Observation of highly vibrationally excited $\tilde{X}^1\Sigma^+$ HCP by stimulated emission pumping spectroscopy

Yit-Tsong Chen, David M. Watt, and Robert W. Field

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Kevin K. Lehmann

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

(Received 16 April 1990; accepted 24 May 1990)

We have observed stimulated emission pumping (SEP) spectra of 16 000 cm$^{-1}$–19 000 cm$^{-1}$ vibrationally excited methinophosphide (HCP) $\tilde{X}^1\Sigma^+$. The observed vibrational levels have most of their energy localized in the bending coordinate. The turning point in the bending vibration is approximately halfway (2HCP $\approx$ 90°) from HCP to another chemical network, “HPC”, which corresponds to a saddle point on the potential energy surface. This system was earlier studied at lower energy and resolution by dispersed fluorescence spectroscopy. SEP spectra of HCP, and of HCN obtained recently by Wodtke et al., provide an opportunity for a comparison of the intramolecular dynamics in these two isovalent molecules. The spectroscopic data for HCP $\tilde{X}^1\Sigma^+$ will test methods for dealing with large amplitude vibrations (rigid and nonrigid bender Hamiltonians, discrete variable representation–distributed Gaussian basis, and other methods).

The SEP experiment has been described previously and we only discuss conditions unique to the present setup. A 15 ns, $\sim$2 mJ PUMP pulse (frequency doubled output of a Nd:YAG pumped dye laser) excites a selected rovibrational level of the HCP $\tilde{A}^1A^+$ electronic state (band origin at 34 746 cm$^{-1}$). A DUMP pulse of $\sim$5 mJ, delayed 20 ns with respect to the PUMP, stimulates emission from the HCP $\tilde{A}^1A^+$ state to rovibrational levels of $\tilde{X}^1\Sigma^+$. The SEP spectrum is detected as dips in the side-fluorescence intensity. HCP was synthesized by pyrolysis of CH$_3$PCl$_2$ at $\sim$900 °C in a 30 cm long, 7 mm diam quartz tube packed with crushed quartz. The gaseous products were passed through a KOH trap at 200 K, which removed HCl and low volatility products. A second trap at 77 K collected the HCP product and passed CH$_4$ and other low boiling products. HCP (and an CH$_3$ pyroproduct) was evaporated from the second trap at 130 K. HCP could be stored indefinitely in a glass tube at 77 K.

A sample SEP spectrum ($\sim$0.5 cm$^{-1}$ resolution) of HCP is shown in Fig. 1. The PUMP transition was HCP $\tilde{A}^1A^+ (0,3,0)$ $\rightarrow 6 \tilde{X}^1\Sigma^+ (0,0,0)$, $J' = 6 \rightarrow \tilde{X}^1\Sigma^+$ ($v_1', v_2', v_3'$) = (0, 0, 0). The $J' = 2$ state is found at higher energy than the $J'' = 0$ state. Most observed transitions are broadened (FWHM $\sim$1.5 cm$^{-1}$), and are upward transitions to weakly predissociated higher excited vibronic states in the previously examined 50 000 cm$^{-1}$–56 000 cm$^{-1}$ region (masked by C$_2$H$_2$ absorption in the previous UV absorption study of HCP). We are analyzing this new electronic band system.

The sharper (FWHM $\sim$0.5 cm$^{-1}$, laser linewidth-limited) but weaker SEP signals are distinguished from upward transitions by comparing the $Q(6)$ and $Q(7)$ PUMP spectra. The $Q(6)$ and $Q(7)$ PUMP spectra contain transitions into $J'' = 6$ and 7 levels in common. If the $Q(7)$ spectrum must be shifted to higher (lower) frequency by $7B' + C' \approx 8.0 \text{ cm}^{-1}$ to bring it into partial coincidence with the $Q(6)$ spectrum, the transition is upward (downward). By this method, two sets of SEP signals to the vibrational states (0,250,0) at $\sim$17 530 cm$^{-1}$ and (0,300,0) at $\sim$18 690 cm$^{-1}$ above HCP $\tilde{X}^1\Sigma^+$ (0,0,0) have been identified in Fig. 1 (top). The vibrational assignments are based on predictions from the earlier dispersed fluorescence study, in which $v_3'\leq27$ levels were observed. A higher resolution SEP spectrum (FWHM $\sim$0.03 cm$^{-1}$, absolute accuracy of line centers, 0.005 cm$^{-1}$) is shown in Fig. 1 (bottom). SEP spectra characterize the (0,260,0), (0,280,0), (0,300,0), (0,240,1) and (0,261,1) levels which contain 16 000 cm$^{-1}$–19 000 cm$^{-1}$ vibrational energy. The parity splittings in $J'' = 2$ doublets ($\approx 0.1 \text{ cm}^{-1}$ at $J'' = 10$ in the excited vibrational states, due to $l$-type resonance between $J'' = 0$ and one component of the $l'' = 2$) have been observed. The SEP transitions, which were sampled for several $J''$ values between 1 and 13 for each vibrational state, have been least-squares fit to a standard Hamiltonian for a linear triatomic molecule (including the off-diagonal matrix element responsible for the $l$-type resonance). The molecular constants for highly vibrationally excited HCP $\tilde{X}^1\Sigma^+$ are listed in Table I.

Accurate $B$ values for both HCP and DCP should characterize the changes in C–H and C==P bond lengths as a function of bending angle. Ab initio estimates indicate that both should lengthen in the transition region between C–H and P–H bonding. The observed decrease in $B$ values from the (0,260,0) to the (0,300,0) vibrational state is consistent with the predicted lengthening of the C==P bond. The separa-

---

NSF, Predoctoral Fellow.
The SEP spectrum of HCP at \(-0.5\) cm\(^{-1}\) resolution. A sample pressure of \(-200\) mTorr of HCP was used. The \(Q(6)\) line of the \(\tilde{A}^1\tilde{A}^+ - \tilde{X}^1\Sigma^+\), \((0,0,0)^{1}\) \(-\) \((0,0,0)^{2}\) band was used as the PUMP transition. The polarizations of PUMP and DUMP lasers are parallel to each other. The strong and broadened (FWHM \(-1.5\) cm\(^{-1}\)) features are upward transitions to higher excited electronic states. Two sets of SEP signals to \((0,28^{03},0)\) at \(-17530\) cm\(^{-1}\) and to \((0,30^{03},0)\) at \(-18690\) cm\(^{-1}\) above the \((0,0,0)^{2}\) level of HCP \(\tilde{X}^1\Sigma^+\) have been identified. (Lower) The 0.03 cm\(^{-1}\) resolution SEP spectrum of \((0,28^{03},0)\) at \(-17530\) cm\(^{-1}\) in HCP \(\tilde{X}^1\Sigma^+\). The rotational features \(J^*\) = \(6,5,6,7\), follow the selection rule \(K^* = |I^*| = 1\), for a perpendicular band system. The spectra were background corrected by subtracting the average of the 25 nearest nonpeak bins (4 bins per 0.03 cm\(^{-1}\)) from each point in the spectrum. The peaks (typical fluorescence dip \(-5\%\)) were selected manually. The very weak lines near \(J^* = 6\), were not reproducible in repeated scans. However, a few unassigned weak extra SEP signals near the \((0,24,1), (0,26,1),\) and \((0,30,0)\) vibrational states have been detected.

The correlation between \(g_{22}(\text{eff})\) and \(B\) has shown that a 0.6 cm\(^{-1}\) change in \(g_{22}(\text{eff})\) of HCN corresponds to a \(-0.06\) cm\(^{-1}\) change in \(B\) value. Our HCP data do not show a linear variation of \(g_{22}(\text{eff})\) vs \(B\) (as for HCN), and the change in \(B(\Delta B \sim 0.015\) cm\(^{-1}\) vs \(-0.06\) cm\(^{-1}\)) is much smaller for HCP than HCN. As the bending quantum number in HCP \(\tilde{X}^1\Sigma^+\) is increased, from \(v_2 = 0\), the \(B\) value first increases and then decreases; in contrast \(g_{22}(\text{eff})\) increases monotonically with \(v_2\). The \(l\)-type resonance parameter, \(q\), changes only \(-18\%\) from \((0,2,0)\) to \((0,30,0)\), a surprisingly harmonic behavior for such large amplitude vibration.

The major result reported here is observation of SEP transitions into highly excited \(v_2 \leq 30\) bending states with only 0 or 1 quantum of \(\tilde{C} = \tilde{P}\) stretch. This is in contrast with HCN, where the highest observed levels have 14 or fewer quanta of bending excitation and up to 7 quanta in the \(\tilde{C} = \tilde{N}\).
<table>
<thead>
<tr>
<th>Vibrational state</th>
<th>(0,2,0)</th>
<th>(0,26,0)</th>
<th>(0,28,0)</th>
<th>(0,30,0)</th>
<th>(0,24,1)</th>
<th>(0,26,1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_0 )</td>
<td>1334.9812(6)</td>
<td>16318.692(3)</td>
<td>17489.333(8)</td>
<td>18648.087(6)</td>
<td>16224.149(4)</td>
<td>17389.563(9)</td>
</tr>
<tr>
<td>( \tilde{g}_{22} )</td>
<td>5.0442(4)</td>
<td>5.522(1)</td>
<td>5.585(2)</td>
<td>5.651(2)</td>
<td>5.536(1)</td>
<td>5.588(2)</td>
</tr>
<tr>
<td>( B_0 )</td>
<td>0.6671(30(24)</td>
<td>0.65248(9)</td>
<td>0.65104(26)</td>
<td>0.64812(16)</td>
<td>0.65158(8)</td>
<td>0.64945(19)</td>
</tr>
<tr>
<td>( \gamma_v \times 10^4 )</td>
<td>0.058(15)</td>
<td>1.01(18)</td>
<td>1.77(40)</td>
<td>1.22(25)</td>
<td>1.37(14)</td>
<td>1.67(28)</td>
</tr>
<tr>
<td>( D \times 10^6 )</td>
<td>0.696(18)</td>
<td>0.11(7)</td>
<td>5.2(14)</td>
<td>1.3(9)</td>
<td>2.0(5)</td>
<td>2.0(10)</td>
</tr>
<tr>
<td>( q \times 10^3 )</td>
<td>2.322(37)</td>
<td>1.934(31)</td>
<td>1.915(49)</td>
<td>1.898(29)</td>
<td>1.928(24)</td>
<td>1.814(39)</td>
</tr>
</tbody>
</table>

*The spectroscopic constants (1σ uncertainties in parentheses) of highly vibrationally excited \( \tilde{X}^1 \Sigma^+ \) HCP have been obtained from least-squares fits to a Hamiltonian for a linear tristatic molecule with a diagonal matrix element of

\[
E = v_0 + \tilde{g}_{22} l^2 + (B_0 + \gamma_v l^2) (J(J+1) - l^2) - D (J(J+1) - l^2)^2,
\]

and an off-diagonal l-type resonance term between \( l = 0 \) \( \{ \Psi_0 = |v_0, J, l = 0 \rangle \} \) and one of the \( l = 2 \) \( \{ \Psi_{2+} = (|v_0, J, l = 2 \rangle + |v_0, J, l = -2 \rangle) / \sqrt{2} \} \) levels.

\[
\langle \Psi_{2+} | \alpha (q', J', l') + q_\perp (J, l) | \Psi_0 \rangle = (q/4) \sqrt{(l_2 + 2) / (J(J+1) - 2)}.
\]

The centrifugal distortion constant \( D \) is assumed to be identical for both \( l = 0 \) and \( l = 2 \) levels in the fits.

The rms deviation in the least-squares fit of each of these five vibrational bands is \( \lesssim 0.01 \) cm\(^{-1}\).

From Ref. 8.


In HCP, at \( v^c_2 \approx 30 \), the H atom is approaching the point where the chemical bonding changes from predominantly C-H to P-H and the bending coordinate must change from an arc around the C to an arc around the P. By pumping higher bending vibrational levels of the HCP \( \tilde{A}^1 \Delta^+ \) intermediate state, we expect that \( v^c_2 > 30 \) of \( \tilde{X}^1 \Sigma^+ \) should be accessible, thus allowing us to explore levels in the HCP\( \Leftrightarrow \)HPC transition region. In this region, the C-H bond length must lengthen, and thus \( v^c_3 \) should "light up" in the spectrum. The rotational structure shows that \( B^* \) changes by \( \sim 3 \% \) despite large amplitude motion corresponding to bending vibrations of \( \sim 90^\circ \) away from linearity. The \( g_{22}(\text{eff}) \) constant, which reflects the energy difference of purely planar \( (l = 0) \) vs slightly elliptical \( (l = 2) \) bending, increases only 12% from \( (0,2,0) \) to \( (0,30,0) \), thus illustrating the unexpectedly harmonic nature of this large-amplitude bending motion.

We thank G. W. Adamson for experimental assistance and Dr. S. L. Coy and Dr. S. C. Ross for stimulating discussions. This research was supported by a grant from the Air Force Office of Scientific Research (AFOSR-88-0062).