CP's Triple-bond Strength Experienced in its THz Spectrum

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The submillimeter-wave rotational spectrum of the CP radical in the electronic and vibrational ground state ($X^2\Sigma^+$) was recorded in the frequency region between 572 GHz and 1.05 THz, covering rotational quantum numbers from $N = 11$ up to 21. The CP radical has been produced by discharging CH_4 over red phosphorus buffered with Ar at liquid nitrogen temperature. Analysis of the new rotational data of CP together with those available in the literature allows the derivation of an accurate set of molecular constants, including rotational, B_0 = 23859.91521(28) MHz and the centrifugal distortion constant D_0 = 39.8140(19) kHz, the fine structure and hyperfine structure parameters. The stiffness of the CP bond can be inferred by requiring only one distortion constant D_0 to fit the measured rotational spectrum.

Introduction

The CP molecule is isoelectronic with CN and hence they possess the same electronic ground state, i. e. $X^2\Sigma^+$. The two molecules are also comparable with respect to their rotational and fine structure parameters. In contrast to CN, however, not so much spectroscopic knowledge has been gathered about the CP radical. Thorne et al. estimated bond energies of several simple phosphorus containing molecules like PH, PH_2, P_2, CP, etc. and they conclude that the CP radical has the highest bond energy among them [1]. In the laboratory, the CP radical was first studied by Herzberg in 1930 [2], who identified this molecule via its electronic $B^2\Sigma^+ - X^2\Sigma^+$ transition. By investigating the $A^2\Pi - X^2\Sigma$ band in the infrared with Fourier-transform spectroscopy, Ram and Bernath [3] derived rotational parameters for the $A^2\Pi$ electronic and the $X^2\Sigma$ vibrational ground state. Based upon these parameters, Saito and coworkers [4] measured the pure rotational spectrum of CP below 335 GHz using a source-modulated millimeter-wave spectrometer. Due to the small rotational quantum numbers $N \leq 7$ of these investigations [4], the hyperfine structure could be resolved for most of the measured transitions, which is in contrast to our current measurements between 572 and 1050 GHz.

Hitherto CP and PN are the only phosphorus containing species, which have been detected in the interstellar space. The CP molecule was discovered by Guélin et al. [5] in 1990 in the carbon star envelope IRC+10216. They observed the rotational transitions $N = 2 \rightarrow 1$, $N = 3 \rightarrow 2$, $N = 5 \rightarrow 4$ at 95, 143, 238 GHz with the IRAM 30 m telescope. In the interstellar medium, the production of molecules with bond strength comparable to CP or larger might be favoured in processes involving grain vaporization. Therefore CP may have a high abundance in circumstellar envelopes and warm clouds.

In the present paper we extend the frequency region of the laboratory-observed rotational transitions into the terahertz region for the electronic and vibrational ground state. Our data, together with those in the literature allow to obtain an accurate set of molecular parameters for CP which may help to detect transitions of CP in high excitation regions in the interstellar medium. In addition, these measurements of CP should also partly be seen as an effort to investigate the sub-mm-wave spectra of other phosphorus containing molecules, some of them with potential astrophysical significance, such as PH [6] and PS [7].

Experimental

The Cologne terahertz spectrometer has been described in some detail by Winnewisser [8]. For the measurements concerning the CP radical we used two high-frequency and broadband tunable backward wave oscillators (BWOs) as radiation sources (frequency range: 530-710 GHz, output power: ≃ 2 mW and 880 - 1100 GHz, 0.5 mW supplied from the

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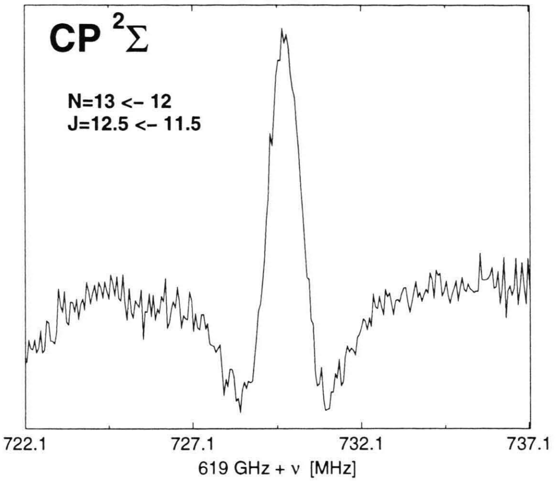

Fig. 1. Rotational transition of the CP radical at 619 GHz.

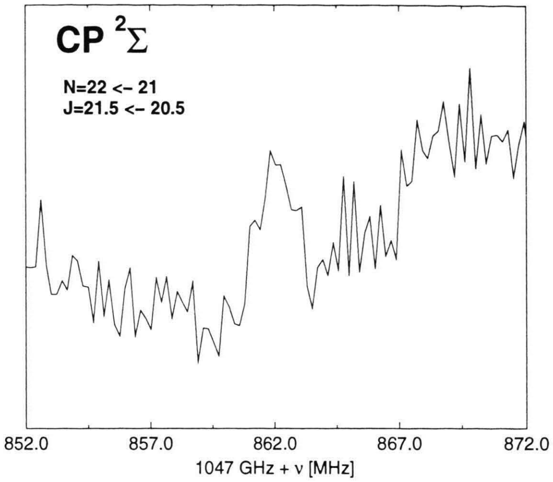

Fig. 2. CP transition at 1.04 THz.

ISTOK company). These BWOs were digitally frequency and phase locked to the higher harmonics of a 78 - 118 GHz local oscillator supplied by the KVARZ company. The BWO radiation was frequency-modulated by a double step function of 7 kHz and detected by a magnetically tuned hot electron InSb bolometer. Former measurements below 335 GHz by Saito et al. [4] were done by producing the CP molecule in the discharge of a PH_3/CH_4-mixture. Nevertheless, based on the good results with recent measurements of PH [6], we decided to produce CP by immersing red phosphorus in the dc glow discharge of CH_4 buffered with Ar. Additionally it was necessary to cool down the absorption cell to liquid nitrogen temperature in order to obtain sufficent absorption of the microwave radiation. Optimal parameters for the production of CP in the discharge were found to be:

- partial pressures of (Ar/CH_4): (90/10) μbar
- discharge current: 400 mA

For well-isolated and strong lines, the measurement accuracy of our spectrometer in the Doppler-limited mode is better than ± 5 kHz [9]. Moreover, this measurement accuracy can be increased to ± 500 Hz in cases where sub-Doppler measurements are possible [10]. The CP spectra have been measured with less accuracy for a variety of reasons such as blending of hyperfine components, baseline problems, and the rather low production rate of the molecule. The measurement accuracy is estimated to be typically 80 kHz for the stronger lines and 250 kHz for the weaker ones. Sample spectra of our measurements at 619 and 1047 GHz are shown in Figs. 1 and 2. The difference between the signal to noise ratios for these two lines corresponds to the different output power of the two BWOs. Integration time was about 3 minutes for the measurement at 619 GHz and – limited by the possible duration of the discharge – about 20 minutes for the lines at 1 THz.

Theory and Analysis

The unpaired electron of CP gives rise to a $^2\Sigma^+$ electronic ground state. The Hamiltonian H describing the CP rotational energy levels in the vibrational and electronic ground state consists of three parts:

$$H = H_{\rm rot} + H_{\rm fs} + H_{\rm hfs} , \qquad (1)$$

where the subscripts rot, fs, and hfs refer to the rigid-body rotational, fine structure and hyperfine structure contributions, respectively. The Hamiltonian is evaluated in a Hund's case (b_{β_J}) representation [11], in which the rigid-body angular momentum $\boldsymbol{N}$ and the electronic spin $\boldsymbol{S}$ first couple together to form a resultant $\boldsymbol{J}$, which then couples with the nuclear spin $\boldsymbol{I}$ to form the total angular momentum $\boldsymbol{F}$:

$$\boldsymbol{J} = \boldsymbol{N} + \boldsymbol{S} \quad \text{and} \quad \boldsymbol{F} = \boldsymbol{J} + \boldsymbol{I}. \qquad (2)$$

As typical for the Hund's (b) vector coupling scheme, $H_{\rm rot}$ yields the largest contribution to the Hamiltonian for $^2\Sigma$ radicals. Hence the energy levels are first ordered according to the rotational quantum number

N in contrast to molecules with electronic orbital angular momentum (i. e molecules with Π or Δ ground state). The fine structure arising from the coupling of the electronic spin ($S = \frac{1}{2}$) with the rotational motion of the molecule leads to the so called ρ-type doublet structure, with levels characterized by quantum numbers $J = N \pm \frac{1}{2}$. Moreover the magnetic hyperfine contributions of the phosphorus nucleus ($I = \frac{1}{2}$) have to be considered. The values of the total angular momentum quantum number F are therefore $F = J \pm \frac{1}{2}$. The matrix elements for H used in the Hund's case (b_{β_J}) representation are

$$\begin{aligned}
&\left\langle N'(S=\frac{1}{2})(I=\frac{1}{2})J'F \mid \hat{H} \mid N(S=\frac{1}{2})(I=\frac{1}{2})JF \right\rangle \\
&= \left\{ [B - DN(N+1)]N(N+1) + \gamma\frac{1}{2}[J(J+1) - N(N+1) - \frac{3}{4}] \right\} \delta_{N',N}\delta_{J',J} + 3(-1)^{J'+F+1} \qquad (3) \\
&\cdot \sqrt{(2J+1)(2J'+1)} \left\{ \begin{Bmatrix} F & J' & 1 \\ 1 & 1 & J \end{Bmatrix} \left\{ b_F(-1)^{N+J+\frac{3}{2}} \begin{Bmatrix} \frac{1}{2} & J' & N \\ J & \frac{1}{2} & 1 \end{Bmatrix} \delta_{N',N} \right.\right. \\
&\left.\left. - t\sqrt{30}(-1)^{N'} \sqrt{(2N+1)(2N'+1)} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ N' & N & 2 \\ J' & J & 1 \end{Bmatrix} \begin{pmatrix} N' & 2 & N \\ 0 & 0 & 0 \end{pmatrix} \right\} \right\} .
\end{aligned}$$

The newly measured lines are listed in Table 1. For all these transitions the hyperfine splitting collapses to values which lie within the Doppler-width because of the relatively high J values. All lines were fitted to the effective Hamiltonian as given above. Our data yield a set of very precise molecular parameters (see Table 2), where the rotational constant B, the centrifugal distortion parameter D and the fine structure constant γ could be obtained with high accuracy. The magnetic hyperfine constants b_F and t are obtained from low N transitions, measured by Saito et al. [4], which were also included into the fit.

Compared with the isoelectronic radical CN, the fine-structure splitting is considerably larger for CP, as is clearly visible from the relationship between the rotational constant B and the fine structure constant γ: $\frac{\gamma_{\mathrm{CP}}}{B_{\mathrm{CP}}} \approx 5 \cdot \frac{\gamma_{\mathrm{CN}}}{B_{\mathrm{CN}}}$, where the values for $\gamma_{\mathrm{CN}} = 217.4988(57)$ MHz and $B_{\mathrm{CN}} = 56693.4703(17)$ MHz were taken from [12]. In addition it is very remarkable that there was no need to include higher order centrifugal distortion terms than D into the fit, although high N quantum numbers up to 21 were involved. This has to be seen as a manifestation of the strong triple bond of the CP molecule. The appropriate force constant k can be obtained by

$$2\pi\nu_0 = \sqrt{\frac{k}{\mu}}, \tag{4}$$

where ν_0 and μ are the frequency of the first normal mode and the reduced mass of the molecule. Taking into account $\nu_0 = 1236.38\ \mathrm{cm}^{-1}$ given by Kawaguchi et al. [13] one obtains $k_{\mathrm{CP}} = 5.22 \cdot 10^8$

Table 1. Observed Rotational Transitions of CP (in MHz).

N'	J'	$\leftarrow$	N''	J''	ν_{obs}	O – C
12	11.5		11	10.5	572084.772	0.029
12	12.5		11	11.5	572640.609	–0.256
13	12.5		12	11.5	619729.786	0.050
13	13.5		12	12.5	620285.905	–0.099
14	13.5		13	12.5	667362.480	–0.039
14	14.5		13	13.5	667918.431	–0.347
19	18.5		18	17.5	905306.434	0.201
19	19.5		18	18.5	905862.870	0.206
20	19.5		19	18.5	952844.446	0.104
20	20.5		19	19.5	953400.922	0.129
21	20.5		20	19.5	1000363.276	–0.065
21	21.5		20	20.5	1000919.827	0.019
22	21.5		21	20.5	1047862.109	–0.166
22	22.5		21	21.5	1048418.610	–0.147

Table 2. Estimated molecular constants of CP in the electronic and vibrational ground state ${}^2\Sigma^+$ (in MHz); the values in parentheses denote the uncertainties in units of the last digits.

H_{rot}	B	23859.91521(28)
	D	0.0398140(19)
H_{fs}	γ	556.6324(70)
H_{hfs}	B_F	–132.54(25)
	t	151.340(67)

$\frac{1}{\mathrm{cm}^2\mathrm{amu}}$. This may be compared with the corresponding values of PS and PH: $k_{\mathrm{PS}} = 3.34 \cdot 10^8 \ \frac{1}{\mathrm{cm}^2\mathrm{amu}}$ (with $\nu_{0_{\mathrm{PS}}} = 733.55 \ \mathrm{cm}^{-1}$ [13]) and $k_{\mathrm{PH}} = 1.96 \cdot 10^8 \ \frac{1}{\mathrm{cm}^2\mathrm{amu}}$ (with $\nu_{0_{\mathrm{PH}}} = 2276.21 \ \mathrm{cm}^{-1}$ [14]). Therefore the ratio $k_{\mathrm{CP}} \approx 1.5 \ k_{PS} \approx 2.6 \ k_{\mathrm{PH}}$ suggests a triple bond between the C and P atoms in contrast to a double bond character for the PS molecule and a single bond for PH. This is conforms with Thorne et al. [1], who reported that the CP radical has the highest bond energy among various phosphorus containing molecules. In comparison, the CN triple bond produces $k_{\mathrm{CN}} = 1.08 \cdot 10^9 \ \frac{1}{\mathrm{cm}^2\mathrm{amu}}$ (with $\nu_{0_{\mathrm{CN}}} = 2062.13 \ \mathrm{cm}^{-1}$ [15]) about twice the value of k_{CP}.

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[1] L. R. Thorne, V. G. Anicich, S. S. Prasad, and W. T. Huntress, ApJ. **280**, 139 (1984).

[2] G. Herzberg, Nature (London), **126**, 131 (1930).

[3] R. S. Ram, and P. F. Bernath, J. Mol. Spec. **122**, 282 (1987).

[4] S. Saito, S. Yamamoto, K. Kawaguchi, M. Ohishi, H. Suzuki, S. Ishikawa, and N. Kaifu, ApJ, **341**, 1114 (1989).

[5] M. Guélin, J. Cernicharo, G Paubert, and B. E. Turner, Astron. Astrophys. **230**, L9 (1990).

[6] E. Klisch, H. Klein, G. Winnewisser, E. and Herbst, Z. Naturforsch. **53 a**, 733 (1998).

[7] H. Klein, E. Klisch, and G. Winnewisser, Z. Naturforsch. **54 a**, ... (1999).

[8] G. Winnewisser, Vib. Spectrosc. **8**, 241 (1995).

[9] S. P. Belov, F. Lewen, Th. Klaus, and G. Winnewisser, J. Mol. Spec., **174**, 606 (1995).

[10] G. Winnewisser, S. P. Belov, Th. Klaus, and R. Schieder, J. Mol. Spec., **184**, 468 (1997).

[11] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, Dover Publications, Inc., New York 1975.

[12] E. Klisch, Th. Klaus, S. P. Belov, G. Winnewisser, and E. Herbst, Astron. Astrophys. **304**, L5 (1995).

[13] K. Kawaguchi, E. Hirota, M. Ohishi, H. Suzuki, S. Takano, S. Yamamoto, and S. Saito, J. Mol. Spec. **130**, 81 (1988).

[14] J. R. Anacona, P. B. Davies, and P. A. Hamilton, Chem. Phys. Lett. **104**, 269 (1984).

[15] G. Herzberg, Molecular Spectra and Molecular Structure (Vol. I), Krieger Publishing Company, Malabar, Florida 1989.