

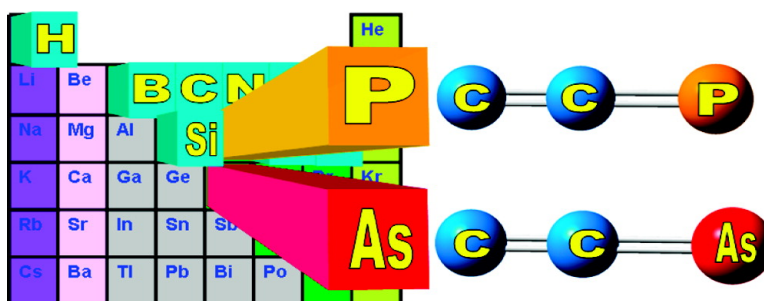
Communication

Spectroscopic Identification of CP and CAs, Two New Main Group Dicarbides

Fumie X. Sunahori, Jie Wei, and Dennis J. Clouthier

J. Am. Chem. Soc., **2007**, 129 (31), 9600-9601 • DOI: 10.1021/ja0738475 • Publication Date (Web): 13 July 2007

Downloaded from <http://pubs.acs.org> on February 16, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 3 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Spectroscopic Identification of C₂P and C₂As, Two New Main Group Dicarbides

Fumie X. Sunahori, Jie Wei, and Dennis J. Clouthier*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

Received May 28, 2007; E-mail: dclaser@uky.edu

Of the 44 possible main group dicarbides, only eight (C₂X, X = H, B, C, N, O, Si, S, and Cl) have been spectroscopically characterized. While the CCN radical has been studied extensively, the isovalent CCP species was hitherto unknown although it had been predicted to be a likely interstellar molecule.¹ A literature search did not reveal any experimental information or theoretical predictions for the CCAs radical. Solid-state phosphorus² and arsenic³ carbides are of current interest because of their potential to form very durable films and crystals with interesting electrical properties. We have been engaged in spectroscopic studies of gas-phase main group reactive intermediates for some time, and in this communication, we report the discovery of two new dicarbide free radicals, CCP and CCAs.

The radicals were prepared in a supersonic discharge jet source using techniques described in detail elsewhere.⁴ For the majority of the experiments, a mixture of PCl₃ or AsCl₃ vapor and CH₄ in high pressure argon was used as the precursor which facilitated isotopic substitution experiments with ¹³CH₄. A pulsed DC discharge at the exit of a pulsed molecular beam valve fragmented the precursor molecules yielding a variety of atomic, radical, and ionic species which reacted downstream prior to supersonic expansion cooling. The jet-cooled products were probed using laser-induced fluorescence (LIF) and wavelength-resolved emission spectroscopic techniques.

During LIF experiments on HCP⁺, we discovered a new set of bands in the 490–630 nm region. Isotopic substitution experiments showed that the carrier of this spectrum did not contain hydrogen. The same bands were observed with greater intensity using a PCl₃/CH₄/Ar precursor mixture. The low-resolution emission spectrum obtained by exciting the lowest energy LIF band at 626 nm (see Figure 1) exhibited at least three distinct vibrational intervals and an obvious doubling with an almost constant interval of 140–147 cm⁻¹. Similar experiments with ¹³CH₄ gave LIF and emission spectra with significant vibrational isotope shifts but isotope-invariant doublings, which must then be interpreted as spin-orbit splittings.

Strong evidence that the carrier of the spectrum contains two carbon atoms comes from LIF experiments using a precursor gas mixture of PCl₃ and equal amounts of ¹²CH₄ and ¹³CH₄. A band at 17 780 cm⁻¹ in the ¹²CH₄ spectrum was augmented by three additional bands, indicative of the formation of four isotopomers ¹²C¹²CX, ¹²C¹³CX, ¹³C¹²CX, and ¹³C¹³CX. The nature of the species X attached to the two carbon atoms can be deduced from the 0.1 cm⁻¹ resolution LIF spectrum shown in Figure 2. The band has all the characteristics of a ΔΛ = ±1 transition of a linear molecule and the partially resolved rotational structure gives a ground state rotational constant of ca. 0.19 cm⁻¹. Since a phosphorus-containing molecule is necessary in the precursor gas mixture to obtain the spectrum, the most obvious candidate is the CCP free radical which has a theoretically predicted⁵ ground state B value of 0.208 cm⁻¹. The absence of any intensity alternation in the rotational branches

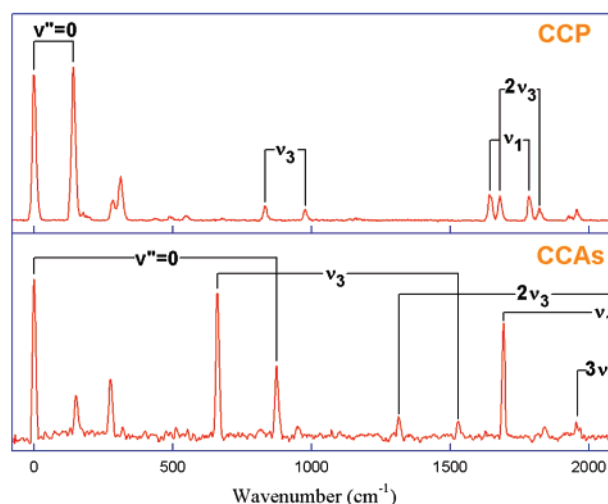


Figure 1. Single vibronic level emission spectra of CCP (above) and CCAs (below) obtained by pumping the 0–0 band Q-branch maxima at 15 971 and 14 606 cm⁻¹, respectively. The wavenumber scale is displacement from the excitation laser and gives a direct measure of the ground state energy of each band in the spectrum. Each vibronic transition consists of two features, both originating from $v' = 0$ in the upper state and terminating on one of the spin-orbit components (see text) in the ground state. The left-hand feature of the $v'' = 0$ transition was attenuated as it was obscured by scattered laser light.

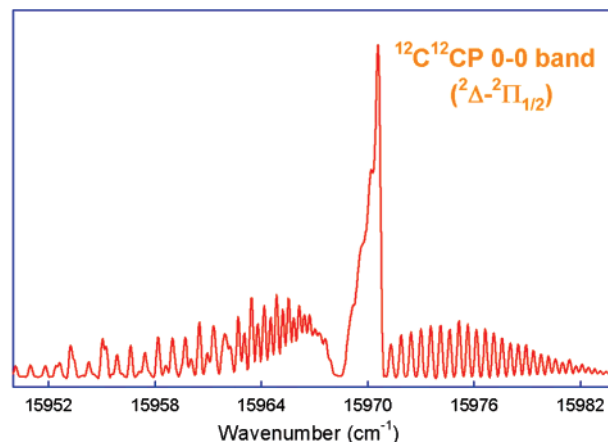


Figure 2. Medium-resolution LIF spectrum of the 0–0 band of CCP.

further indicates that the molecular structure is CCP rather than CPC, which is calculated⁶ to have substantially higher (88.0 kcal/mol) energy.

Like CCN, the CCP radical is expected to be linear in the ground state (²Π), and its electronic configuration is

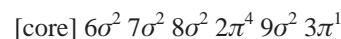


Table 1. Experimental and Theoretical Ground State Parameters of the $^{12}\text{C}^{12}\text{CX}/^{13}\text{C}^{13}\text{CX}$ ($X = \text{P}, \text{As}$) Free Radicals^a

	$^{12}\text{C}^{12}\text{CP}/^{13}\text{C}^{13}\text{CP}$		$^{12}\text{C}^{12}\text{CAs}/^{13}\text{C}^{13}\text{CAs}$	
	expt	theory ^b	expt	theory ^b
ν_1	1644/1594	1726/1659	1692/1627	1749/1680
ν_2	—	225/217 ^c	—	184/176 ^c
ν_3	833/813	847/829	661/641	675/655
A^d	142/145	—	874/874	—
$r(\text{C}-\text{C})$ (\AA) ^b		1.314		1.293
$r(\text{C}-\text{X})$ (\AA) ^b		1.626		1.734

^a All quantities except the geometric parameters are in cm^{-1} . ^b B3LYP/ aug-cc-pVTZ values. ^c Due to the Renner–Teller effect, theory gives two nondegenerate bending frequencies. The value given is the average of the two values. ^d Spin–orbit splitting.

The 140 cm^{-1} ground state intervals can then be assigned as the splitting produced by the spin–orbit coupling interaction due to the unpaired electron in the highest occupied molecular orbital (HOMO). The magnitude of the splitting is very similar to the 147 cm^{-1} spin–orbit interval in the ground state of the HCP^+ free radical.⁷ Promotion of an electron from the 9σ orbital to the 3π HOMO gives rise to three possible electronic excited states: $^2\Sigma^+$, $^2\Sigma^-$, and $^2\Delta$. The partially resolved rotational structure in Figure 2 is most consistent with assigning the observed electronic transition as $^2\Delta-^2\Pi$, similar to that observed⁸ in CCN at $21\,259\text{ cm}^{-1}$.

Similar experiments with $\text{AsCl}_3/\text{CH}_4/\text{Ar}$ mixtures gave a new set of LIF bands in the $570\text{--}685\text{ nm}$ region whose contours were similar but less well-resolved than that in Figure 2, consistent with expectations for the CCAs free radical. The emission spectrum (Figure 1) is in many ways similar to that of CCP but exhibits much larger isotope-independent spin–orbit splittings of $860\text{--}874\text{ cm}^{-1}$, comparable to the 1026 cm^{-1} spin–orbit interval in the $^2\Pi$ ground state of AsO .⁹ Experiments with $\text{SbCl}_3/\text{CH}_4/\text{Ar}$ mixtures did not reveal any new bands that could be assigned as due to the CCSb species, probably because it has a lower dissociation energy.

On the basis of the ^{13}C isotope effects, the carbon–carbon (ν_1) and carbon–phosphorus (ν_3) stretching vibrations were readily identified in the emission spectra of both radicals. For CCP, ν_3 is prominent in the spectrum with a frequency of 833 cm^{-1} , which decreases to 813 cm^{-1} on ^{13}C substitution. The C–C stretching fundamental was found at 1644 cm^{-1} with a ^{13}C isotope effect of 50 cm^{-1} . The CCAs emission spectrum consists of prominent C–As ($\nu_3 = 661\text{ cm}^{-1}$) and C–C ($\nu_1 = 1692\text{ cm}^{-1}$) stretching progressions. The experimental results are summarized in Table 1. There are also low-frequency bands associated with the bending mode of each radical, but the assignments are more complicated due to angular momentum coupling (the Renner–Teller effect) in the ground state, which will require more detailed investigation.

We have used our own theoretical predictions of the ground state properties of CCP and CCAs to support our assignments and analyses of the spectra. Density functional calculations using the Becke three parameter hybrid density functional¹⁰ with the Lee, Yang, and Parr correlation functional¹¹ (B3LYP) and Dunning's correlation consistent triple- ζ basis set augmented by diffuse functions¹² (aug-cc-pVTZ) predicted unscaled CCP ν_1 and ν_3 stretching frequencies of 1726 and 847 cm^{-1} , respectively, in good agreement with experiment. The theoretically predicted $^{12}\text{C}^{12}\text{CP}-^{13}\text{C}^{13}\text{CP}$ isotope shifts of 67 cm^{-1} (ν_1) and 18 cm^{-1} (ν_3) are also in accord with the experimental values of 50 and 20 cm^{-1} . Similar agreement between theory and experiment is found for the ground state vibrational frequencies of CCAs. The experimental values and the theoretical predictions are compared in Table 1.

All of the data obtained in this work lead to the firm conclusion that the species detected are the CCP and CCAs free radicals. It is noteworthy that only two phosphorus-containing interstellar molecules (CP and PN)^{13,14} are known. Since ab initio theory predicts a CCP ground state dipole moment^{5,6} of at least 3 Debye, it may be possible to observe this radical by radioastronomy. Our ongoing high-resolution studies of the rotational structure of the electronic bands of CCP will provide suitable molecular constants to search for the microwave spectrum. Collaborative efforts in microwave spectroscopy are currently in progress.

Acknowledgment. F.X.S. is grateful to the University of Kentucky Graduate School for an Academic Year Fellowship. We thank the National Science Foundation for support of this research.

References

- (1) Millar, T. J. *Astron. Astrophys.* **1991**, *242*, 241.
- (2) Claeysens, F.; Fuge, G. M.; Allan, N. L.; May, P. W.; Ashfold, M. N. R. *J. Chem. Soc., Dalton Trans.* **2004**, 3085.
- (3) Hu, C.; Feng, Y. P. *Phys. Rev. B* **2006**, *74*, 104102.
- (4) (a) Harjanto, H.; Harper, W. W.; Clouthier, D. J. *J. Chem. Phys.* **1996**, *105*, 10189. (b) Harper, W. W.; Clouthier, D. J. *J. Chem. Phys.* **1997**, *106*, 9461.
- (5) Largo, A.; Barrientos, C.; López, X.; Ugalde, J. M. *J. Phys. Chem.* **1994**, *98*, 3985.
- (6) El-Yazal, J.; Martin, J. M. L.; François, J.-P. *J. Phys. Chem. A* **1997**, *101*, 8319.
- (7) King, M. A.; Klapstein, D.; Kroto, H. W.; Maier, J. P.; Nixon, J. F. *J. Mol. Struct.* **1982**, *80*, 23.
- (8) Merer, A. J.; Travis, D. N. *Can. J. Phys.* **1965**, *43*, 1795.
- (9) Anderson, V. M.; Callomon, J. H. *J. Phys. B: At. Mol. Opt. Phys.* **1973**, *6*, 1664.
- (10) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (11) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (12) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- (13) Turner, B. E.; Bally, J. *Astrophys. J.* **1987**, *321*, L75.
- (14) Guélin, M.; Cernicharo, J.; Paubert, G.; Turner, B. E. *Astron. Astrophys.* **1990**, *230*, L9.

JA0738475