are expected to develop, which may be difficult to be described by extending pictures appropriate at much lower energies. Thus, either some new models have to be formulated or, alternatively, the problem has to be approached from a different perspective, that is, the exact solution of the Schrödinger equation using a global potential energy surface (PES).

Significant advances have been made in the last years, at least for small molecules, in generating accurate PESs and in solving the multidimensional Schrödinger equation using these surfaces.$^{2,3}$ A recent and prominent example is HCO.$^{4–6}$ Nonetheless, when one considers highly excited molecules, the density of states is large and consequently hundreds or even thousands of eigenfunctions have to be calculated, which is still a formidable task. Moreover, even if we are able to accurately compute a dense spectrum of vibrational levels, something which becomes more and more feasible with modern computers, the inspection of all these wave functions and their assignment to sets of quantum numbers as well as the extraction of dynamics information from the spectrum are still big challenges.

Because of the problems related to the “understanding” of spectra—with “understanding” we mean not just the assignment to quantum numbers, which anyhow becomes more and more questionable with increasing energy, but primarily the distillation of dynamical information encoded in the spectra—in the last years tremendous efforts have been made to develop techniques for recognizing patterns and hierarchical coupling in highly congested and complex spectra. We can broadly divide these techniques into statistical and dy-
namical. In the first category we classify methods which employ a special kind of sorting the spectral lines for pattern recognition. Among these techniques we mention the hierarchical tree method of Davis,8,9 and the extended crosscorrelation function method of Field and co-workers.9 The second category incorporates all semiclassical methods which try to establish a correspondence between quantum states and some classical objects.10 Once, such a correspondence has been achieved the extraction of dynamics is facilitated through visualization of the nuclear motions offered by classical mechanics.

The validity of semiclassical correspondence is still an open problem, especially at high energies where the classical dynamics turns to be predominantly chaotic. However, after the pioneering works of Gutzwiller11–13 and Heller,14,15 numerous numerical applications have demonstrated the importance of classical mechanics and especially of periodic orbits (PO) in understanding the localization of wave functions in configuration space, which in turn is helpful for understanding spectral patterns.16–19

The concept of POs for tracing the dynamical and spectroscopic characteristics of a polyatomic molecule becomes particularly powerful when it is applied in conjunction with continuation techniques in order to compute families of POs and their energy dependence.20 This then leads to the construction of continuation/bifurcation diagrams, which are exceedingly helpful for recognizing how spectra change from the bottom of the potential well to highly excited states. The usefulness of POs has been demonstrated for a number of triatomic molecules,19 and recently even for acetylene, a prototypical tetrameric molecule.21 A few interesting phenomena have been discovered such as the importance of saddle-node states22 and their connection to the isomerization processes as well as the phenomenon of complex instability.23 A molecule, for which the understanding of its energy spectrum—on the basis of only the bare quantum mechanical calculations—would be difficult without POs and their continuation/bifurcation diagrams, is HCP in its ground electronic state. In this article we demonstrate how these classical tools can be used to elucidate the patterns in the quantum mechanical spectrum of HCP calculated with an ab initio PES.

Recently, the dispersed fluorescence and stimulated emission pumping spectroscopy of phosphaethyne, HCP, performed by Ishikawa et al.,24 have raised attention. HCP is similar to HCN. Both of these molecules have linear equilibrium geometries, but they differ in the stability of their linear isomers. While CN–H is a stable isomer, CP–H corresponds to a saddle point on the potential energy surface. The latter has been confirmed by a number of ab initio calculations at several levels. Lehmann and co-workers25 carried out MP4 type calculations for the bending potential and showed that CP–H is a maximum and the same result has been obtained by us with CASSCF/MRSDCI calculations (Sec. II).

Electronic, vibrational, and rotational spectra of HCP have helped to determine the equilibrium geometries and spectroscopic constants of the ground and the first excited electronic states.25–29 In order to find signatures of large-amplitude angular motion, i.e., isomerization, Field and co-workers have exploited the A–X and C–X transition bands in an attempt to access high lying bending vibrational states.24 The former band is believed to follow the pure bending overtones (0,v2,0), with v2 ranging from 26 to 42, which span an energy interval of ~3 eV above the vibrational ground state. This energy regime is expected to be sufficiently high to allow large-amplitude motion of the H atom around CP.

By fitting the spectra to well known spectroscopic models for linear molecules it was established, however, that despite the energetic opening of a whole new portion of the coordinate space the spectrum is surprisingly regular, as was also found by Lehmann et al.25 some time ago. Nevertheless, two quite surprising observations were made which indicate that indeed a structural change from mainly H–CP to CP–H motion may be entangled. First, with v2 ≥ 32 perturbations of the pure bending overtones set in which were absent at lower excitations. Second, the vibrational fine structure constants of the (0,v2,0) levels change abruptly around v2 = 36. For example, the rotational constant B0 rises suddenly by about 8% from v2 = 34 to v2 = 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 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 could lead to the sudden turning on of perturbations as well as the abrupt changes in the fine structure constants.24

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 a recent communication (which will be referenced as paper I in what follows) we have presented some preliminary results from our classical and quantum mechanical calculations.30 The main result was the finding of two distinct families of bending states; one with wave functions 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 provided a clear-cut assignment. The different types of bending motion lead to distinctly different moments of inertia and therefore to different rotational constants. Even though the accuracy of the PES is not good enough to allow direct comparison with the experimental data, it is safe to conjecture that the experimental observations bear some relationship with our predictions of different types of bending motion.

Inspired by our results, Ishikawa et al.31 have performed new SEP experiments in the energy region of 13 400–17 500 cm−1 and indeed found strong evidence for the existence of two distinct families of bending states, which they attributed to normal-mode and isomerization-type states, as predicted by the periodic orbit analysis. These new experiments, in turn, encourage us to continue our the-
II. AB INITIO POTENTIAL ENERGY SURFACE

The HCP ground-state potential energy surface (PES) has been calculated by *ab initio* methods on the multireference configuration interaction (MRCI) level using all singly and doubly excited reference wave functions obtained by complete active space self-consistent field (CASSCF) calculations. A triple-zeta-polarization atomic basis set is employed. For the CASSCF calculations we have chosen 6 electrons and 7 orbitals as the active space giving rise to 142 and 260 reference configuration state functions for linear and bent nuclear geometries, respectively. The MRCI calculations then result in ~78 000 and 156 000 configurations for the two symmetry classes. The calculations have been performed with the MOLPRO program package.32

We have computed a total of 157 energies for different geometries sampling a large portion of the coordinate space, especially along the isomerization path. The points are subsequently fitted to an analytical expression of the Sorbie–Murrell form,33

\[ V(R_1, R_2, R_3) = V^{(3)}(R_1, R_2, R_3) + \sum_{i=1}^{3} V^{(2)}(R_i), \]  

with \( R_1, R_2, \) and \( R_3 \) being the HC, CP, and HP separations, respectively. The two-body terms are of the form

\[ V^{(2)}(R_i) = -D_i(1 + a_{1i}r_i + a_{2i}r_i^2 + a_{3i}r_i^3) \times \exp(-a_{1i}r_i), \]

where \( r_i = R_i - R_i^e \) and the \( R_i^e \) are the equilibrium bond lengths of the three diatoms. The three-body term is written as

\[ V^{(3)}(R_1, R_2, R_3) = V_{\text{PES}}^{(3)}(R_1, R_2, R_3) = \sum_{k} c_k P_k(s_1, s_2, s_3), \]

where the \( P_k(s_1, s_2, s_3) \) are functions in the variables

\[ s_1 = 0.4161 \delta_1 - 0.0975 \delta_2 + 0.9041 \delta_3, \]

\[ s_2 = -0.9060 \delta_1 + 0.0400 \delta_2 + 0.4213 \delta_3, \]

\[ s_3 = -0.0772 \delta_1 - 0.9944 \delta_2 - 0.0717 \delta_3 \]

(see Table II), and \( \delta_i = R_i - R_i^e \). The two-body parameters \( a_{1i}, a_{2i}, \) etc. and the coefficients \( c_k \) in Eq. (4) have been taken from Refs. 34 and 35. The coefficients \( c_k \) and the reference geometries \( R_i^e \) in the three-body term are fitted to the *ab initio* points. All parameters of the potential function are summarized in Tables I and II.

The subsequent classical and quantum mechanical calculations are performed in Jacobi coordinates \( R \), the distance from H to the center-of-mass of CP, \( r \), the CP separation, and \( \gamma \), the angle between the vectors \( R \) and \( r \) (with \( \gamma = 0 \) for linear HCP; see the inset in Fig. 2). In what follows all energies are quoted with respect to the minimum of H+CP \((r_e)\), i.e., the constant \( D_e^{\text{CP}} = 5.3568 \) eV is added to the full potential. In this normalization the energy at the equilibrium

<table>
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<th>TABLE I. Parameters of diatomic potentials.</th>
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<td>( \alpha_j/A )</td>
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</tr>
<tr>
<td>CH(( ^2\Sigma^+ ))</td>
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<td>CP(( ^2\Sigma^+ ))</td>
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<td>HP(( ^2\Sigma^+ ))</td>
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\[ V^{(3)}(R_1, R_2, R_3) = V_{\text{PES}}^{(3)}(R_1, R_2, R_3) = \sum_{k} c_k P_k(s_1, s_2, s_3), \]

(3)

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<table>
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<th>TABLE II. Parameters of the three-body potential.</th>
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<tr>
<td>( P_k(s_1, s_2, s_3) )</td>
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<tr>
<td>( s_1 )</td>
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<td>( s_{31} )</td>
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<td>( s_{33} )</td>
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</table>

\[ V_{\text{PES}}^{(3)}(R_1, R_2, R_3) = \sum_{k} c_k P_k(s_1, s_2, s_3), \]
coordinates of the CP–H saddle point are $2\,\text{g}$ and $2\,\text{h}$.

Figure 1. Contour plots of the HCP potential energy surface as functions of $r$ and $\gamma$ for fixed value of $R$ (a), $R$ and $\gamma$ for fixed value of $r$ (b), and $R$ and $r$ for $\gamma=0$ (c). Energy normalization is so that H+CP($r_0$) corresponds to $E=0$. The highest contour is for $E=0$ and the spacing is $\Delta E=0.5\text{ eV}$. Also shown are the projections of selected classical periodic orbits; (a) and (b) short dashes, [B], $E=2.509\text{ eV}$; long dashes, [r1A], $E=-2.500\text{ eV}$; solid line, [SN1A], $E=-2.582\text{ eV}$; (c) long dashes, $[\gamma]$, $E=-2.507\text{ eV}$; dashed–dotted line, $[R]$, $E=-2.501\text{ eV}$.

Two-dimensional contour plots of the HCP PES are depicted in Fig. 1. Note, that there is no minimum for the CP–H linear configuration but only a saddle point; the upper part of Fig. 1 is misleading, because $R$ is fixed in this representation. The potential contour along the minimum energy path in the angular coordinate is shown in Fig. 2; in order to calculate this energy profile, the potential has been minimized in $R$ and $r$ for a fixed value of $\gamma$. The energy and the coordinates of the CP–H saddle point are $-1.8935\text{ eV}$, $R=3.5634\,a_0$, $r=3.0904\,a_0$, and $\gamma=180^\circ$, respectively. For the subsequent discussion it is worth underlining that, as seen in Figs. 1(a) and 1(b) as well as in Fig. 2, the behavior of the PES changes quite dramatically in the angular interval between $60^\circ$ and $90^\circ$. This is the region where the bonding changes its character and H–CP begins to more and more go over to CP–H.

Neither the level of the ab initio calculations nor the number of calculated points and the analytical fit have been designed to reproduce the true PES near the equilibrium with greatest possible accuracy. Our focus is the vibrational dynamics of highly excited states near the H–CP↔CP–H isomerization. Therefore it does not come as a surprise that the fundamental excitation energies are reproduced only with modest success. The experimental energies for the second overtone of the bending mode, $0(20)$, and the first overtones of the CP stretching, $0(01)$, and the H–CP stretching, $1(00)$, modes are $1332.3\text{ cm}^{-1}$, $1280.9\text{ cm}^{-1}$, and $3216.9\text{ cm}^{-1}$, respectively (Table XI of Ref. 36). The corresponding calculated values are $1283\text{ cm}^{-1}$, $1234\text{ cm}^{-1}$, and $3330\text{ cm}^{-1}$. Two recently published ab initio calculations concentrate on the region around the equilibrium and therefore yield much better agreement with these experimental data.$^{37-39}$

III. PERIODIC ORBITS AND PHASE SPACE STRUCTURE

Periodic classical orbits (POs) are located by multiple shooting algorithms and by damped and quasi-Newton iterative methods.$^{40}$ According to the Weinstein and Moser theorems,$^{41,42}$ for a system with $N$ degrees of freedom there are at least $N$ families of periodic orbits, which emanate from the stable equilibrium points of the potential energy surface. These families are called principals and correspond to the $N$ different vibrational modes at energies not too high above the minimum. At a saddle point of a potential one can also find principal families of POs which, however, are unstable in those directions along which the potential descends. By following the evolution of the principal families with total energy, one can locate new families of POs, which bifurcate from the parent ones; they have either the same periods as the original POs or multiples of them. The theory of bifurcations of POs as well as their stability analysis is well developed, and the representation of numerical results is commonly given by a continuation/bifurcation diagram.$^{43-45}$
Periodic orbits are either stable or unstable. A periodic orbit is stable when trajectories, that are launched close to it, depart exponentially from the PO which is then called singly or doubly unstable, respectively. For systems with three or more degrees of freedom it may also happen that four eigenvalues are related to each other according to \( \lambda, 1/\lambda, \lambda^* \), and \( 1/\lambda^* \) with modulus different from one; the PO is then called complex unstable.

In Fig. 3(a) we show a projection of the continuation/bifurcation diagram of HCP in the \((E, r)\) plane. The diagram is constructed by plotting the initial value of one particular degree of freedom (the CP bond distance \( r \) in the present case) of the POs as a function of the total energy \( E \).\(^{46}\) If the energy of the system is changed smoothly, then the initial conditions of the PO are also expected to change smoothly, except at bifurcations. The actual shape of the curves in Fig. 3(a) is of course irrelevant; important are only the localizations of bifurcations of families of POs. Continuous lines in the figure represent stable periodic orbits, whereas dots mark unstable ones. We do not distinguish in this diagram the particular type of instability; we note however, that some families do show double and even complex instability, at least for small energy intervals as will be discussed later on. The lower part of Fig. 3 depicts the periods of the periodic orbits vs energy. In Table III we list the period and the initial conditions of the POs as a function of the total energy.

There are three principal families of POs, one for each normal vibrational mode. They will be denoted by \([R]\), \([r]\), and \([B]\), respectively (\(B\) stands for bending). Because of the linearity of HCP at the equilibrium point the two stretching periodic orbits, \([r]\) and \([R]\), are constrained to lie in the \(y=0\) plane for all times. The \([r]\)-type POs represent mainly motion along the CP bond \( r \), whereas \([R]\)-type POs show motion mainly along the H–CP stretch coordinate \( R \); examples are depicted in Fig. 1(c). For very low energies, the third principal PO illustrates motion predominantly along the bending angle \( \gamma \). At higher energies, however, it represents a

![FIG. 3. (a) Continuation/bifurcation diagram. Plotted is the variation of the initial CP stretching coordinate (Ref. 46) as function of energy. The continuous lines represent stable periodic orbits whereas the dots indicate unstable POs. See the text for more details. The arrow indicates the energy of the \((0,0,0)\) ground vibrational state. (b) The periods of the \([B]\)-, \([R]\)-, \([r]\)-, \([r1A]\)-, and \([SN]\)-type POs as functions of the energy.](image)

<table>
<thead>
<tr>
<th>PO</th>
<th>(E/\text{eV})</th>
<th>(T^a)</th>
<th>(R^b)</th>
<th>(r)</th>
<th>(\gamma)</th>
<th>(p_x)</th>
<th>(p_y)</th>
<th>(p_\gamma)</th>
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<td>([r])</td>
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<td>2.8870</td>
<td>2.396 178.3</td>
<td>1.920 793.4</td>
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<td>0.449 898 9</td>
<td>-1.103 293 1</td>
<td>0.000 000 0</td>
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<td>5.8350</td>
<td>2.446 729.7</td>
<td>1.856 564.6</td>
<td>0.106 422 2</td>
<td>0.129 082 9</td>
<td>-1.964 504 7</td>
<td>1.983 991 0</td>
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<td>2.577 725.5</td>
<td>1.545 207 1</td>
<td>0.000 000 0</td>
<td>1.078 571 3</td>
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<td>0.000 000 0</td>
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<td>2.6269</td>
<td>2.590 402.0</td>
<td>1.492 402 2</td>
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<td>0.000 000 0</td>
</tr>
<tr>
<td>([B])</td>
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<td>5.5700</td>
<td>2.119 118.6</td>
<td>1.467 732 0</td>
<td>0.230 794 2</td>
<td>-0.160 271 6</td>
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<td>2.227 777 0</td>
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<td>1.608 939 2</td>
<td>0.098 053 3</td>
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<td>-4.026 377 6</td>
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<td>9.9900</td>
<td>2.237 286 2</td>
<td>1.564 291 9</td>
<td>0.124 621 2</td>
<td>-0.061 508 8</td>
<td>-0.142 299 9</td>
<td>-4.484 219 0</td>
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<td>([SN3A])</td>
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<td>16.8320</td>
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<td>1.584 481 7</td>
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<td>-0.056 191 9</td>
<td>-4.599 228 1</td>
</tr>
</tbody>
</table>

\(^a\) One time unit corresponds to 10.18 fs.

\(^b\) Distances in Å, angle in rad, and masses in units of 1/12 of \(^{12}\)C.
mixture of bending and CP stretching motion as will be discussed below.

The family of \([R]\)-type POs remains stable up to about 3 eV above the bottom of the well. It becomes singly unstable at \(-2.454\) eV but turns stable again at \(-1.954\) eV. Then, it stays stable up to \(-0.707\) eV where again it becomes singly unstable. However, the real eigenvalue of the monodromy matrix never exceeds the value of 1.2, that is, the POs of type \([R]\) remain reasonably stable for almost the entire energy regime up to the dissociation threshold. A bifurcating family, denoted by \([R1A]\) (branch \(A\) of the first bifurcation), comes into existence at \(-2.454\) eV, where the \([R]\)-type POs become unstable for the first time. These POs are also confined onto the \(\gamma=0\) plane. The period of the new family is roughly twice as large as for the original \([R]\) PO.

The bend family, \([B]\), is also found to be stable up to energies close to dissociation. A prototype is shown in Figs. 1(a) and 1(b) and more examples can be found in Figs. 1 and 2 in paper I. The characteristic feature of these POs is their confinement to relatively small angles; they never explore angles greater than \(40^\circ-50^\circ\) irrespective of the total energy. This behavior seems to be counterintuitive; by pumping more and more energy into the bending mode one expects the bending-type orbit to follow the isomerization path in Fig. 1(b). However, that is not the case. Increasing the energy gradually pushes the orbit towards stretching of the CP mode rather than increasing \(\gamma\). This rather unexpected behavior is the result of strong mixing between the bending and the CP stretching mode.

Contrary to the other two principal families, the \([r]\) family shows an early bifurcation at \(-4.872\) eV, i.e., only \(0.358\) eV above the minimum. For comparison, the energy of the ground vibrational state is \(-4.866\) eV, that is, the bifurcation occurs even below the lowest quantum mechanical state. (In the next section we shall show that there are no quantum mechanical states with wave functions following the \([r]\)-type PO.) At the bifurcation point a pair of eigenvalues of the monodromy matrix is equal to \(-1\), i.e., this is a bifurcation by reflection, and we denote the bifurcating family as \([r1A]\) (branch \(A\) of the first bifurcation). Beyond the point of bifurcation the \([r]\) family becomes singly unstable and remains singly unstable up to \(+0.401\) eV. However, the real eigenvalue of the monodromy matrix, which characterizes the degree of the instability of these POs, never exceeds the value of \(1.74\). The bifurcating POs, \([r1A]\), are stable and remain stable up to \(-2.056\) eV, where they abruptly cease to exist. Actually, from the bifurcation diagram we can see that the \([r1A]\) family originates from a reverse saddle-node bifurcation occurring at the energy of \(-2.056\) eV. Here it merges with a branch of unstable periodic orbits, which is termed \([r1B]\). We found it very difficult to propagate this unstable branch backwards in energy. Numerical difficulties arose because of nearby unstable POs which cause problems in the convergence of the Newton–Raphson procedure, rather than the magnitude of the instability of the \([r1B]\)-type POs. In contrast to the \([r]\) POs, the POs of type \([r1A]\) are not confined to the \(\gamma=0\) plane but sample regions of coordinate space with nonlinear geometries. Actually, they are symmetric with respect to \(\gamma=0\) and therefore their period is roughly twice the period of the \([r]\) POs [see Fig. 3(b)]. An example is shown in Figs. 1(a) and 1(b) (see also Figs. 1 and 2 in paper I). They show a behavior in the \((r,\gamma)\)-plane, which is opposite to the behaviour of the \([B]\)-type POs.

As seen in Table III as well as Fig. 3(b) the periods of the \([B]\) and \([r1A]\) POs are almost identical; the same is obviously true for the quantum mechanical frequencies belonging to the states, which correspond to these POs. It is this accidental coincidence of periods which causes the resonance and polyad structure governing the entire HCP spectrum up to high energies. It is important to underline that the \([r1A]\) POs, like their counterparts of type \([B]\), are confined to small bending angles. In other words, none of the periodic orbits emanating from the bottom of the well samples the isomerization path.

The first POs that extend to angles larger than \(40^\circ\), i.e., towards the CP–H side of the PES, are found to occur suddenly at an energy of \(-3.1526\) eV or \(2.08\) eV above the bottom of the well. They emerge from a saddle-node (SN) bifurcation and therefore we denote them as \([SN1]\). There are again two branches, a stable one, which will be denoted by \([SN1A]\), and an unstable one, \([SN1B]\), which we did not follow as function of \(E\). A representative example for branch \(A\) is depicted in Figs. 1(a) and 1(b) (see also Figs. 1 and 2 in paper I). The \([SN1]\)-type POs follow closely the minimum energy path in the \((r,\gamma)\)-plane. However, in contrast to the \([B]\)- and \([r1A]\)-type periodic orbits they show only little variation in the \(r\) coordinate, less than about \(0.2\) a.u.

The originally stable POs of the \([SN1A]\) family become singly unstable at \(-2.927\) eV, change into complex unstable at \(-2.899\) eV, and then become again stable at \(-2.781\) eV. Finally, they become once more singly unstable at \(-2.668\) eV and remain singly unstable up to the highest energy we have followed them. The \(SN1\) branch does continue to energies higher than shown in Fig. 3. However, it becomes more and more difficult to find these types of trajectories and therefore we did not systematically follow the \(SN1\) branch any further. At higher energies we have located additional saddle-node bifurcations at \(-2.612\) eV and \(-2.522\) eV, giving rise to new types of periodic orbits. These POs, which are denoted as \([SN2]\) and \([SN3]\), penetrate deeper and deeper into the CP–H hemisphere. The \([SN3]\)-type POs show some oscillatory behaviour in the \((r,\gamma)\)-plane close to their turning points at larger angles. From Fig. 3(b) it is apparent that, in contrast to the \([B]\)- and \([r1A]\)-type orbits, the periods of the orbits of the \([SN1]\) and \([SN2]\) families strongly increase with energy. This is readily understandable because the \([SN]\) orbits extend to larger and larger angles where the potential becomes gradually flatter (see Fig. 2).

The overall dynamical behavior of HCP, as it emerges from the continuation/bifurcation diagram, is rather regular, despite the early appearance of a bifurcation and the approximate 1:1 relationship between the vibrational periods of the \([B]\)- and the \([r1A]\)-type POs. Instability is developed at relatively high energies and only when the bending angle extends well into the CP–H side of the potential. Because the bending family remains stable for the entire energy interval.
studied, the unstable regions in phase space are essentially related to the unstable \([r1B]\) family. We will show in the next section that the POs are extremely useful for understanding the quantum mechanical wave functions and their development with energy.

IV. VIBRATIONAL LEVELS AND EIGENFUNCTIONS

A. Variational calculations

We have performed quantum mechanical variational calculations for determining the vibrational energies as well as the corresponding wave functions. The total angular momentum is \(J=0\) in all cases. The Hamiltonian is represented in a highly contracted/truncated 3D basis as described in detail in Ref. 48. The variational program requires basically two parameters. The energy \(E_{\text{cut}}\) up to which all internally contracted basis functions are included and the maximal distance in the dissociation coordinate, \(R_{\text{max}}\). All other parameters are chosen automatically. In the present calculations we used \(E_{\text{cut}}=-0.2\;\text{eV}\) and \(R_{\text{max}}=7.5\;\text{a0}\) resulting in about 9000 basis functions. The estimated error due to limitations of the basis size is less than 1 meV for levels up to 3 eV above the bottom of the well, the energy region most interesting for the present study. Since our PES does not have spectroscopic accuracy, slight errors in the vibrational energies are not considered to be crucial. It is well known that wave functions converge more slowly than energy levels. Nevertheless, we are confident that the main results of this work are not affected by convergence problems as calculations with fewer basis functions have demonstrated.49,50

We have visually examined, by both 2D projections and 3D representations, the lowest 700 wave functions in an attempt to assign the vibrational levels. As we will demonstrate, the spectrum is straightforwardly assignable up to an energy of roughly \(-3\;\text{eV}\), i.e., \(2.25\;\text{eV}\) above the minimum. Around this energy regime some of the wave functions begin to behave drastically differently, which gradually complicates an unique assignment. Interestingly, this is the same energy regime, in which the saddle-node POs, \([\text{SN}1]\), suddenly come into existence. In the following subsections we will describe the assignment of the levels and the relationship between the localization of the quantum wave functions on one hand and the periodic orbits on the other. The effect of the different behaviors of the wave functions on the rotational constants will be elucidated in the next section.

In the subsequent discussion we will use the following notation: \(v_1, v_2\), and \(v_3\) are the H–CP stretch mode associated with \(R\), the bending mode, and the CP stretch mode related to motion in \(r\), respectively. As mentioned in Sec. III, the periods associated with the \([r1A]\)- and the \([B]\)-type POs are very close, and therefore both types of orbits show a strong mixing of CP-stretching and bending motion. The same resonance effect obviously governs the quantum mechanical dynamics with the consequence that the wave functions are arranged in the \((r,\gamma)\)-plane rather than along the angular axis or the CP stretching mode. Therefore, the assignment in terms of bending and CP stretching states is quite arbitrary (see below). As will become apparent later on, the wave functions of the two progressions \((0,v_2,0)\) and \((0,v_2,3)\) qualitatively behave in a similar way as far as the symmetry with respect to linearity is concerned. For this reason we prefer an assignment which treats both modes correspondingly and therefore we identify in both cases the quantum numbers \(v_2\) and \(v_3\) with the number of nodes along the ‘backbone’ of the respective wave functions in the interval \([0\leq \gamma \leq \pi]\). This facilitates, as we think, the subsequent discussion. Thus, in order to compare with the usual nomenclature for a linear molecule (including the notation used by us in paper I) the quantum number \(v_2\) has to be multiplied by 2.

B. Polyad structure

The energy spectrum of HCP is governed by a pronounced anharmonic resonance between the bending and the CP stretching modes leading to a distinct polyad structure in the energy level spectrum. This resonance and the corresponding mode mixing is intriguingly illustrated by continuously changing one parameter in the Hamiltonian, for example the mass of the hydrogen atom.6,51 In Fig. 4(a) we plot the excitation energies [measured with respect to the \((0,0,0)\) ground vibrational state] for the two lowest excited states as a function of \(m_X^{1/2}\) from \(m_X=0.7\) to \(\approx 1.6\) \((m_X\) is measured in terms of the mass of the hydrogen atom). The CP stretching frequency is, in a diatomic sense, almost independent of the mass of the attached atom X, whereas the bending frequency varies approximately linearly with \(m_X^{1/2}\). However,
according to Wigner’s noncrossing rule, the two energy curves are not allowed to cross and therefore are forced to avoid each other. The resulting avoided crossing occurs (accidentally) around \( m_X \approx 1.1 \), i.e., just in the region of HCP.

At small values of \( m_X \) the CP stretching (bending) state is the lower (upper) one and the wave function is clearly aligned along the \( r \)-\( (\gamma) \)-axis (see Fig. 5 and Ref. 52). As the mass of the atom \( X \) increases these two local-mode wave functions mix which results in a rotation in the \((r, \gamma)\)-plane. At larger values of \( m_X \) the wave functions are again aligned along either the one or the other axis and the assignment in terms of local modes is again straightforward.

The effect of mixing is also illustrated by the variation of the expectation values of the kinetic energies in coordinates \( x = r \) or \( y \). The lower part of Fig. 4 depicts \( T_r \) as a function of \( m_X \), for the two states considered. The location of the avoided crossing at \( m_X \approx 1.1 \) is well predicted by this quantity. In view of this figure it appears that for HCP the upper state has more character of bending motion and therefore should be assigned as \((0, 1, 0)\), while the lower state has more character of motion along \( r \) and thus must be assigned as \((0, 0, 1)\). This nomenclature is in accordance with the experimental assignment.\(^{36}\)

Incidentally we note that for HCP there is no state with nodes aligned purely along the \( r \) axis, which is in accord with the bifurcation into \([r]\) and \([r1A]\)-type POs occurring very early, below the vibrational ground state.

The two adiabatic wave functions can be approximately represented by linear combinations of zero-order or local-mode type wave functions according to

\[
\Psi_1(r, \gamma) = \cos \eta \ \phi^{(1)}_{k=1}(r) \phi^{(1,0)}_0(\gamma) - \sin \eta \ \phi^{(1)}_{k=0}(r) \phi^{(1,2)}_0(\gamma),
\]

\[
\Psi_2(r, \gamma) = \sin \eta \ \phi^{(1)}_{k=1}(r) \phi^{(1,0)}_0(\gamma) + \cos \eta \ \phi^{(1)}_{k=0}(r) \phi^{(1,2)}_0(\gamma),
\]

where \( \eta \) is the mixing angle and \( \phi^{(1)}_{k}(r) \) and \( \phi^{(1,0)}_{0}(\gamma) \) are one-dimensional oscillator wave functions in \( r \) and \( \gamma \) with \( k \) and \( l \) quanta, respectively. The wave functions for HCP are well represented by \( \eta = \pi/4 \).

Because of the resonance in the bending and the CP stretching frequencies, the energy spectrum of HCP consists of well defined polyads \((v_1, P - n, n)\) with polyad quantum number \( P = v_1 + v_3 \). Figure 6 shows a portion of the spectrum in the energy region of \( P = 8-10 \). Each polyad, for a fixed value of \( v_1 \), consists of \( P + 1 \) levels. The highest one, \((v_1, P, 0)\), is the pure overtone of the bending mode, while the lowest member \((v_1, 0, P)\) is the overtone of the CP stretching mode associated with \( r \). In order to illustrate the development of the nodal pattern in the low-energy regime we show in Fig. 7 wave functions in polyads \( P = 1-3 \). The relationship of the \((0, P, 0)\) and the \((0, 0, P)\) wave functions is clearly seen. The potential plot also includes the POs of the \([B]\)- and the \([r1A]\)-type for the energies of the states (0,3,0) and (0,0,3), respectively. As expected, they follow closely the “backbone” of the corresponding wave functions.\(^{19}\)

In full accordance with the classical calculations, both the bending wave functions as well as the CP stretch wave functions are well confined to small angles and this does not change when the energy increases. They do not follow the minimum energy path in the \((R, \gamma)\)-plane but are more and more pushed aside, to larger respectively smaller values of \( r \). The first wave functions that extend well beyond \( 40^\circ \) correspond to the \([SN]\)-type periodic orbits found in the classical analysis. How these states emerge as a function of energy and how they fit into the polyad structure described above is the topic of the next subsection.

Vibrational resonances and polyads are well known topics in molecular spectroscopy (see Refs. 53 and 54, and references therein). We described the polyad structure for HCP.
in some detail in order to highlight the structural changes that occur at higher energies.

C. The genesis of saddle-node states

All states up to \( P = 12 \) can be—without any real problems—uniquely assigned. In order to illustrate how the wave functions change, within a given polyad, from the lowest to the highest level, we show in the upper panel of Fig. 8 selected wave functions for \( P = 10 \). The transition from \((0,10,0)\), the highest state in this polyad, to \((0,0,10)\), the lowest level, is very "smooth." Coming from the top of the polyad, the number of nodes in the \([r1A]\)-type mode gradually increases at the expense of the number of nodes in the \([B]\)-type mode. Between states \((0,6,4)\) and \((0,4,6)\) the overall character of the wave function changes from predominantly \([B]\) to \([r1A]\) type. As we have shown in paper I, the backbone of the wave functions closely follow the \([B]\) and the \([r1A]\) POs (see also Fig. 7). The assignment in terms of two quantum numbers \( v_2 \) and \( v_3 \) is straightforward; \( v_1 \) is zero for all these examples. Polyad \( P = 11 \) behaves in an almost identical manner.

All the wave functions for \( P = 12 \), shown in the lower panel of Fig. 8, are still more or less straightforwardly assignable in terms of nodes along their backbone. However, careful inspection reveals that the nodal pattern of the lower members, e.g., \((0,1,11)\)–\((0,4,8)\), are slightly distorted in comparison to the corresponding \( P = 10 \) wave functions. While all wave functions for \( P = 10 \) are directed either "up" (towards larger values of \( r \)) or "down" (towards smaller values of \( r \)), thereby avoiding the isomerization path, the wave functions at the bottom of polyad \( P = 12 \) show some tendency for pointing to larger angles, i.e., in the direction of the CP–H channel. States with a new type of bending wave functions are about to emerge! The lowest member, \((0,0,12)\), however, has again the expected clear structure as all other \((0,P)\) wave functions for \( P = 11 \).

Something really new begins with \( P = 13 \). This can be seen both in the energy-level structure, Fig. 9, and in the wave functions, Fig. 10. While for \( P \leq 12 \) all polyads are complete, i.e., there are \( P + 1 \) levels, with \( P = 13 \) they begin to become "incomplete." What do we mean by that? At the lower end of this polyad, where the lowest state for \( P = 13 \), \((0,0,13)\), is expected, there is no state which would readily fit into the \((0,P = 13)\) scheme. There is a level with a slightly lower energy. However, its wave function does not have the general shape of \((0,0,P)\)-type wave functions observed for \( P \leq 12 \) (see Figs. 7 and 8). While the \((0,0,P \leq 12)\) wave functions show curvature in the \((r,\gamma)\)-plane, this wave function runs almost parallel to the \( r \) axis, but at the same time clearly extends to larger angles. It is very much reminiscent of the \([SN]\)-type POs discussed above (see Fig. 14 and paper I) This wave function has 13 nodes along its backbone and therefore we include it to the \( P = 13 \) polyad, despite the fact that its energy does not fit to the polyad structure. However, one should keep in mind that this state is somewhat different. In order to distinguish it and other examples from the "pure" \((v_1,v_2,v_3)\) states we will use the index \( SN \).
first clear-cut SN-type state occurs at an energy just slightly higher than the first [SN]_type PO (Fig. 2).

The trend observed for $P=13$ continues to higher polyads and actually becomes even more pronounced. For example, for $P=14$ already two states are missing at the lower end of this polyad, $(0,1,13)$ and $(0,0,14)$. There are two pairs of levels at significantly lower energies, which cannot be clearly assigned (Nos. 246 and 248, respectively, 254 and 255). One level of the lower pair is certainly $(0,0,14)$ SN, and one level of the upper pair is state $(0,1,13)$ SN. However, due to substantial mixing with states of the $P=11$ polyad with $v_1=1$ the corresponding wave functions have a very bizarre nodal structure.

For $P=15$ three levels are missing at the lower end of the polyad. At the same time two states of the $(1,P=12)$ polyad are absent. Altogether, there are now five states in this energy regime, which do not readily fall into the polyad structure as it is found at lower energies. The wave functions, three of which are plotted in the lower panel of Fig. 10, all have a clear [SN]-type behavior and are assigned to $(0,0,15)$ SN, $(0,1,14)$ SN, and $(0,2,13)$ SN. The remaining two states are assigned to $(1,0,12)$ SN and $(1,1,11)$ SN. This kind of evolution continues at higher energies, that is, more and more states at the lower end of a polyad turn into [SN]-type states. However, because the density of states and therefore the mixing between states gradually increases, the assignment becomes more and more tedious and fewer and fewer states can be uniquely assigned.

Close inspection of the wave functions has revealed that starting with polyad $P=13$ the lower states of a polyad gradually change their character from $[r_1A]$- to [SN]-type. The onset of this new type of behavior is reflected also by the energy dependence of the various progressions. Figure 11 depicts the energy levels for the two progressions $(0,P,0)$ and $(0,0,P)$.
and (0,0,P); according to the discussion above, the (0,0,P >12) states are really (0,0,P)\text{SN} states. The (0,P,0) progression shows a rather small anharmonicity up to very high levels. This is in line with the observation that the period of the corresponding \([B]\) PO does not change much with energy. The other progression, (0,0,P), is slightly more anharmonic with the result that the gap between the two ladders slowly increases. It exists only up to \(P=12\), where the \((0,0,P)\text{SN}\) progression abruptly sets in. The latter is highly anharmonic, which explains why the corresponding levels do not fit well into the general polyad structure but appear at significantly lower energies than expected. The \([\text{SN}]\)-type wave functions have a completely different structure than the \([r1A]\)-type wave functions and extend more towards the isomerization path. Since the potential becomes gradually flatter along the minimum energy path, it is not surprising to observe a significant reduction in the energy spacing and therefore an increase of the anharmonicity (see Fig. 2).

The dashed line in Fig. 11 is an extrapolation of the \([r1A]\) progression derived from a fit to the energies up to level (0,0,12). It appears that the structural change of the wave functions begins just where the (0,0,P) and the (0,0,P)\text{SN} curves "bifurcate." Expressed differently, while climbing up the ladder, the quantum mechanical wave functions follow the \([\text{SN}]\)-type path rather than the \([r1A]\) route at the bifurcation.

The structural change of the states is also encoded in the energy spacing between adjacent levels, \(\Delta E_P(n)=E_{(0,P-n,n)}-E_{(0,P-n-1,n+1)}\), within a particular polyad. For the lower polyads \(\Delta E_P(n)\) monotonically increases from the lowest to the highest level as can be seen in Fig. 12, i.e., the spacing is smallest at the bottom of a polyad and largest at the top. This monotonic behavior holds true up to \(P=9\) and 10. Starting with \(P=11\), \(\Delta E_P(n)\) becomes nonmonotonic having a minimum at \(n=9\). This minimum shifts to \(n=11\) for \(P=13\) and then stays at 11. The two different branches for the higher polyads indicate the change from the \([r1A]\) - to the \([B]\)-type behavior at the lower end of a polyad. Whether this minimum in the energy spacing has the same origin as the one predicted in the effective Hamiltonian analysis of Kellman and co-workers\(^{53}\) has to be investigated in the future.

Up to now we exclusively analyzed levels without excitation in the third coordinate, \(R\). The general behavior discussed for the \(v_1=0\) states does not qualitatively change when \(v_1\neq 0\). Around the same energy, where the \((0,v_2,0)\) states show a transition from the \([r1A]\)-type wave functions to the \([\text{SN}]\) wave functions, the wave functions for states with excitation in \(R\) show a similar change. Examples for two polyads, \((1,P=12)\) and \((2,P=10)\), are depicted in Fig. 13. However, in comparison with the \(v_1=0\) states the transition occurs more gradually and not so abrupt. Thus, although the polyad structure and the change of the structure of the molecule is not strongly dependent on \(R\), the motions in \(r\) and \(\gamma\) on one hand, and in \(R\), on the other, are not completely decoupled. The distinctly different level spacings within polyads for different quantum numbers \(v_1\) further support this conjecture (see Figs. 6 and 9).\(^{56}\)

Despite the fact that substantial mixing of all three modes gradually prohibits the complete assignment of states for higher and higher energies, it is possible to assign all of the \([B]\)-type and most of the \([\text{SN}]\)-type overtones. In Table IV we list the energies and the energy differences, \(\Delta E\), between adjacent levels of the \((0,v_2,0)\) and the \((0,0,v_3)\text{SN}\) states. Examples of higher-order \([\text{SN}]\)-type wave functions are depicted in Fig. 14. It is clearly seen how the \([\text{SN}]\)-type wave functions penetrate deeper and deeper into the CP–H hemisphere of the PES as the energy increases. For comparison we show one \([\text{SN}]\) PO in the upper two panels together with a contour plot of the potential. Because at these high energies several families of \([\text{SN}]\) orbits coexist, it is not clear which type corresponds to a particular wave function. For the \((0,v_2,0)\) states \(\Delta E\) decreases in a very regular manner with increasing quantum number, which indicates that this progression is very robust and is not significantly perturbed by coupling to other modes. In contrast, \(\Delta E\) for the \(\text{SN}\) states has a less gradual dependence. In view of the energy spacings there seem to be at least two different families of \(\text{SN}\)-type states; a third one might begin with the highest overtone considered, which we reluctantly assigned to \((0,0,26)\text{SN}\) (unclear assignments are put in double brackets). Since the states \((0,0,14)\text{SN}\), \((0,0,19)\text{SN}\), and \((0,0,25)\text{SN}\) are missing in the table (because of substantial mixing with other states, the wave functions do not have a clear nodal structure), the overall picture is somehow blurred. Although a direct correlation

![FIG. 12. Energy spacing between adjacent levels within a particular polyad, \(\Delta E_P(n)\), as function of \(n\). \(n=0\) marks the top of the polyad. (See text for further details.)](image-url)
of wave functions and POs of the different [SN]-type or energy spacings and classical periods is difficult, the rather abrupt change of the energy spacing in the saddle-node states indicates that the quantum mechanical states are indeed influenced by the different [SN]-type classical orbits.

V. ROTATIONAL CONSTANTS

In a spectroscopic experiment one measures energy differences rather than wave functions. Information about the structure of a particular vibrational state can be extracted only indirectly from intensities or, more precisely, from fine structure constants such as, for example, rotational constants. In the case of HCP, the two quite different bending motions, represented by the \([B]\)- and the \([rA]\)-type wave functions, on one hand, and wave functions with [SN] character, on the other, result in substantially different rotational constants and therefore rotational constants are helpful quantities for identifying different structures of vibrational states.\(^3\)

In the present work we determined the rotational constants for each of the 700 vibrational levels by calculating the expectation values of the inverse of the moments of inertia with the \(J=0\) eigenfunctions. The moments of inertia have been calculated by diagonalizing the inertia tensor. Of course, this procedure for calculating rotational constants is an approximation and effects due to modifications of the vibrational wave functions as a consequence of overall rotation and 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, \(B_{\text{rot}}\), is close to the spectroscopic \(B_0\) measured by Ishikawa \textit{et al.}\(^2\)

In general, the \(B_{\text{rot}}\) values for the states with wave functions of the [SN]-type are substantially larger than those for the \([B]\)- and \([rA]\)-type states. The differences can be qualitatively explained in terms of the quite different amplitudes of bending motion for the three families of states. The main contribution to the moment of inertia results from rotation of CP around the axis, while the contribution from the much lighter H atom is exceedingly smaller. However, in the case of the small-amplitude angular motion of the \([B]/[rA]\) states, the hydrogen atom is always far away from the rotation axis with the result that its contribution is not negligible, but of the order of at least a few percent of the contribution of 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 (\(\gamma=90^\circ\)) so that its net contribution is indeed unimportant. Since the rotational constant is proportional to the inverse of the moment of inertia, the \([B]/[rA]\) states have a rotational constant which is a few percent smaller than for the [SN] states.

First, we consider the variation of \(B_{\text{rot}}\) inside a particular polyad. In Fig. 15(a) we plot \(B_{\text{rot}}\) for states \((0,P-n,n)\) with \(n=0\) (the highest member of the polyad) through \(n=P\) (the lowest member of the polyad). For small values of \(P\), the rotational constant monotonically decreases with \(n\) from the top to the bottom of the polyad, with the exception of the lowest level. This general behavior can be qualitatively explained by the more or less monotonic decrease of the expectation value \(\langle \gamma \rangle\) from state \((0,P,0)\) to \((0,0,P)\) (see for

---

**TABLE IV.** Assigned overtone states of the \([B]\) and the [SN] type.

<table>
<thead>
<tr>
<th>([B]) State</th>
<th>(E/\text{cm}^{-1})</th>
<th>(\Delta E/\text{cm}^{-1})</th>
<th>([\text{SN}]) State</th>
<th>(E/\text{cm}^{-1})</th>
<th>(\Delta E/\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0,0)</td>
<td>0</td>
<td></td>
<td>(0,13,0)</td>
<td>16 931</td>
<td>1720*</td>
</tr>
<tr>
<td>(0,1,0)</td>
<td>1 283</td>
<td>1283</td>
<td>(0,16,0)</td>
<td>19 421</td>
<td>739</td>
</tr>
<tr>
<td>(0,2,0)</td>
<td>2 568</td>
<td>1285</td>
<td>(0,18,0)</td>
<td>20 493</td>
<td>1272</td>
</tr>
<tr>
<td>(0,3,0)</td>
<td>2 690</td>
<td>1272</td>
<td>(0,20,0)</td>
<td>21 428</td>
<td>769</td>
</tr>
<tr>
<td>(0,4,0)</td>
<td>5 124</td>
<td>1274</td>
<td>(0,22,0)</td>
<td>22 458</td>
<td>320</td>
</tr>
<tr>
<td>(0,5,0)</td>
<td>6 388</td>
<td>1264</td>
<td>(0,24,0)</td>
<td>23 625</td>
<td>277</td>
</tr>
<tr>
<td>(0,6,0)</td>
<td>7 639</td>
<td>1251</td>
<td>(0,26,0)</td>
<td>24 721</td>
<td>896</td>
</tr>
</tbody>
</table>

*The italic numbers do not correspond to nearest neighbors spacings.
example polyad $P = 3$ in Fig. 7). The smaller $\langle \gamma \rangle$ the larger is the distance of H from the rotation axis and, as a consequence, the smaller is the rotational constant. With increasing polyad quantum number the behavior changes slightly in that $B_{rot}$ first stays approximately constant before it decreases near the lower end of the polyad.

The overall picture changes quite substantially with $P = 12$ where the perturbations of the wave functions in the low-energy portion of the polyad become more distinct. The rotational constants for states $(0,2,10)$ and $(0,1,11)$ are much larger than they are expected to be. The corresponding wave functions shown in Fig. 8 have some clear admixture of SN character, which explains this increase of $B_{rot}$. State $(0,0,12)$ is again a "normal" $[r1A]$ state and its rotational constant is again much smaller than for the next two higher levels. The first real [SN]-type state occurs in the $P = 13$ polyad and for reasons discussed above the corresponding rotational constant is significantly larger than the constants for all lower states. Figure 15(a) shows, for $P = 10$, similar results for states with excitation in the $v_1$ mode. With increasing excitation in the H–CP stretching mode the transition from $[B]$- or $[r1A]$-type behavior to [SN]-type behavior occurs at higher and higher members in the polyad (smaller values of $n$) and the rotational constants clearly show this. In conclusion, the rotational constant reflects in a remarkable manner the structure of the vibrational states, especially the extent of the angular motion.

In Fig. 16(a) we plot the rotational constants for the 700 lowest states as a function of energy. One can clearly distinguish two regimes: States whose $B_{rot}$ constants are below the rotational constants belonging to the $(0,P,0)$ progression and states above this borderline. The $(0,P,0)$ states can be uniquely identified up to very high energies and their rotational constants vary exceedingly smoothly with $P$ [Fig. 16(b)]. In accord with experiment they first rise with en-
energy and then monotonically decrease with $P$. The $B_{rot}$ values for progression $(0,0,P)$ monotonically decrease with $P$ up to $P=12$. In accord with our calculations, the measured value for $(0,0,1)$ is slightly lower than the rotational constant for the vibrational ground state (Table VIII in Ref. 36). As discussed in Sec. IV the $(0,0,P)$ progression only extends to $P=12$. State $(0,0,13)$ is of the [SN] type and because of the essentially different angular shape, this state has a much larger rotational constant. States $(0,0,14)$ and $(0,0,19)$ are strongly perturbed and therefore not included in the progression. The many states between the $(0,P,0)$ progression on one hand and the $(0,0,P)_{SN}$ progression on the other have more or less pronounced [SN] character and therefore rotational constants which are larger than those for the pure $[B]$-type states.

Except for the lower states of the $(0,P,0)$ progression, the rotational constants for states $(0,P,0)$ and $(0,0,P)$ decrease with energy. This behavior can be explained by the continuous increase of the expectation value of the CP stretching coordinate, $\langle r \rangle$, with the degree of excitation. On the other hand, $\langle r \rangle$ remains approximately constant with $P$ for the [SN] states and so does the corresponding $B$ value.

**VI. DISCUSSION**

Demonstrating how the vibrational energy spectrum of HCP, a relatively simple triatomic molecule, changes with energy and how new types of motions appear when climbing up the ladder were the main purposes of the foregoing sections. Classical mechanics, especially the concept of periodic orbits and their continuation/bifurcation diagram, have been proven to be exceedingly helpful in understanding the development of the quantum mechanical states. Nevertheless, if one wants to obtain a clearest picture, it is absolutely necessary to visually inspect all wave functions, even though that is a tremendous task. Automatic assignments in terms of, for example, projections of wave functions on zero-order wave functions, works at low energies, but is bound to fail when mixing of (zero-order) states becomes too strong.

The most surprising finding was the gradual change of the polyad structure at the bottom of the polyad, when the states $(0,0,P)$ with wave functions quite restricted in the H–C–P bending angle turn into $(0,0,P)_{SN}$ states, whose wave functions have a completely different bending behavior. Although this transition sets in rather abruptly in a narrow energy regime, early signs of these structural changes are already found at lower energies. The onset of this change is accurately predicted by classical mechanics in form of the birth of saddle-node periodic orbits. In contrast to classical mechanics where the [SN]-type POs come into existence at a precise energy, in quantum mechanics the structural change is, as expected, somehow smeared out. It should be noted that the $[r1A]$-type wave functions do not completely cease to exist. At higher energies one can find wave functions that have, if the contours plotted are chosen in a special way, the character of $(0,0,P)$ wave functions. However, the examples found by us were strongly mixed with other states in the energetic proximity. In other words, quantum mechanics still “feels” the existence of the underlying $[r1A]$ POs.

There are several interesting questions to be asked and classical mechanics can provide possible answers to them. First, why does the change begin at the bottom of the polyads and not at the top, i.e., why do the $(0,0,P)$ states turn into the saddle-node wave functions rather than the $(0,P,0)$ levels? We think the answer to this question has to do with the different stabilities of the $[B]$- and $[r1A]$-type POs. The $[B]$ periodic orbits and likewise the corresponding wave functions are comparably robust and exist up to very high energies; in addition the anharmonicity is quite small in this mode. One reason for this pronounced stability might be the existence of the potential trough seen at small angles and larger CP bond distances (Fig. 1), which—loosely speaking—“guides” the $[B]$ orbits. The sibling POs of the $[r1A]$-type avoid this region of the PES and intuitively are expected to be less stable. Actually, they eventually cease to exist at around $-2$ eV, an energy where the $[B]$ orbits are still intact. Moreover, the classical bifurcation analysis showed that there is a second branch of trajectories, $[r1B]$, which are unstable and therefore create regions of instability in their neighborhood. Thus, it appears that first the quantum mechanical states, which follow the less stable POs, change their character.

Second, why do the SN POs and the corresponding quantum states come into existence so suddenly with energy? According to general results of non-linear dynamics
theories, saddle-node bifurcations occur as a consequence of tangencies of the stable and unstable manifolds of unstable periodic orbits. As predicted by the Newhouse theorem, when these invariant objects (the manifolds) touch each other, new periodic orbits emerge. By way of this mechanism classical trajectories find ways to penetrate into regions of phase space, which were not sampled by periodic orbits at lower energy. Characteristic examples are the saddle-node bifurcations which appear above potential barriers. The unstable POs that originate at the top of the barrier give rise to periodic orbits which can visit the minima on both sides of the barrier. The remarkable observation is that these saddle-node POs create stability in otherwise highly unstable regions of phase space. Studies like the present one demonstrate how quantum mechanics can “recognize” these regions and accommodates the eigenfunctions accordingly.

Saddle-node bifurcations may also appear inside potential wells when the curvature of the potential changes abruptly. This is the case for HCP. As we can see from Fig. 2 the saddle-node bifurcations emerge when the minimum energy path signals changes in the slope of the PES. It is really astonishing that the quantum mechanical states of the SN type appear at about the same energies and show distinct progressions with different energy spacings. This underlines the strong influence the different [SN]-type POs have on the quantum mechanical world.

The third question concerns the relative importance of kinetic energy coupling and coupling of the modes due to the potential. In the initial phase of our study we believed that it is the pronounced potential trough mentioned above that explains the bowed shape of the \( B \)-type POs and the corresponding wave functions. However, if that were true, how can we explain—in terms of the shape of the PES—the particular form of the \( r1A \) POs and wave functions? In doing the mass variation study discussed in Sec. IV we found out that the interplay between the kinetic energy term and the potential is important. In Fig. 17 we show wave functions for HCP in polyad \( P = 10 \) in comparison to the corresponding wave functions for DCP. Although there is some mixing between \( r \) and \( \gamma \), the wave functions for DCP have a much stronger local-mode character, i.e., they are much better aligned along the \( r \) and the \( \gamma \) axis. The \( (0, P, 0) \) bending states extend along the isomerization path and this behavior is not just found at high energies but even for the lowest excited states.

A detailed discussion of DCP will be published at a later date.

The accuracy of our PES is not sufficient to compare directly the calculated transition energies and rotational constants with the experimental results. For example, the discrepancy for the fundamental of the \( (0, P, 0) \) progression is 53 cm\(^{-1}\), which accumulates up to about 300 cm\(^{-1}\) for the 14th overtone. Beyond \( P = 15 \) the deviation becomes smaller again. This large mismatch and the relatively large density of states makes it impossible to uniquely relate the measured transitions to the vibrational levels calculated. Therefore, we are unable to identify the calculated levels that correspond to the levels for which unusually large rotational constants have been measured. At present time the comparison can only be made qualitatively.

It is plausible to speculate that the onset of the perturbations detected in the \( (0, v_2, 0) \) progression\(^{24} \) with \( v_2 > 16 \) (in our notation) is caused by the structural changes of the quantal wave functions found in the present study. Between \( v_2 = 17 \) and 19 the measured \( B_{\text{rot}} \) value changes substantially by about 8% and takes on values which are in very good agreement with the calculated rotational constants for the SN states. Although this agreement might be coincidence, we have the impression that the sudden increase signals some structural changes of the kind described by us. In an attempt to assess the existence of the [SN]-type states, Ishikawa et al.\(^{31} \) performed an additional SEP experiment and indeed found bands having the characteristics of the \( (0,0,P)_{\text{SN}} \) states; relatively large rotational constants, a large anharmonicity, and an energetic origin in reasonable agreement with our predictions.

What is needed is a better potential energy surface in order to directly compare with the experimental spectra. At present time the \textit{ab initio} calculations of Koput\(^{38} \) are extended to cover the full angular regime from H–CP to CP–H. Once this PES is available we should be in the position to make a rigorous contact with experiment.

Recently there has been some interest in extracting information about periodic orbits and their bifurcations from quantum mechanical spectra alone, without actually searching for POs.\(^{61,62} \) The tool is a windowed Fourier transformation of the quantum mechanical spectrum (called vibrogram\(^{63} \)), i.e.,

\[
A(T,E) = \int_{-\infty}^{+\infty} \Sigma(\epsilon)f(E-\epsilon)e^{-iET}d\epsilon,
\]

where the spectrum \( \Sigma(\epsilon) \) is given by

\[
\Sigma(\epsilon) = \sum_{n} \delta(\epsilon - \epsilon_n),
\]

and the sliding window \( f(\epsilon) \) is a Gaussian. The results, which we obtained when taking the calculated vibrational energies without any weighting, were not satisfactory. Especially the sudden occurrence of the saddle-node POs could not be seen. A clearer picture emerged, however, when absorption-type spectra, calculated with localized initial-state
wave functions, were Fourier transformed. Thus, in order to see, for example, the \([B]\) POs we put Gaussian wave functions on the corresponding orbits, calculated the overlap with all vibrational states and used this spectrum in Eq. (6). The same was done with wave packets localized on the \([SN]\) periodic orbits. Various vibograms were compiled into a total vibrogram with the interference between different wave packets taken into account. An example is shown in Fig. 18. One clearly sees the bifurcation around \(-3\) eV. For comparison, we also depict the half-periods of the \([B]\) and \([SN1A]\) periodic orbits and good overall agreement is observed. (Because in the classical calculations the angular coordinate is allowed to vary between \(-180^\circ\) and \(+180^\circ\), it is \(T/2\) that corresponds to \(2\pi/\Delta E\), where \(\Delta E\) is the energy spacing between two levels.) Thus, information about the time-energy relationship of classical periodic orbits can be obtained from only the quantum mechanical calculations, provided the “spectra” are prepared in a particular manner. This requires, however, that some knowledge about the POs is already available.

VII. Conclusions

Our classical and quantum mechanical calculations for the energy spectrum of HCP in the ground electronic state, using an \textit{ab initio} PES, have revealed the following clues:

1. The spectrum is governed by a 1:1 (1:2, if conventional spectroscopic nomenclature is used) resonance between CP stretching and H–C–P bending motion leading to a substantial mixing of local-mode states. The spectrum, which consists of clearly defined polyads, as well as the normal-mode wave functions are astonishingly regular, even at energies where anharmonic couplings due to the potential are prominent.

2. All states below some critical energy are confined to the H–CP hemisphere, i.e., the (Jacobi) angle \(\gamma\) remains smaller than 40° or so, even if the energy is sufficiently high for following the isomerization path to CP–H.

3. A new class of states, which follows the isomerization path all the way to the CP–H side with increasing energy, suddenly comes into existence at a relatively high energy. At the same time the polyad structure gradually disintegrates with the wave functions at the bottom of the polyad turning into the isomerization bending states.

4. Classical periodic orbits quantitatively describe all the findings observed in the quantum calculations. In particular, they closely follow the backbone of the quantal wave functions and explain the sudden appearance of the isomerization-type bending states as the consequence of a saddle-node bifurcation. They even predict the abrupt change of energy spacing between neighboring saddle-node overtones through the generation of new saddle-node periodic orbits at higher energies.

5. The two classes of bending states, those which are confined in the angular coordinate and those which follow the isomerization path, 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 agree well with the two regimes observed in recent SEP spectroscopy experiments.

6. Although a direct comparison with experimental data is, because of the limited accuracy of the potential energy surface used, not possible, our calculations qualitatively explain several observations such as the abrupt onset of perturbations observed in the experimental SEP spectra, the existence of states with two classes of rotational constants, as well as the reality of states with unusually large anharmonicity.

Acknowledgments

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45 Of course, a periodic orbit does not have an initial point in the phase space. With initial point we mean here that particular point at which the tracing of the periodic orbit from $E$ to $E + dE$ is started. A more rigorous procedure would be to choose, for example, the maximum value of $r$ along the PO for a particular energy. That would change the various curves in the bifurcation diagram but not the general appearance nor the bifurcation points.
46 More information about the calculated periodic orbits can be found at the www site http://www.cc.foforth.gr/farantos/articles/hcp/data/
48 The accuracy of the quantum mechanical calculations can be approximately assessed by comparing the number of quantum mechanical states at a particular energy with the corresponding number extracted from the volume of the classical phase space. For the energy of the 250th state, $E_{250}$, the phase-space volume gives 253. For $E_{500}$, $E_{750}$, and $E_{1000}$ the corresponding classical numbers are 506, 755, and 1004, respectively. Because of the polyad structure the quantum mechanical number of states $N(E)$ is not a smooth function of $E$, which partly explains the relatively large deviations for the smaller energies. Overall, however, the agreement is very good.
49 The results of the quantum mechanical calculation together with the assignment can be obtained by anonymous ftp from ftp.gwdg.de, directory/ftp/public/mpst/schinke/hcp/quantum.results.
51 All the wave function plots shown in this article have been obtained from a 3D plotting routine, which allows to rotate objects, that depend on three variables, in space. In all cases we show one particular contour $\epsilon(R, r, y) = \sin(\gamma)\Psi(R, r, y)$ with the value of $\epsilon$ being the same within one figure. The plots are always viewed along the $R$ axis, i.e., in the direction perpendicular to the $(r, y)$-plane. Especially the wave functions of highly excited states (or their backbones) are not confined to the $(r, y)$-plane but arranged in the 3D space. Therefore, showing 2D projections, with one coordinate fixed or integrated over, makes their appearance less informative. The shading emphasizes the 3D character of the wave functions. After testing various ways of plotting we came to the conclusion that these representations are optimal.
54 In paper I the $(0, 0, P)_{1N}$ states had been labeled $(0, P, 0)_{1N}$ because these states substitute the real $[r,1A]$-type states $(0, 0, P)$. We have changed the nomenclature.
55 We also performed classical as well as quantum mechanical two-dimensional calculations with $R$ fixed at its equilibrium for $\gamma = 0$ and found that the 2D and 3D molecules are remarkably different, which shows that all three modes are coupled.