Observation of the Highly Excited Vibrational Levels of HCP: Application of IR-UV-SEP Triple Resonance Spectroscopy

Haruki Ishikawa,* Chioko Nagao, and Naohiko Mikami

*Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578*

Highly excited vibrational levels of HCP involving both CH stretch and bend modes excitation, vibrational energy of which is 15600 - 17000 cm^{-1}, in the ground electronic state were observed by IR-UV double resonance pumped dispersed fluorescence and stimulated emission pumping spectroscopies.

In general, isomerization reaction of triatomic monohydrides, HAB $\leftrightarrow$ ABH, proceeds in a high energy region in the ground electronic state. Thus, an analysis of vibration-rotation eigenstates in the high energy region should provide the information about the isomerization reaction. In order to extract dynamical information from a spectroscopic observation, we have been investigating highly excited vibrational levels of HCP.[1-3] Recently, theoretical studies predicted an existence of "isomerization" states in the high energy region, wave function of which exhibits a distinct nodal pattern compared with those of vibrational level in lower energy region.[4,5] We have carried out dispersed fluorescence (DF) and stimulated emission pumping (SEP) spectroscopies and observed a number of vibrational levels in the energy region where the "isomerization" states are expected to appear. We have analyzed the vibrational level structure by means of an eigenvector analysis of the effective Hamiltonian matrix based on an anharmonic resonance between the bend (ν_2) and the CP stretch (ν_3) modes.[3] This analysis has revealed that the generation of the "isomerization" states can be interpreted by a polyad structure.

In order to extend our study in much higher energy region where an interaction between the bend and the CH stretch (ν_1) modes must be significant, the observation of the highly excited vibrational levels involving both the ν_1 and ν_2 modes excitation is necessary. DF and SEP spectroscopies are very powerful techniques to observe highly excited vibrational levels. However, it is difficult to observe vibrational levels with $v_1 \neq 0$ by these methods, since there is a Franck-Condon selectivity of $\Delta v_1 = 0$ in the electronic transition. To overcome this difficulty, IR pumping of the ν_1 mode will be quite effective prior to a pump transition of DF or SEP spectroscopies as shown in Figure 1. In this way, we can observe highly excited vibrational levels involving the ν_1 mode in the $\tilde{X}$ state by DF and SEP spectroscopies. Hereafter, these IR-UV double resonance pumped DF or SEP methods are referred to as IR-UV-DF or IR-UV-SEP, respectively. In this letter, we report the first observation of the highly excited vibrational levels of HCP involving the ν_1 and the ν_2 modes excitation.

We used almost the same apparatus used in the IR-UV double resonance spectroscopy of HCP reported elsewhere.[6] The IR laser light ($\tilde{\nu}_{IR} \sim 3200$ cm^{-1}) was generated by difference frequency mixing between the second harmonic of outputs of an injection-seeded Nd:YAG laser (Continuum Powerlite 8000) and a Nd:YAG pumped dye laser (Continuum ND6000) in a LiNbO$_3$ crystal. The frequency doubled out-
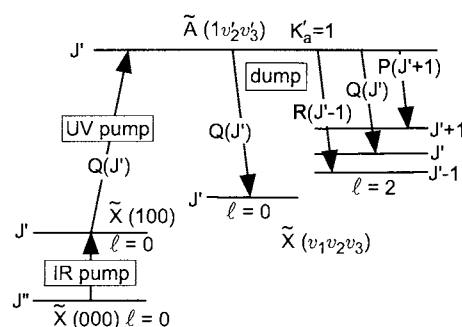
Figure 1. Excitation scheme of the IR-UV-SEP spectroscopy. ℓ represents a vibrational angular momentum quantum number in the $\tilde{X}$ state.

puts of a dye laser (LAS LDL20505) pumped by another Nd:YAG laser (Continuum Surelite III) was used for the UV pump transition ($\tilde{\nu}_{UV} = 36200 - 37150$ cm^{-1}). The IR and UV beams were introduced into a fluorescence cell counter-propagating with each other. The UV laser was irradiated about 20 ns after the IR laser light pulse and the delay time between the two laser pulses was controlled by a digital delayed pulse generator (SRS DG535). In the present study, the $\tilde{X}(100)-\tilde{X}(000)$ and $\tilde{A}(130)$or$(131)-\tilde{X}(100)$ bands were used for the IR and UV pump transitions, respectively. Wavenumbers of the IR and UV transitions are listed in Ref. 7 and 6, respectively. In the case of the IR-UV-DF spectroscopy, a 25 cm monochromator was set in front of a photomultiplier tube. In the case of the IR-UV-SEP spectroscopy, outputs of another Nd:YAG pumped dye laser (Lumonics HD-500) were used as the dump laser pulse ($\tilde{\nu}_{dump} = 22450 - 23800$ cm^{-1}). This dump laser beam was combined with the UV pump laser beam by a dichroic mirror. In general, a fluctuation of the fluorescence intensity from an intermediate level makes lower S/N of the spectrum. To reduce this effect, the dump laser pulse was optically delayed to the UV pump pulses and the fluorescence intensities before and after the dump laser pulse were integrated independently. Then, the fluorescence intensity after the dump laser pulse was normalized by shot to shot. HCP was synthesized by a pyrolysis of CH$_3$PCl$_2$. Details of the synthesis were presented elsewhere.[8] Total pressure of the HCP sample was 500 - 700 mTorr. (1 Torr = 133.322 Pa)
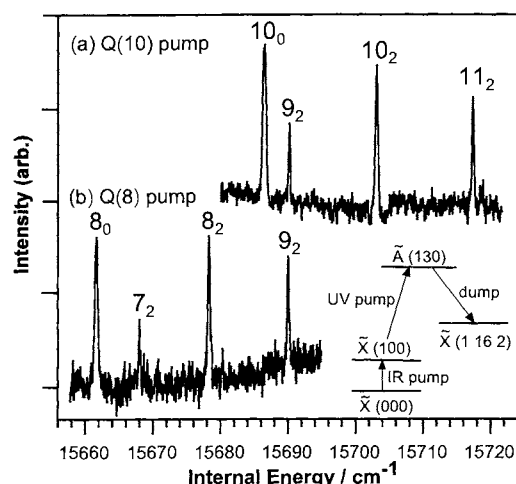
Figure 2 shows IR-UV-DF spectra of the $v_1 = 1$ levels, as well as the $v_1 = 0$, recorded in the present study. As indicated in the figure, $\tilde{A}$ $^1A''$ (130) and (131) levels were used as intermediate states. An even-v_2 progression starting the $\tilde{X}$ (100) level can be clearly recognized in each spectrum. Splittings appearing in the highly excited v_2 levels are due to the polyad structure between the ν_2 and the ν_3 modes as known in the case of $v_1 = 0$ levels.[1] Franck-Condon intensity patterns are very similar among these spectra. Only the offset
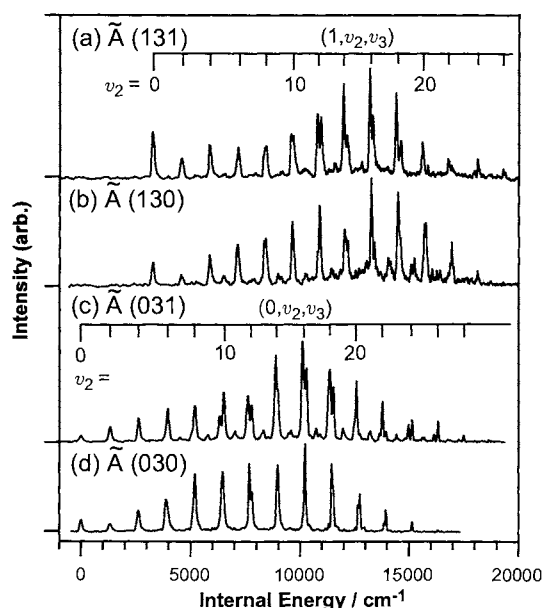
Figure 2. IR-UV-DF spectra of HCP. The abscissa represents internal energy in the $\widetilde{X}$ state. Intermediate vibrational levels in the $\widetilde{A}$ state are (a) (131), (b) (130), (c) (031), and (d) (030). The $\widetilde{X}$ (100) level was used as the intermediate state of the IR-UV double resonance transition.

Figure 3. IR-UV-SEP spectra of HCP. The abscissa represents internal energy in the $\widetilde{X}$ state. The inset shows the excitation scheme of the IR-UV-SEP spectroscopy. Rotational quantum numbers of the termination levels in the $\widetilde{X}$ state are indicated as J_ℓ.

Table 1. Molecular constants of the vibrational levels observed in the present study. $\tilde{\nu}_{\mathrm{calc}}$ represents vibrational term values calculated by using molecular constants reported in Refs. 3 and 7.

Level	$\tilde{\nu}_{\mathrm{obs}}/\mathrm{cm}^{-1}$	B/cm^{-1}	g_{22}/cm^{-1}	$\tilde{\nu}_{\mathrm{calc}}/\mathrm{cm}^{-1}$
(1 20 0)	15 753	0.640	4.14	15 773
(1 18 1)	15 679	0.650	4.12	15 695
(1 16 2)	15 615	0.659	4.16	15 628
(1 22 0)	16 943	0.646	4.32	16 974
(1 20 1)	16 866	0.632	4.30	16 892

is shifted by the energy of the $\widetilde{X}$ (100) level (3216.9 cm^{-1}). Our resolution of the IR-UV-DF spectrum was not enough to resolve all the vibronic bands.

We have also succeeded in recording the IR-UV-SEP spectra. Figure 3 shows the IR-UV-SEP spectra observed. Although this technique involves a triple resonance spectroscopy, the S/N was very good. Four rotational lines appear in the SEP spectrum due to the rotational selection rules, $\Delta J = 0, \pm 1$ and $\Delta |K_a' - \ell''| = 1$. At the present stage, five vibrational levels with $v_1 = 1$ were observed. Vibrational term values obtained, $\tilde{\nu}_{\mathrm{obs}}$, were listed in Table 1. Although our previous polyad structure analysis did not contain the anharmonic resonance between the ν_1 and the ν_2 modes,[3] vibrational term values were predicted by adding harmonic and anharmonic terms, ω_1^0, x_{11}, x_{12}, and x_{13}, reported in the IR study[7] into the effective Hamiltonian. The energy region covered by the present study is very narrow so that an assignment was a tentative one.[9] A detailed rotational analysis has not yet been carried out, since the number of the rotational level observed is not large enough. Preliminary rotational constant, B, and an energy separation between the $\ell = 0$ and 1 levels, g_{22}, are listed in Table 1. The B-values of the (1 v_2 v_3) levels are somewhat smaller than those of the (0 v_2 v_3) levels.[3] This can be attributed to the elongation of the CH bond length. The vibrational levels observed in the present study were assigned to be "normal-mode-type" states in Ref. 3, which exhibit less contribution to the isomerization. This is why our naive prediction of the vibrational term values worked well. However, the g_{22}-value of the (1 22 0) level increases by $\sim 3\%$ compared to that of the (1 20 0) level. In the case of the (0 v_2 0) levels, such a large increase was observed at higher bent state ($v_2 = 32$).[8] Thus, this large increase may indicate the effect

of the ν_1 excitation on the isomerization reaction. In order to discuss details of the isomerization reaction of HCP, it is necessary to measure many vibrational levels with $v_1 \neq 0$.

In conclusion, we reported the observation of highly excited vibrational levels involving both ν_1 and ν_2 modes excitation by means of IR-UV-DF and IR-UV-SEP spectroscopies. They are promising techniques to extend our study into much higher energy region.

Reference and notes

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