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Elavenil Ganesan, Thomas Custer, Arun-Libertsen Lawzer, Jean-Claude Guillemin, Robert Kolos. Unusual Quartet-Doublet Phosphorescence from the Phosphaethynyl Radical, CP. *Angewandte Chemie International Edition*, 2022, 61 (43), pp.e202210521. 10.1002/anie.202210521 . hal-03781315

**HAL Id: hal-03781315**

**<https://hal.science/hal-03781315>**

Submitted on 26 Oct 2022

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## COMMUNICATION

# Unusual Quartet-Doublet Phosphorescence from the Phosphaethynyl Radical, CP

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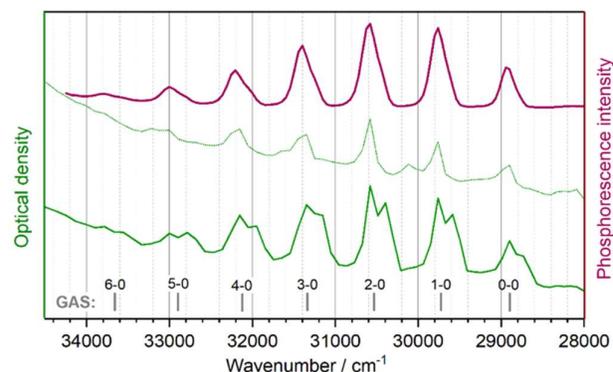
**Abstract:** We report the first detection of phosphorescence from the phosphaethynyl radical. This rare instance of quartet-doublet emission, studied here in solid argon, is presumably promoted by efficient intersystem crossing from the originally photoexcited doublet ( $B^2\Sigma^+$ ) to the adjacent second quartet state,  $1^4\Delta$ . Vibronic progressions were traced for the  $a^4\Sigma^+-X^2\Sigma^+$  and  $a^4\Sigma^+-A^2\Pi$  systems from their origins up to  $(v'=0)\rightarrow(v''=5)$  and  $(v'=0)\rightarrow(v''=2)$  bands, respectively. The measured phosphorescence lifetime is  $108 \pm 3$  ms.

Spectroscopic studies on CP (phosphaethynyl radical, carbon monophosphide) began almost a century ago when the  $B^2\Sigma^+-X^2\Sigma^+$  fluorescence, analogous to the violet system of CN, was detected by Herzberg.<sup>[1]</sup> Shortly thereafter, its rotational structure was described by Bärwald *et al.*<sup>[2]</sup> Two other electronic systems,  $B^2\Sigma^+-A^2\Pi$  in the visible<sup>[2],[3]</sup> and  $A^2\Pi-X^2\Sigma^+$  in near infrared, have also been observed.<sup>[4]</sup> Analysis of the microwave spectrum<sup>[5]</sup> of CP led to its detection around the carbon star IRC +10°216.<sup>[6]</sup> Except for ESR measurements carried out in rare-gas cryogenic matrices,<sup>[7]</sup> CP has only been studied in the gas-phase.

Although they were never observed experimentally, high-spin electronic states of CP have been the subject of a number of computational studies.<sup>[8][9][10][11][12]</sup> In particular, Qin *et al.*<sup>[11]</sup> as well as Zhang and Zhu<sup>[12]</sup> predicted the shapes of several potential energy curves, including those for the first and second quartet states of  $4^4\Sigma^+$  and  $4^4\Delta$  symmetries.

Here we report on electronic absorption and emission spectroscopy of CP photochemically generated from HCP.

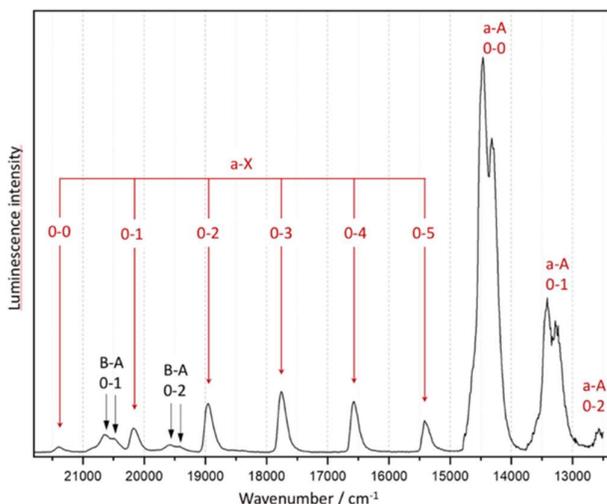
Precursor molecules were isolated in solid argon at 6 K. A xenon microwave discharge lamp provided the far-UV radiation (150–190 nm) for HCP photolysis. Preparative synthesis procedures are described in the Supporting Information, together with further details concerning the cryogenic and spectroscopic instrumentation.



**Figure 1.**  $B^2\Sigma^+-X^2\Sigma^+$   $v'\leftarrow(v''=0)$  progression of CP observed following the far-UV photolysis of HCP trapped in solid argon. Bottom trace: UV absorption. Center: UV absorption after annealing at 25 K. Top: luminescence excitation spectrum for the emission detected at 565 nm ( $17\,700\text{ cm}^{-1}$ ). See Table S1 (Supporting Information) for the wavenumber values. Markings above the wavenumber scale refer to the location of band heads reported by Bärwald *et al.*<sup>[2]</sup> for gas-phase CP.

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As photolysis of HCP proceeds, the UV absorption spectrum of CP appears (Fig. 1) and the  $v' \leftarrow (v''=0)$  progression of the  $B^2\Sigma^+ - X^2\Sigma^+$  system ( $v'$  from 0 to 6) can be discerned. The bands of the progression emerge as doublets with stronger components appearing within ca. 100  $\text{cm}^{-1}$  of the respective gas-phase positions and weaker components red-shifted by ca. 200  $\text{cm}^{-1}$ . The intensities of the weaker components decrease dramatically or vanish completely upon annealing (transient warm-up) to 25 K (Fig. 1). This indicates that the radicals are originally trapped in two distinct microenvironments ("matrix sites").



**Figure 2.** Luminescence of CP radical with band progressions due to  $a^4\Sigma^+ - A^2\Pi_i$ ,  $a^4\Sigma^+ - X^2\Sigma^+$ , and  $B^2\Sigma^+ - A^2\Pi_i$  systems, as measured following the  $B^2\Sigma^+ \leftarrow X^2\Sigma^+$  ( $v'=3 \leftarrow v''=0$ ) excitation (31 450  $\text{cm}^{-1}$ ).

Photoexcitation of the  $B^2\Sigma^+$  state results in luminescence (Fig. 2 and Tab. 1) which allows new electronic systems to be identified. Choosing any of the features from Figure 2 for monitoring while scanning the excitation wavenumber produces a spectrum (Fig. 1, top trace) which mirrors that of the  $B^2\Sigma^+ - X^2\Sigma^+$  absorption of CP (Fig. 1, bottom trace). Fig. S1 of Supporting Information provides the corresponding 3-dimensional excitation-emission maps.

We assign the series of bands originating at 21 430  $\text{cm}^{-1}$  as the  $(v'=0) \rightarrow v''$  progression of the  $a^4\Sigma^+ - X^2\Sigma^+$  phosphorescence of CP, with  $v''$  changing from 0 to 5. The theoretically predicted<sup>[12]</sup> vibrationless energy gap between the ground doublet and the lowest quartet state, 2.64 eV, is close to the observed value (2.66 eV), supporting this assignment. Further support comes from the separation between the first two bands of the progression which is  $1230 \pm 20 \text{ cm}^{-1}$ . This value matches well with the 1226.45  $\text{cm}^{-1}$  separation between the  $v''=0$  and  $v''=1$  levels of the  $X^2\Sigma^+$  state observed in gas-phase for CP radical.<sup>[4c]</sup>

Emission features due to another previously unobserved quartet-doublet system of CP,  $a^4\Sigma^+ - A^2\Pi_i$ , can also be seen. The first three elements of the  $(v'=0) \rightarrow v''$  progression appear to the red of the  $a^4\Sigma^+ - X^2\Sigma^+$  phosphorescence (Fig. 2), starting with the strong origin band around 14 400  $\text{cm}^{-1}$ , *i.e.*, 1.79 eV. This is in good agreement with theory which predicts a value of 1.81 eV.<sup>[12]</sup> These features are doubled due to the presence of  $A^2\Pi_{1/2}$  and  $A^2\Pi_{3/2}$  sublevels. Maxima of the partly overlapping components are separated by  $150 \pm 10 \text{ cm}^{-1}$  which is close to a previously measured gas-phase splitting of 157.87  $\text{cm}^{-1}$ .<sup>[3b]</sup> The  $0 \rightarrow 1$  band

appears  $1057 \pm 10 \text{ cm}^{-1}$  below  $0 \rightarrow 0$ , while the gas-phase  $\omega_e$  value reported<sup>[4b]</sup> for  $A^2\Pi_i$  is 1062.5  $\text{cm}^{-1}$ . The predicted<sup>[12]</sup> change in the equilibrium C-P distance is significantly larger for the  $a^4\Sigma^+ \rightarrow X^2\Sigma^+$  transition than for  $a^4\Sigma^+ \rightarrow A^2\Pi_i$  (-0.16 Å vs. -0.07 Å). This may qualitatively explain the difference in relative strengths (Franck-Condon factors) of  $(v'=0) \rightarrow (v''=0)$  bands within the two vibronic progressions (see Fig. 2).

The monoexponential decay time of undispersed phosphorescence is  $108 \pm 3 \text{ ms}$  (Fig. S2). Emission lifetimes measured separately for the selected bands of  $a^4\Sigma^+ \rightarrow X^2\Sigma^+$  and  $a^4\Sigma^+ \rightarrow A^2\Pi_i$  were identical, within the experimental error (see Fig. S3). The radiative lifetimes theoretically predicted<sup>[12]</sup> for the vibrationally relaxed  $a^4\Sigma^+_{1/2}$  and  $a^4\Sigma^+_{3/2}$  levels of gas-phase CP are 59.7 ms and 129.5 ms, respectively, but our data do not provide evidence for a biexponential decay.

Fluorescence progressions of the  $B^2\Sigma^+ - X^2\Sigma^+$  and  $B^2\Sigma^+ - A^2\Pi_i$  systems, known from previous gas-phase emission studies,<sup>[1],[2]</sup> appeared with their origins in the vicinities of 29 000 and 22 000  $\text{cm}^{-1}$ , respectively (see Fig. S4, S5 and Tab. S2, S3 of Supporting Information). In general, fluorescence was weaker than the phosphorescence.

**Table 1.** Phosphorescence bands of CP in solid Ar following  $B^2\Sigma^+ \leftarrow X^2\Sigma^+$  ( $v'=1 \leftarrow v''=0$ ) excitation (29 760  $\text{cm}^{-1}$ ).

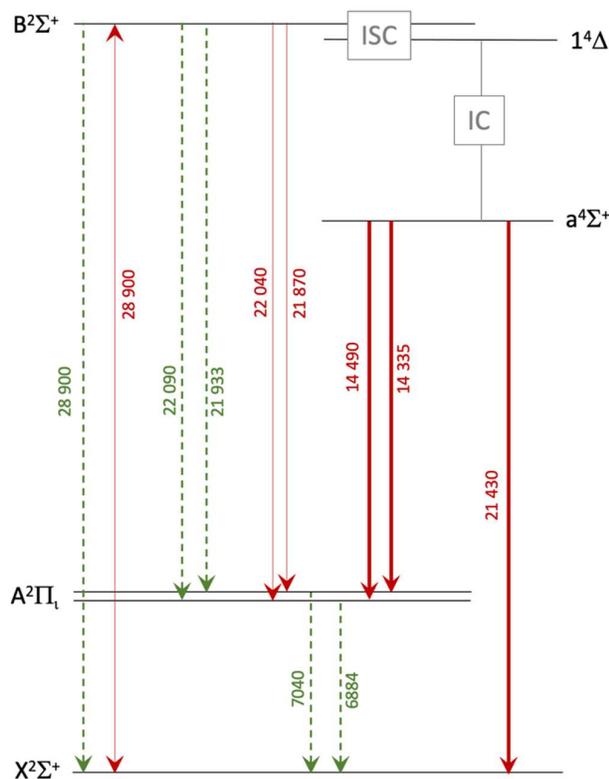
| $v''$  | Wavenumber ( $\text{cm}^{-1}$ ) <sup>a</sup> |
|--|--|
| $a^4\Sigma^+ - X^2\Sigma^+$ , ( $v'=0$ ) $\rightarrow v''$           |  |
| 0  | 21 430                                       |
| 1  | 20 195                                       |
| 2  | 18 970                                       |
| 3  | 17 770                                       |
| 4  | 16 590                                       |
| 5  | 15 420                                       |
| $a^4\Sigma^+ - A^2\Pi_i$ , ( $v'=0$ ) $\rightarrow v''$ <sup>b</sup> |  |
| 0  | 14 490                                       |
|  | 14 335                                       |
| 1  | 13 445                                       |
|  | 13 285                                       |
| 2  | 12 560                                       |
|  | -- <sup>c</sup>                              |

[a] Measurement accuracy changes from  $\pm 10 \text{ cm}^{-1}$  at the top to  $\pm 5 \text{ cm}^{-1}$  at the bottom. [b] Lower and upper row values correspond to  $\Omega=1/2$  and  $\Omega=3/2$  sublevels of the  $A^2\Pi_i$  state, respectively. [c]  $\Omega=1/2$  band falls beyond the wavelength detection limit of 800 nm.

Application of Hund's rule leads to a triplet as the lowest excited state of a closed-shell molecule. For free radicals, an analogous pattern, *i.e.* a higher-spin (quartet) state located below the first excited doublet, is not expected<sup>[13]</sup> excluding radicals having a degenerate ground state such as  $\text{NO}^{[14]}$  (Fig. S6 provides simplified electronic orbital schemes). Consequently, a photoexcited quartet-doublet phosphorescence has been specifically identified in few cases (*e.g.* for  $\text{NO}^{[14]}$ ,  $\text{BiO}^{[15]}$  and decacyclene anion<sup>[16]</sup>). The  $X^2\Sigma^+$  electronic configuration of CP,  $2\pi^{\alpha\beta\alpha\beta} 7\sigma^{\alpha} 2\pi^0$  (inner orbitals not shown), changes mainly to  $2\pi^{\alpha\beta\alpha} 7\sigma^{\alpha\beta} 2\pi^0$  in  $A^2\Pi_i$ , and to  $2\pi^{\alpha\beta\alpha} 7\sigma^{\alpha} 2\pi^{\alpha}$  for the lowest quartet,<sup>[11]</sup> making the quartet state more energetic than  $A^2\Pi_i$ . A nonradiative passage to a quartet state from an originally excited doublet higher than  $A^2\Pi_i$  (*e.g.*  $B^2\Sigma^+$ ) might not seem likely. Such an intersystem crossing would have to prevail over very fast internal conversion and vibrational relaxation. The case of CP is remarkable, however. According to theoretical predictions,<sup>[12][11]</sup> the second excited quartet,  $1^4\Delta$ , is almost coincident with  $B^2\Sigma^+$  across a broad range of interatomic distances. This coincidence,

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we presume, encourages efficient intersystem crossing from the photoexcited  $B^2\Sigma^+$  to the  $1^4\Delta$  state (Fig. 3). This is followed by fast internal conversion to  $a^4\Sigma^+$ . No luminescence originating directly from  $1^4\Delta$  could be observed.



**Figure 3.** Electronic transitions observed for CP. System origins given in wavenumbers. Dashed green arrows are previously reported gas-phase transitions.<sup>[2][3b][4c]</sup> Solid (red) arrows are transitions we detected in solid argon. Bold solid arrows represent phosphorescence. ISC and IC stand for intersystem crossing and internal conversion.

For the extensively studied N-bearing analogue, CN, the relative energies of the three lowest states ( $X^2\Sigma^+$ ,  $A^2\Pi$ ,  $B^2\Sigma^+$ ), and hence the corresponding doublet-state spectroscopy, are quite similar to what is observed for CP.<sup>[17]</sup> However, CN radical quartet states<sup>[18]</sup> are not close in energy to any doublets. Intersystem crossing cannot effectively compete with internal conversion and no quartet-doublet emission is observed. Information concerning  $a^4\Sigma^+$  and  $b^4\Pi$  states of CN comes exclusively from perturbations they cause in doublet-doublet transitions.<sup>[19]</sup> Neither has phosphorescence from CAs been reported and theoretical predictions<sup>[20]</sup> of the potential energy curves do not give grounds to expect it. No relevant calculations or measurements are available for CSb and Cbi.

In conclusion, phosphorescence has been observed for the diatomic radical species CP isolated in a cryogenic matrix. A theoretical justification for this unusual case of quartet-doublet emission is proposed. This phosphorescence is strong (especially the red  $a^4\Sigma^+ \rightarrow A^2\Pi_1$  bands) and therefore useful for the sensitive detection of CP in low temperature solid environments.

## Acknowledgements

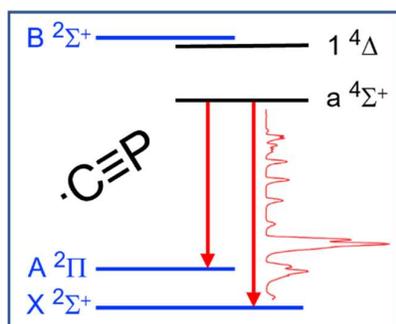
We thank Dr. Marcin Gronowski for fruitful discussions. J.C.G. thanks the Centre National d'Etudes Spatiales (CNES) for a grant and the French national programme "Physique et Chimie du Milieu Interstellaire" (PCMI) of CNRS/INSU with INC/INP co-funded by CEA and CNES.

**Keywords:** Quartet-doublet emission • Radical phosphorescence • CP radical • Carbon monophosphide

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## Entry for the Table of Contents



CP is generated by photolysis of phosphoethyne (HCP) isolated in solid argon. Phosphorescence of the radical, observed after the  $\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+$  photoexcitation, is assisted by an intersystem crossing from  $\text{B}^2\Sigma^+$  to the adjacent second quartet state,  $1^4\Delta$ . Intense, well-resolved vibronic progressions were traced for  $\text{a}^4\Sigma^+ - \text{X}^2\Sigma^+$  and  $\text{a}^4\Sigma^+ - \text{A}^2\Pi$  emission systems. Phosphorescence lifetime is on the order of 0.1 s.