

Photoluminescence of tetrachloroarsenate(III)

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Abstract

Glasses of $(\text{NBu}_4)\text{AsCl}_4$ in ethanol at 77 K show a red emission at $\lambda_{\text{max}} = 617$ nm with $\phi \approx 10^{-4}$ and $\tau = 0.46$ μs . It is suggested that this luminescence originates from the sp excited state $^3\text{P}_1$ of the As^{3+} ion. The excited state properties of AsCl_4^- are discussed in comparison to those of SbCl_4^- and BiCl_4^- .

1. Introduction

While Blasse and his group have studied the luminescence of As^{3+} 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 AsCl_4^- for the present investigation. This choice was based on our previous study of the emission behavior of the complexes MCl_4^- and MCl_6^{3-} with $\text{M} = \text{Sb}$ and Bi [2,3]. We expected to see distinct differences in the luminescence properties between the heavy metal complexes SbCl_4^- and BiCl_4^- and the corresponding chloro complex of the lighter congener 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 $(\text{NBu}_4)\text{AsCl}_4$ 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 $(\text{NBu}_4)\text{AsCl}_4$ in an ethanol glass with that of europium thenoyltrifluoroacetate ($\lambda_{\text{max}} = 612$ 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 AsCl_4^- in acetonitrile (Fig. 1) shows a weak band at $\lambda_{\text{max}} = 359$ nm ($\epsilon = 12.3$ $\text{M}^{-1} \text{cm}^{-1}$) and an increase of the extinction towards shorter wavelength. Weak shoulders appear around 310 and 270 nm. While at room temperature AsCl_4^- was not emissive, a red photoluminescence at $\lambda_{\text{max}} = 617$ nm was observed in ethanol glasses at 77

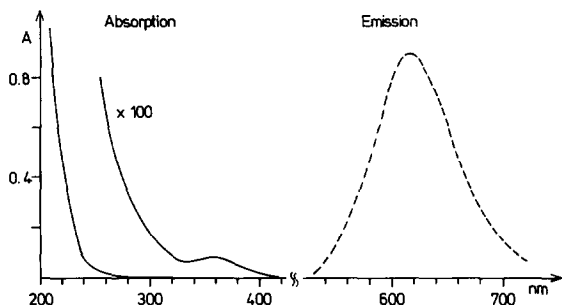


Fig. 1. Electronic absorption (—) and emission (---) spectra of $(\text{NBu}_4)\text{AsCl}_4$. Absorption: 9.20×10^{-5} M in acetonitrile under argon at room temperature, 1 cm cell. Emission: 10^{-2} M in ethanol at 77 K, $\lambda_{\text{exc}} = 300$ nm, intensity in arbitrary units.

K (Fig. 1). The excitation spectrum was quite featureless but agreed qualitatively with the absorption spectrum. The emission quantum yield was roughly $\phi = 10^{-4}$ at $\lambda_{\text{exc}} = 300$ nm. The emission decayed with a lifetime of $\tau = 0.46 \pm 0.03$ μs .

4. Discussion

In analogy to SbCl_4^- and BiCl_4^- [2,3] the long-wavelength absorptions of AsCl_4^- are assigned to sp transitions of the central s^2 ion. The A band ($^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition) of AsCl_4^- at $\lambda_{\text{max}} = 359$ nm is much weaker than those of SbCl_4^- and BiCl_4^- 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 SbCl_4^- and BiCl_4^- become partially allowed by strong spin-orbit coupling of the heavier metals antimony and bismuth. The B ($\lambda_{\text{max}} \approx 310$ nm) and C ($\lambda_{\text{max}} \approx 270$ nm) bands of AsCl_4^- which are assigned to the $^1\text{S}_0 \rightarrow ^3\text{P}_2$ and $^1\text{S}_0 \rightarrow ^1\text{P}_1$ 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 s^2 ions [3,5]. In the case of AsCl_4^- the LMCT assignment is supported by the observation that UV irradiation of AsCl_4^- in CH_3CN leads to a photoredox decomposition with the formation of elemental arsenic. The sp absorptions of

As^{3+} in $\text{Cs}_2\text{NaScCl}_6$ matrix appear at shorter wavelengths (A band at $\lambda_{\text{max}} = 308$ nm, B band at 281 nm, C band at 250 nm) [1] than the corresponding absorptions of AsCl_4^- .

In analogy to many other chloride complexes of s^2 ions [3] the emission of AsCl_4^- at $\lambda_{\text{max}} = 617$ nm is assigned to the $^3\text{P}_1 \rightarrow ^1\text{S}_0$ transition. Its spin-forbidden character is in accordance with the observation that this emission appears only at low temperatures while the luminescence of SbCl_4^- and BiCl_4^- can be clearly seen in solution at room temperature [2,3]. A rough estimate of the radiative lifetime of AsCl_4^- based on the emission quantum yield ($\phi \approx 10^{-4}$) and lifetime ($\tau = 0.46$ μs) yields a reasonable value of approximately 10 ms which compares with 2.5 ms for As^{3+} in $\text{Cs}_2\text{NaScCl}_6$.

The Stokes shift of the $^1\text{S}_0 \leftrightarrow ^3\text{P}_1$ transition of AsCl_4^- amounts to 11650 cm^{-1} . Stokes shifts of this magnitude were also observed for SbCl_4^- and BiCl_4^- . It is suggested that this shift is caused by a structural change from disphenoidal (C_{2v}) [6] in the ground state toward a tetrahedral geometry in the $^3\text{P}_1$ excited state [2,3]. It is quite interesting that the Stokes shift of AsCl_4^- is comparable to that of As^{3+} in $\text{Cs}_2\text{NaScCl}_6$ ($\Delta\bar{\nu} = 12200$ cm^{-1}) [1]. It was assumed that in the latter case the large shift is related to the fact that As^{3+} 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 As^{3+} in $\text{Cs}_2\text{NaScCl}_6$ might be smaller than 6, possibly 4 as for AsCl_4^- .

As an alternative, the long radiative lifetime of AsCl_4^- may have a different origin. Generally, the lowest energy sp transition which takes place between the $^1\text{S}_0$ ground state and the $^3\text{P}_0$ state is not seen in either absorption or emission since it is strongly forbidden [7]. If in the case of AsCl_4^- the $^3\text{P}_0$ 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 $^1\text{S}_0/{}^3\text{P}_1$ transition because the undetected $^1\text{S}_0 \rightarrow ^3\text{P}_0$ absorption should be located at lower energy than the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ absorption.

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