Observation of the "isomerization states" of HCP by stimulated emission pumping spectroscopy: Comparison between theory and experiment

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Highly excited vibrational states of HCP $\widetilde{X}\,^1\Sigma^+$ were investigated by stimulated emission pumping spectroscopy. Two distinct families of vibrational states were observed in the 13400–17500 cm^{-1} energy region. One of them is ''normal-mode-type'' states, well characterized by polyads involving the bending (ω_2) and CP stretching (ω_3) vibrations. The other is delocalized ''isomerization states'' whose existence has been predicted by a recent theoretical study [J. Chem. Phys. **104**, 10055 (1996)]. The present spectroscopic observations agree well with the theoretical predictions. © *1997 American Institute of Physics.* [S0021-9606(97)03207-8]

Molecular isomerization processes occur often at high levels of vibrational excitation in the electronic ground state. On the basis of a time-independent picture, the isomerization process can be characterized by analysis of rotation-vibration eigenstates in the high energy region. Therefore, investigations of highly excited vibrational levels are very important for gaining fundamental insights into isomerization. Among various kinds of isomerization reactions, the isomerization of a triatomic monohydride, HAB, is the simplest one: the hydrogen migration reaction, HAB↔ABH. This system is most fundamental for both experimental and theoretical studies. Recent spectroscopic[1-3] and theoretical[1,4] studies of HCP have revealed many clues to an understanding of the HCP↔CPH isomerization. In the case of HCP, many theoretical calculations have predicted that the CPH configuration corresponds to a saddle point rather than a local minimum on the potential surface,[1,4,5] unlike the case of the homologue, HCN. However, one can consider the HCP–CPH system as a prototype of isomerization, especially in respect of the change in the nature of the HC vs HP chemical bond.

Stimulated emission pumping (SEP) and dispersed fluorescence (DF) spectroscopies are very useful techniques to investigate highly excited vibrational levels in the electronic ground state.[6] These methods have already been applied to the HCP system. Lehmann *et al.* observed 94 vibrational levels having a vibrational energy (E_{VIB}) in the $\widetilde{X}$ state, up to $E_{\mathrm{VIB}}=16917$ cm^{-1}, in $\widetilde{A}\,^1A''\rightarrow\widetilde{X}\,^1\Sigma^+$ DF spectra. [The zero of energy, $E_{\mathrm{VIB}}=0$, is chosen at $J=0$ in the (0,0,0) level.][1] They assigned all of the levels observed as combination levels of the bend and the CP stretching modes, as denoted by (0,v_2,v_3), where v_2 and v_3 refer to the quantum numbers of the bending (ν_2) and CP stretching (ν_3) modes. They also fitted the vibrational energies using a rigid bender model and obtained a good fit. Later, Field and co-workers observed HCP $\widetilde{A}\rightarrow\widetilde{X}$ SEP spectra that sampled pure bend overtone levels, (0,v_2,0) with $v_2=26-42$, in the $\widetilde{X}$ state.[2,3] They found an abrupt change of the rotational, B, and vibrational fine structure constants in the vicinity of $v_2=36$. For

example, the B-value first increases slightly with v_2 for $v_2 = 0 - 2$.[7] At some point, it turns around and then decreases slowly. The B-value observed by SEP first slowly decreases with v_2 for $v_2 = 26$ to 34 and then increases rapidly above $v_2=36$. They claimed that this feature is caused by a change in the curvature of the potential energy surface sampled indirectly (via second order Coriolis interactions of the form $\Delta v_2 = -3\Delta v_1$) by the high-$v_2$ vibrational states. They also observed $\widetilde{C}\,^1A'\rightarrow\widetilde{X}\,^1\Sigma^+$ SEP spectra which sampled vibrational levels in the 22500–23200 cm^{-1} energy region.[3] They found 22 vibrational levels in this energy region. Some of these vibrational levels were found to exhibit anomalously large B-values, $B \geqslant 0.7$ cm^{-1}. These B-values are more than 5% larger than that of the (0,0,0) level. They suggested that these large B-values are due to a Coriolis coupling effect between the H–X stretch (X is the CP center of mass) and the bend and that this Coriolis coupling ''turns on'' when $\omega_{\mathrm{HX}}\sim 3\omega_2$.[3,8]

Very recently Schinke and co-workers calculated a potential energy surface of HCP in the electronic ground state.[4] Their calculation showed that the CPH saddle point occurs at 3.342 eV above the bottom of the HCP well. They obtained more than 700 vibrational levels located at energies up to 3 eV above the bottom of the HCP well by exact quantum mechanical bound-state calculations. They also computed that the zero-point energy is 0.37 eV (2984 cm^{-1}). In addition, they analyzed periodic orbits (POs) and bifurcation–continuation diagrams in classical phase space. They found that the quantum wave functions are clearly localized along the projections of the POs onto the potential surface. Their theoretical study predicted several points of great interest with respect to HCP isomerization: the existence of two distinct families of bending states. One of these families is associated with vibrational levels having the wave function confined to rather small bending angles, that is, normal-mode-type states. On the other hand, the wave functions of the other family of bending states are closely related to the minimum energy isomerization path from H–CP to CP–H.

Therefore the latter type of vibrational levels can be referred to as ''isomerization states.'' In their paper, Schinke and co-workers[4] denoted these states as [SN] levels, since the appearance of this family corresponds to a saddle node bifurcation in the bifurcation–continuation diagram of the POs. The lowest energy [SN] level is located at 2.08 eV (PO analysis) of 2.26 eV (quantum calculation) above the bottom of the HCP well. Since their calculation was restricted to $J=0$ states, they estimated the B-value of each vibrational level from the expectation value of the reciprocal moment of inertia. The calculated B-values of all [SN] levels were found to be about 5% larger (0.685 cm^{-1}) than that of the vibrational ground state (0.652 cm^{-1}). It is evident that the signature of all [SN] levels is large B-values. In this respect, the large-B levels that were observed in the $\widetilde{C} \rightarrow \widetilde{X}$ SEP spectra recorded by Field and co-workers[2,3] seem to be closely related to the [SN] levels. However, the energy region that the SEP spectra sampled, 3 eV above the bottom of the well, is much higher than where the lowest energy computed [SN] level is located. In order to identify the [SN] levels in an SEP spectrum, it would be necessary to find levels with large B-values in the lower E_{VIB} energy region where the first [SN] levels are expected to appear.

In this communication, we report new SEP spectra of $\widetilde{C} - \widetilde{X}$ transitions which have sampled highly excited vibrational levels of HCP $\widetilde{X} \, ^1\Sigma^+$ and the experimental identification of two families of vibrational levels, ''normal-mode-type'' and Schinke's [SN] levels. In the 13400–17500 cm^{-1} energy region, we found five vibrational levels that can be assigned as [SN] levels. The agreement between the theoretically predicted and our experimentally observed [SN] states, such as a large rotational constant, vibrational energy onset, and highly anharmonic vibrational spacing, was quite good.

The experimental conditions are only briefly described here. Two dye lasers (Lumonics HD-500) were pumped by a Nd:YAG laser (Continuum Powerlite 9010). The output of one of the dye lasers was frequency doubled and used as the PUMP pulse. Several vibrational levels of the $\widetilde{C} \, ^1A'$ state were used as intermediates. Depending on the DUMP transition frequency, the fundamental or frequency-doubled output of the other dye laser was used as the DUMP pulse. In order to avoid saturation effects, laser intensities were reduced to 50 and 300 μJ for the PUMP and the DUMP pulses, respectively. The time delay between the PUMP and DUMP pulses was less than 10 nsec. The resolution of both lasers was typically about 0.1 cm^{-1}. Laser wavelengths were calibrated using a wavemeter (Burleigh WA-4500) or a 75 cm monochromator. The absolute accuracy of line positions was 1 cm^{-1}, but the relative accuracy was 0.1 cm^{-1}. When DF spectra were recorded, a 25 cm monochromator (Nikon P-250) was placed in front of a photomultiplier. HCP was synthesized by the method described elsewhere.[2]

Since the equilibrium structure of the HCP $\widetilde{X}$ state is linear, the bending vibration is doubly degenerate. Therefore, a vibrational angular momentum quantum number, ℓ, is necessary to characterize each vibrational level. The values of ℓ
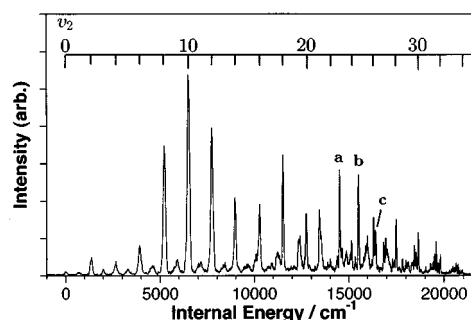

FIG. 1. Dispersed fluorescence spectrum from the $\widetilde{C} \, ^1A'(0,1,1)$ level of HCP. A $P(9)$ rotational line was used as the PUMP transition.

are restricted to $\ell = v_2, v_2 - 2, v_2 - 4, \ldots$, and 0 or 1 for even or odd v_2, respectively. The total angular momentum, J, must be larger than or equal to ℓ, that is, $J \geq \ell$. Due to the rotational selection rule for the $\widetilde{C} - \widetilde{X}$ transition, which is $\Delta|K_a' - \ell''| = 0$, only transitions terminating in $\ell = 0$ levels are allowed in the $\widetilde{C} \rightarrow \widetilde{X}$ DF and SEP spectra. The value of ℓ is easily recognized by following the spectrum to the lowest value of J, which is $J = \ell$.

Figure 1 shows a dispersed fluorescence (DF) spectrum from the HCP $\widetilde{C}$ (0,1,1) level, in which the $P(9)$ line was used as the PUMP transition. The abscissa represents the internal energy of the electronic ground state, $\widetilde{X}$. As indicated in the figure, the most prominent peaks can be assigned as the bands in a bending progression, $(0,v_2,0)$, where $v_2 = 0, 2, 4, \ldots, 34$. Weak bands located between the prominent bands in the lower energy region are tentatively assigned as nominally ''forbidden'' transitions to $\ell = 1$ levels that appear due to the ''axis-switching'' effect.[9] As E_{VIB} increases, the spectral pattern becomes increasingly complicated. As mentioned above, all vibrational levels observed in the $\widetilde{A} \rightarrow \widetilde{X}$ DF spectra reported by Lehmann et al. could be assigned as bend–CP stretch $(0, v_2, v_3)$ combination levels.[1] Many vibrational levels observed in the $\widetilde{C} - \widetilde{X}$ DF spectrum were also assigned as bend–CP stretch combination levels in the same was as for the $\widetilde{A} \rightarrow \widetilde{X}$ transition. However, other levels, which cannot be assigned as $(0, v_2, v_3)$ combination levels, appear in the DF spectrum via transitions with relatively large Franck–Condon intensities. For example, three transitions denoted as **a**, **b**, and **c** in Fig. 1 have relatively large intensities compared with those terminating in the $(0, v_2, v_3)$ levels in the same energy region. In order to obtain more detailed information, SEP spectra in the vicinity of the **a**, **b**, and **c** bands were recorded. A typical SEP spectrum is shown in Fig. 2. This spectrum sampled the (0,26,0) and **c** levels in the $\widetilde{X}$ state. Since $\widetilde{C} \, ^1A' - \widetilde{X} \, ^1\Sigma^+$ is a parallel transition, only $R(J'' - 2)$ and $P(J'')$ lines appear in the $P(J'')$ PUMP $\widetilde{C} - \widetilde{X}$ SEP spectrum. If the $R(0)$ line is observed in the $P(2)$ PUMP SEP spectrum, the vibrational level must contain a $J=0$ level, that is, the vibrational angular momentum quantum number, ℓ, must be zero. For all levels observed in this study, ℓ is equal to zero. The theoretical calculation by Schinke and co-workers was restricted to the case of $J=0$, which necessarily belongs to $\ell = 0$. Therefore, the levels ob-
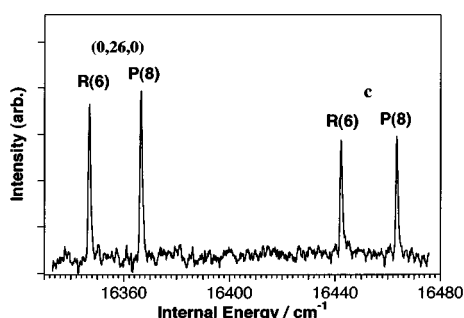
FIG. 2. Stimulated emission pumping spectrum of HCP. The PUMP transition was the $\widetilde{C}\,^1A'(0,1,1) - \widetilde{X}\,^1\Sigma^+(0,0,0)$ $P(8)$ line. Vibrational assignments are indicated on the figure. The level, **c**, is the same as that indicated in Fig. 1.

served in this work can be directly compared to those in the theoretical study.

In Table I the molecular constants of the vibrational levels observed in this study are listed. It is clear that these levels can be classified into two families with respect to their B-value. The levels with ordinary B-values, which are very close to that of the $(0,0,0)$ level, are assigned as bend–CP stretch combinations, $(0,v_2,v_3)$. The normal-mode-type levels analyzed in the theoretical study exhibit the same rotational behavior (see Fig. 3 of Ref. 4). As mentioned above, all of the vibrational levels observed in the $\widetilde{A}\rightarrow\widetilde{X}$ DF spectra by Lehmann *et al.* and many of those observed in the $\widetilde{C}\rightarrow\widetilde{X}$ DF and SEP spectra in this study were well characterized as bending and CP stretching combination levels. It is well known that the bending and CP stretching vibrations interact with each other by 2:1 anharmonic (Fermi) resonance between the $(0,v_2,v_3)$ and the $(0,v_2-2,v_3+1)$ levels.[3,10] Due to this anharmonic resonance, all $(0,P-2m,m)$ levels with $m=0,1,\dots,P/2$ are grouped into one polyad, where $P=v_2+2v_3$. The vibrational energies of the normal-mode like levels can be well reproduced by a calculation based on Dunham expansion for modes 2 and 3 combined with a

$2\omega_2:1\omega_3$ anharmonic resonance. Consequently, the vibrational structure of all $(0,v_2,v_3)$ levels of HCP is well characterized by a $2\omega_2:1\omega_3$ polyad effective Hamiltonian. Schinke and co-workers also reported strong anharmonic interactions between the bend and CP stretch among the normal-model-type states. Thus, all vibrational levels that belong to $(0,P-2m,m)$ polyads can be referred to as ''normal-mode-type'' states. This polyad structure remains valid and plays a central role in assigning the vibrational structure observed in the higher energy region near the isomerization barrier.[3,11] A detailed analysis of this anharmonic resonance will be described in a future publication.[11]

In contrast, the B-values of the levels associated with the **a**, **b**, and **c** bands are $4-10\%$ larger than that of the $(0,0,0)$ level. As mentioned above, the computed B-values of the theoretical [SN] levels are about 5% larger than that of the $(0,0,0)$ level.[4] Thus, we assigned these large-B levels as the ''isomerization'' state or Schinke's [SN] levels. By selecting the $\widetilde{C}$ $(0,1,2)$ level as the intermediate, two additional large-B levels were observed. Note that it is important to distinguish between large B-values computed from $J=0$ expectation values of the reciprocal moment of inertia and these measured from rotational intervals involving at least one $J\neq0$ rotational energy level. The latter type of B-value determination is often susceptible to second-order perturbation theoretic contributions from b- or c-type $(\Delta\ell=\pm1)$ Coriolis perturbations. Of course, short of a global deperturbation, experimentally determined effective B-values could become anomalously large owing to either the inertial effect present in Schinke's calculations or incompletely deperturbed Coriolis effects. Among many types of Coriolis effects, the strongest ones are expected to be $\Delta v_1 = -\Delta v_2 = \pm1$. Matrix elements for the Coriolis perturbations should be large for highly excited bending levels because of the expected $v_2^{1/2}$ scaling of $\Delta v_2 = \pm1$ off diagonal matrix elements. Since all of the ''isomerization'' states presumably have $v_{HX}\neq0$, there will be b,c-type Coriolis perturbers symmetrically both above and below the main state. Perturber levels which are located above and below the level concerned provide opposite effects, decreasing and increasing the B-value, respectively. Thus, the net effect might not be so large. The net Coriolis effect on the effective B-value for our highly excited bending levels was estimated to cause a -0.01 cm^{-1} decrease in the B-value. In this respect, our experimentally observed large B-values are considered to arise mainly from a change in the moment of inertia,[12] precisely the effect predicted by Schinke *et al.*[4] Moreover, two other types of evidence also support our assignment, the onset energy and the large anharmonicity, and these also support our assignment, as described below. In the theoretical calculation, the lowest energy [SN] level is predicted to occur at 2.26 eV above the bottom of the HCP well. Subtracting the zero-point energy, this level is located at 15244 cm^{-1} above the $(0,0,0)$ level. The energy of the lowest vibrational level with large B-value observed in this work is 13424 cm^{-1}, which is slightly lower than that of the theoretical prediction. Taking the accuracy of the theoretical calculation into account, the experimental onset energy agrees

TABLE I. The molecular constants of highly vibrationally excited levels of $\widetilde{X}\,^1\Sigma^+$ HCP observed in the present study. All constants are in units of cm^{-1}.[a]

Vibrational level	G_v	B	$D\times10^6$	
$(0,0,0)$[b]	0.0	0.66632742(16)	0.7025(17)	
$(v_{HX},v_b,v_{CP})_{SN}$	13424.2	0.695(3)	54(19)	
$(v_{HX},v_b+2,v_{CP})_{SN}$	14496.6	0.688(3)	−15(19)	**a** band
$(v_{HX},v_b+4,v_{CP})_{SN}$	15505.1	0.723(3)	72(19)	**b** band
$(v_{HX},v_b+6,v_{CP})_{SN}$	16412.6	0.707(4)	21(18)	**c** band
$(v_{HX},v_b+8,v_{CP})_{SN}$	17172.4	0.725(3)	5(19)	
$(0,26,0)$	16319.6	0.651(4)	−8(18)	
$(0,20,4)$	17151.6	0.655(3)	46(19)	
$(0,24,2)$	17299.0	0.652(3)	20(19)	

[a]G_v values have been obtained from the term value of the $J=0$ rotational level in each vibrational level. B and D constants (1σ uncertainties in parentheses) have been obtained from least-squares fits to the following equations

$$\Delta\nu_{DUMP}(P(J)-R(J-2))=B(4J-2)-D(8J^3-12J^2+12J-4).$$

[b]From A. Cabaña *et al.*, J. Mol. Spectrosc. **96**, 342 (1982).

satisfactorily with that of the theoretical prediction. The other feature of the theoretical [SN] levels is their strong anharmonicity. Schinke and co-workers[4] predicted that the energy difference between the first two members of the [SN] series $(0,26,0)_{SN}$ and $(0,28,0)_{SN}$ was of the order of 850 cm^{-1}, and that the difference rapidly decreases with v_2 because of strong anharmonic effects that occur at larger bending angles. They assigned the value of the v_2 quantum number of the [SN] level by counting the nodes of its wave function along the [SN]-type trajectory. In contrast, it is difficult to determine *experimentally* the bending quantum number of our observed [SN] levels. We have tentatively assigned these levels as $(v_{HX}, v_b, v_{CP})_{SN}$, $(v_{HX}, v_b + 2, v_{CP})_{SN}, \ldots, (v_{HX}, v_b + 8, v_{CP})_{SN}$ in energy order. The observed energy difference, $\Delta G(v_2) = G(v_1, v_2 + 1, v_3) - (v_1, v_2 - 1, v_3)$, rapidly decreases with v_2 as 1072.4, 1008.5, 907.5, and 759.8 cm^{-1}. If the vibrational energy can be well fitted by Dunham expansion through second order (v_2^2), as is generally possible at low E_{VIB}, the energy difference should decrease linearly with v_2. In the case of the pure bend overtones, $\Delta G(v_2)$ exhibited a linear dependence on v_2, $\Delta G(v_2) = 1336.9 - 6.26 \, v_2$.[3] The observed $\Delta G(v_2)$ for the [SN] levels shows a higher than linear order dependence on v_2. Thus, the predicted strong anharmonicity of the [SN] levels is clearly evident in our spectra.

In conclusion, we have observed two distinct families of vibrational levels in the $\widetilde{X}$ state of HCP. The observed spectroscopic features of the two families are in good agreement with theoretical predictions. The [SN]-type or ''isomerization'' levels, have been experimentally identified here for the first time for any molecule.

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[12] An anharmonic resonance assisted Coriolis perturbation could be the cause of a large effective B-value. One possible mechanism for this type of perturbation will be evaluated in Ref. 8.