Photoluminescence of tetrachloroarsenate(III)

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Abstract
Glasses of (NBu₄)AsCl₄ in ethanol at 77 K show a red emission at \( \lambda_{\text{max}} = 617 \) nm with \( \phi \approx 10^{-4} \) and \( \tau = 0.46 \mu s \). It is suggested that this luminescence originates from the sp excited state \( ^3P_1 \) of the As³⁺ ion. The excited state properties of AsCl₄⁻ are discussed in comparison to those of SbCl₄⁻ and BiCl₄⁻.

1. Introduction
While Blasse and his group have studied the luminescence of As³⁺ ions in solid elpasolite, \( \text{Cs}_2\text{NaScCl}_6 \) [1], molecular As(III) compounds have not yet been observed to emit according to our knowledge. We explored this possibility and selected the complex anion AsCl₄⁻ for the present investigation. This choice was based on our previous study of the emission behavior of the complexes MCl₄⁻ and MCl₆⁻ with \( M=\text{Sb} \) and \( \text{Bi} \) [2, 3]. We expected to see distinct differences in the luminescence properties between the heavy metal complexes SbCl₄⁻ and BiCl₄⁻ and the corresponding chloro complex of the lighter congeners arsenic which as a number of the fourth period of the periodic table is characterized by a smaller spin-orbit coupling constant.

2. Experimental
The compound \((\text{NBu}_4)_2\text{AsCl}_4\) was prepared according to published procedures [4]. Solutions of this substance were light sensitive. UV irradiation for longer periods led to the deposition of elemental arsenic as a dark brown precipitate. Absorption spectra were measured in solutions of dry acetonitrile under argon at room temperature on a Hewlett Packard 8452A diode array spectrophotometer. Emission spectra were obtained in ethanol glasses at 77 K on a Hitachi 850 spectrofluorimeter equipped with a Hamamatsu 928 photomultiplier. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations. Luminescence quantum yields were estimated by comparing the integrated emission intensity of \((\text{NBu}_4)_2\text{AsCl}_4\) in an ethanol glass with that of europium thenoyltrifluoroacetone (\( \lambda_{\text{max}} = 612 \) nm, \( \phi = 0.56 \)) under comparable conditions. Emission lifetimes were measured on a luminescence analysis system (model LS-100-07) from Photon Technology International.

3. Results
The absorption spectrum of AsCl₄⁻ in acetonitrile (Fig. 1) shows a weak band at \( \lambda_{\text{max}} = 359 \) nm \( (e = 12.3 \ M^{-1} \ cm^{-1}) \) and an increase of the extinction towards shorter wavelength. Weak shoulders appear around 310 and 270 nm. While at room temperature AsCl₄⁻ was not emissive, a red photoluminescence at \( \lambda_{\text{max}} = 617 \) nm was observed in ethanol glasses at 77
4. Discussion

In analogy to SbCl₄⁻ and BiCl₄⁻ [2,3] the long-wavelength absorptions of AsCl₄⁻ are assigned to sp transitions of the central s² ion. The A band (1⁰S₀→3³P₁ transition) of AsCl₄⁻ at λ_max = 359 nm is much weaker than those of SbCl₄⁻ and BiCl₄⁻ since the spin-selection rule is largely valid for arsenic which belongs to the fourth period of the periodic table. In contrast, the spin-forbidden transitions of SbCl₄⁻ and BiCl₄⁻ become partially allowed by strong spin-orbit coupling of the heavier metals antimony and bismuth. The B (λ_max ≈ 310 nm) and C (λ_max ≈ 270 nm) bands of AsCl₄⁻ which are assigned to 1⁰S₀→3³P₂ and 1⁰S₀→1⁴P₁ sp transitions, respectively, are obscured by another absorption which increases in intensity towards shorter wavelength. We assign this band to a ligand-to-metal charge transfer (LMCT) transition which involves the promotion of a chloride electron to the p orbitals of As(III). Analogous LMCT bands were also identified in the absorption spectra of halide complexes of other s² ions [3,5]. In the case of AsCl₄⁻ the LMCT assignment is supported by the observation that UV irradiation of AsCl₄⁻ in CH₃CN leads to a photoredox decomposition with the formation of elemental arsenic. The sp absorptions of As³⁺ in Cs₂NaScCl₆ matrix appear at shorter wavelengths (A band at λ_max = 308 nm, B band at 281 nm, C band at 250 nm) [1] than the corresponding absorptions of AsCl₄⁻.

In analogy to many other chloride complexes of s² ions [3] the emission of AsCl₄⁻ at λ_max = 617 nm is assigned to the 3³P₁→1⁰S₀ transition. Its spin-forbidden character is in accordance with the observation that this emission appears only at low temperatures while the luminescence of SbCl₄⁻ and BiCl₄⁻ can be clearly seen in solution at room temperature [2,3]. A rough estimate of the radiative lifetime of AsCl₄⁻ based on the emission quantum yield (φ ≈ 10⁻⁴) and lifetime (τ = 0.46 µs) yields a reasonable value of approximately 10 ms which compares with 2.5 ms for As³⁺ in Cs₂NaScCl₆.

The Stokes shift of the 1⁰S₀→3³P₁ transition of AsCl₄⁻ amounts to 11650 cm⁻¹. Stokes shifts of this magnitude were also observed for SbCl₄⁻ and BiCl₄⁻. It is suggested that this shift is caused by a structural change from disphenoidal (C₃ᵥ) [6] in the ground state toward a tetrahedral geometry in the ³P₁ excited state [2,3]. It is quite interesting that the Stokes shift of AsCl₄⁻ is comparable to that of As³⁺ in Cs₂NaScCl₆ (ΔΦ = 12200 cm⁻¹) [1]. It was assumed that in the latter case the large shift is related to the fact that As³⁺ ions which occupy octahedral sites in the halide matrix are rather small. In the ground state they may thus not be located in the center of octahedral sites formed by the chloride ions. Accordingly, the effective coordination number for As³⁺ in Cs₂NaScCl₆ might be smaller than 6, possibly 4 as for AsCl₄⁻.

As an alternative, the long radiative lifetime of AsCl₄⁻ may have a different origin. Generally, the lowest energy sp transition which takes place between the ⁰S₀ ground state and the ³P₀ state is not seen in either absorption or emission since it is strongly forbidden [7]. If in the case of AsCl₄⁻ the ³P₀ state is somehow populated its radiative deactivation should be extremely slow in accordance with our observation. It follows that the Stokes shift of this emission is then smaller than that noted above for the ¹S₀→³P₁ transition because the undetected ¹S₀→³P₀ absorption should be located at lower energy than the ¹S₀→³P₁ absorption.
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References
