

SHORT COMMUNICATIONS

X-RAY ABSORPTION STUDIES OF YbAl_2 AND YbAl_3 INTERMETALLIC COMPOUNDS

V. PRABHAWALKAR and B. D. PADALIA
Department of Physics Indian Institute of
Technology, Bombay 400 076, India.

THE intermetallic compounds YbAl_2 and YbAl_3 crystallize in the MgCu_2 and AuCu_3 -type structures respectively¹. These systems have been extensively studied using various techniques¹⁻⁵. The results on YbAl_2 and YbAl_3 obtained in our laboratory, using x-ray absorption (XAS) technique are discussed here in the light of the available reports on these systems.

The samples were prepared using the standard technique⁴. X-ray absorption spectra were recorded

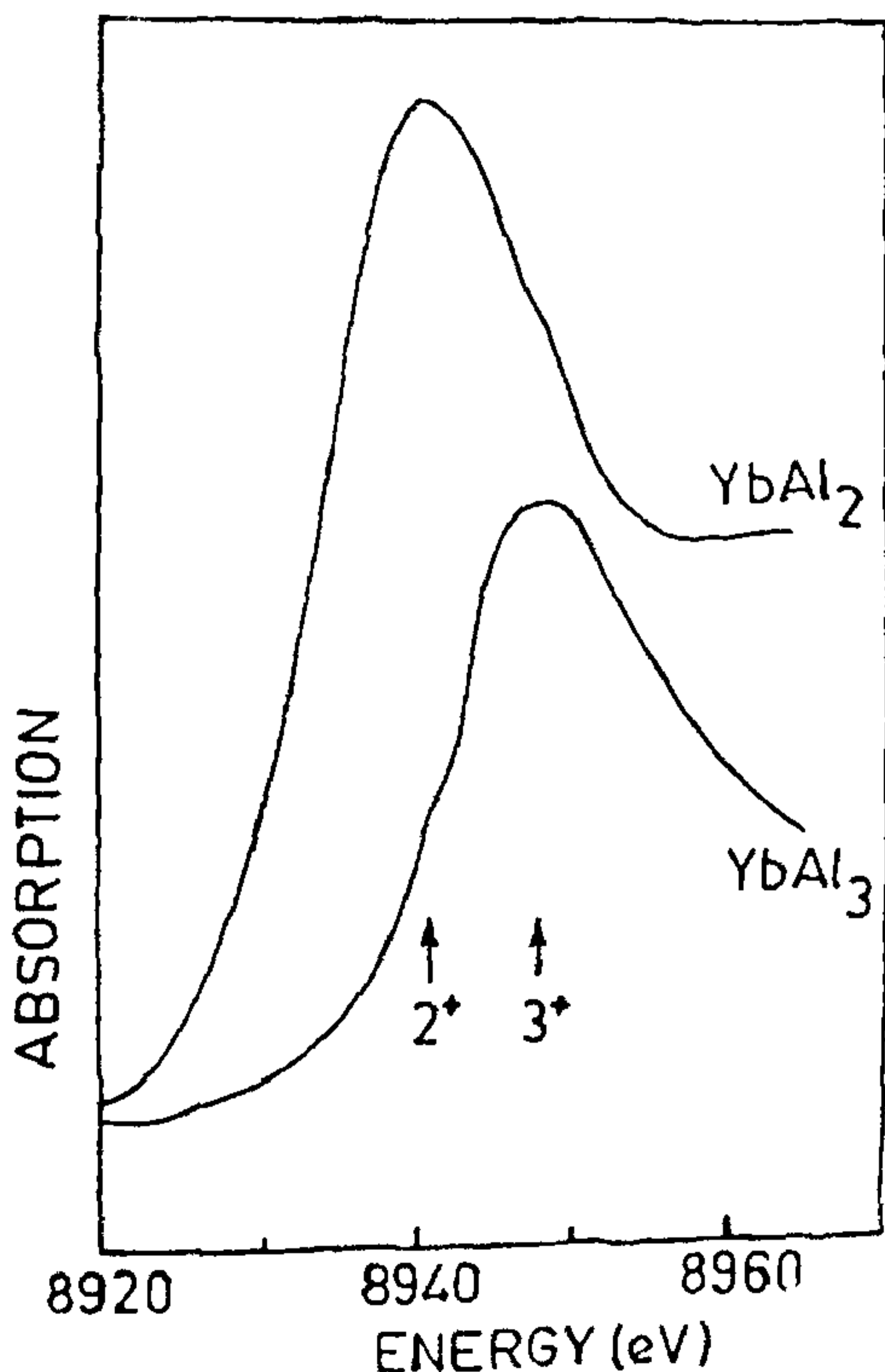


Figure 1. L_3 -absorption spectra of Yb in YbAl_2 and YbAl_3 intermetallics.

using 600 mm x-ray spectrograph of focussing type. Details regarding the experimental set-up and measurements are discussed elsewhere^{6,7}.

Figure 1 shows the L_3 -absorption edge region of Yb in YbAl_2 and YbAl_3 . The absorption spectra for each of these systems, YbAl_2 and YbAl_3 exhibit two peaks separated by ~ 7 eV. The energies of these peaks are measured and compared with the standard divalent and trivalent Yb compounds^{8,9}. Such a comparison reveals that the two peaks appearing in the absorption spectra correspond to Yb^{2+} and Yb^{3+} , thus establishing the mixed valence character of both YbAl_2 and YbAl_3 . The intensities of the absorption peaks indicate that the population of Yb^{2+} in YbAl_2 is larger than that of Yb^{3+} . On the other hand, the population of Yb^{2+} in YbAl_3 is much less than Yb^{3+} .

It is of interest to compare the present results in the light of the available reports on YbAl_2 and YbAl_3 . The lattice constant as well as the magnetic susceptibility measurements on YbAl_2 indicate that Yb in YbAl_2 is in intermediate valence state^{4,5}. These techniques suggest that the average valency of Yb in YbAl_2 is ~ 2.1 at room temperature. Subsequent XAS studies on YbAl_2 using synchrotron radiation² gave nearly the same value of average valency (~ 2.5). The L_3 -absorption spectral features recorded in the present work for YbAl_2 resemble closely to those reported by others².

The magnetic susceptibility and lattice constant measurements^{4,5} on YbAl_3 indicate that Yb in YbAl_3 is in mixed valence state. Further support to mixed valence character of YbAl_3 has been obtained from the $4f$ x-ray photoelectron spectra (XPS)³. The ratio $\text{Yb}^{3+}/\text{Yb}^{2+}$ in YbAl_3 determined from XPS studies is comparable, though smaller than the value estimated by the magnetic susceptibility data³. The present XAS results on YbAl_2 agree well with those reported by others using various techniques³⁻⁵.

It may be concluded that the present XAS results on YbAl_2 and YbAl_3 firmly establish the mixed-valence character of YbAl_2 and YbAl_3 intermetallic compounds.

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ANOMALOUSLY LONG RADIATIVE LIFETIMES OF URANYL ION IN SOLUTIONS

G. C. JOSHI AND D. D. PANT*

Department of Physics, Garhwal University, Srinagar 246 174, India.

* Department of Physics, Kumaun University, Naini Tal 263 001, India.

In uranyl solutions, theoretical calculations of natural lifetimes were reported by Rabinowitch *et al*¹ which correspond to an absorption band in the (400–500 nm) region. The value calculated by them ($\tau_{\text{cal}} \sim 1.5 \times 10^{-4}$ sec) was an order of magnitude less than the experimentally observed lifetimes in many cases. They however, mentioned that a correct value could be obtained if, out of the entire absorption curve, the contribution of the electronic absorption corresponding to the F series alone could be evaluated. On the contrary, Dieke *et al*² calculated it to be of the order of 10^{-1} sec. for $\text{CsUO}_2(\text{NO}_3)_3$. This is a much greater value since the fluorescence quantum yield for this uranyl salt is nearly unity. The lifetime of F electronic band calculated by McClynn³ (4.76×10^{-4} sec) is also shorter than the observed values at low temperatures. In our previous work⁴, we calculated the lifetimes, of various uranyl species and found that, in general, for protonated solutions the $\tau_{\text{cal}} > \tau_{\text{obs}}$. This is an expected result as the shortening of the observed lifetimes are due to general non-radiative processes. In the present

paper we report the results of a study with due consideration of fluorescence yield and the lifetimes in deuterated solvents. It is found that the τ_{cal} values are smaller than τ_{obs} values for most of the cases.

The room temperature absorption spectra were recorded with a Beckman DK-2A spectrophotometer. The absorption spectra of uranyl sulphate solution in sulphuric acid were also recorded at 80° K where it froze into a transparent glass, by recording transmitted light of an incandescent source with a monochromator photomultiplier assembly and calculating the extinction coefficient as compared to pure H_2SO_4 frozen glass. The lifetimes and recordings of emission spectra were measured by usual methods⁴.

The natural lifetimes (τ_{cal}) were calculated using the Strickler and Berg⁵ formula.

$$\frac{1}{\tau} = 2.88 \times 10^{-9} n^2 \langle \nu_f^{-3} \rangle_{\nu}^{-1} g_i / g_u \int \epsilon(\bar{\nu}) d \log \bar{\nu} \text{ sec}^{-1}$$

where n is refractive index, g_i / g_u the multiplicity fac-

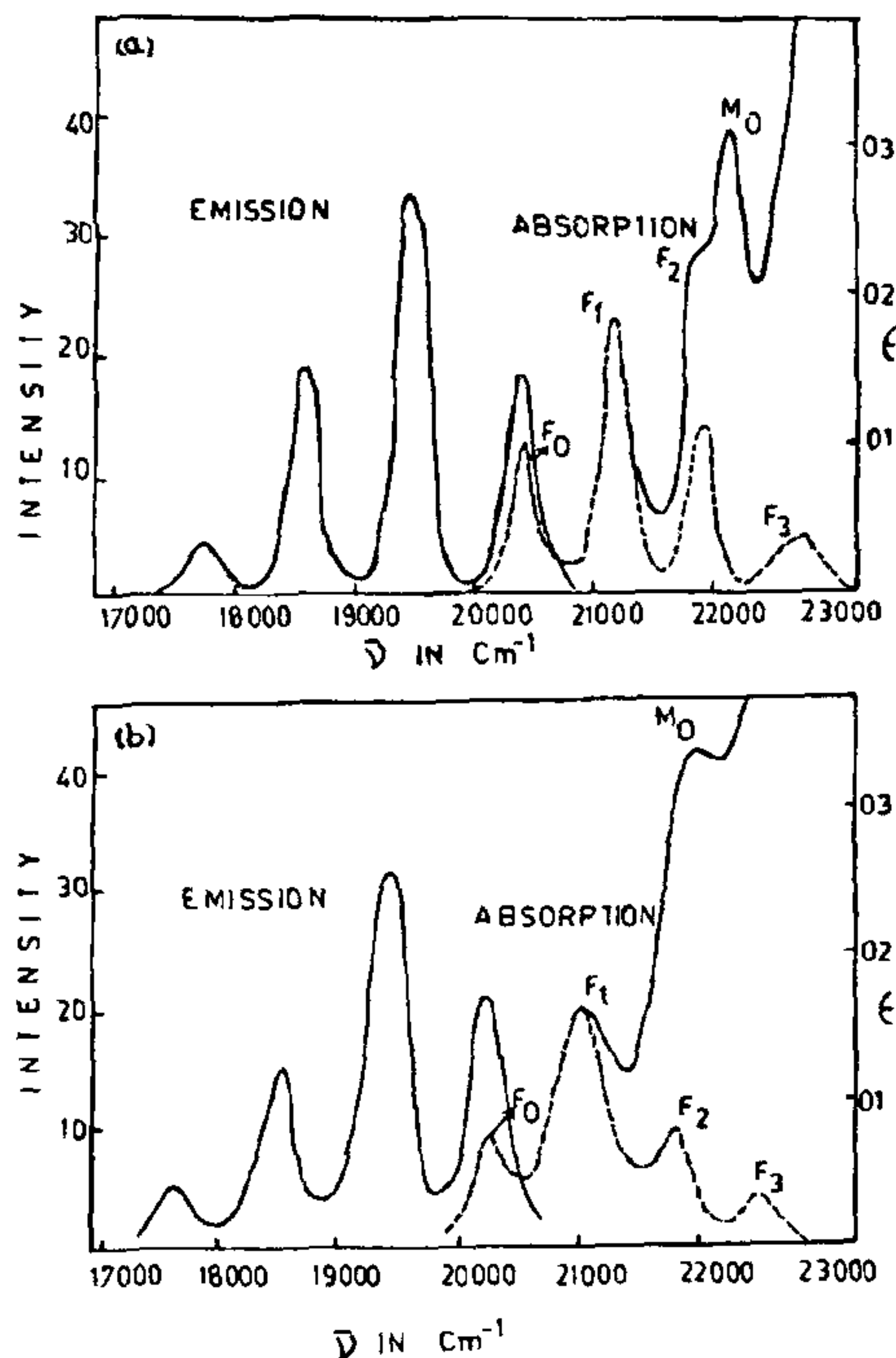


Figure 1. Absorption and emission spectra of the UO_2^{2+} ion in 97% H_2SO_4 solution (a) at 80° K and (b) at 293° K.