

## Short Communication

Vibrational spectra of  $\text{Cd}_2\text{As}_2\text{O}_7$ Enrique J. Baran<sup>1\*</sup> and Matthias Weil<sup>2</sup><sup>1</sup> Centro de Química Inorgánica (CEQUINOR/CONICET, UNLP), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C. Correo 962, 1900-La Plata, Argentina<sup>2</sup> Institut für Mineralogie, Kristallographie und Strukturchemie, Technische Universität Wien, Getreidemarkt 9/171, A-1060 Vienna, Austria

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**The infrared and Raman spectra of  $\text{Cd}_2\text{As}_2\text{O}_7$ , belonging to the thortveitite structural type, were recorded and are discussed on the basis of a factor group analysis and by comparisons with related compounds. Copyright © 2004 John Wiley & Sons, Ltd.**

**KEYWORDS:** cadmium(II) diarsenate; Raman spectra; infrared spectra; factor group analysis

## INTRODUCTION

Numerous divalent metal diarsenates of stoichiometry  $\text{M}_2\text{As}_2\text{O}_7$  crystallize in the thortveitite-type structure.<sup>1–7</sup> In the case of  $\text{Cd}_2\text{As}_2\text{O}_7$ , Calvo and Neelakantan<sup>1</sup> first showed its relation to this structural family and later Juri *et al.*<sup>4</sup> determined its crystallographic data by means of powder diffractometry. Only recently was a definitive structural refinement by single-crystal x-ray diffractometry published by Weil.<sup>8</sup>

So far, for only a few of these thortveitite-type diarsenates have detailed vibrational spectroscopic studies been performed. Therefore, and taking advantage of the now available structural information, we have measured and assigned the infrared and Raman spectra of  $\text{Cd}_2\text{As}_2\text{O}_7$ .

## EXPERIMENTAL

Microcrystalline samples of  $\text{Cd}_2\text{As}_2\text{O}_7$  were prepared by solid-state reaction of the binary oxides in closed silica ampoules at 873 K for 10–12 days.<sup>8</sup>

IR spectra in the range 4000–300  $\text{cm}^{-1}$  were recorded with a Bruker IFS 66 Fourier transform (FT) IR instrument using the KBr pellet technique. A total of 80 scans were accumulated. Raman spectra were measured on powdered samples in a capillary tube using the FRA 106 Raman accessory of the same FTIR instrument. Radiation of 1064 nm from an Nd:YAG solid-state laser was used for excitation.

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## RESULTS AND DISCUSSION

$\text{Cd}_2\text{As}_2\text{O}_7$  crystallizes in the monoclinic space group  $C2/m(C_{2h}^3)$  with  $Z = 2$ . The main structural features are  $\text{As}_2\text{O}_7^{4-}$  groups with a linear As—O—As bridge showing large thermal motion of the bridging O atom perpendicular to the As—O—As axis. The conformation of the  $\text{As}_2\text{O}_7^{4-}$  anion is staggered. The Cd(II) cations conform to edge-sharing  $\text{CdO}_6$  octahedra, which form two-dimensionally infinite honeycomb sheets extending parallel to the *ac* plane with the  $\text{As}_2\text{O}_7^{4-}$  anions situated above and below the vacant sites of these cationic layers.<sup>8</sup>

As the thortveitite-type structure presents linear or practically linear X—O—X bridges, the symmetry of the 'free ions' is approximately  $D_{3d}$  and the 21 internal vibrations of the  $\text{As}_2\text{O}_7^{4-}$  anion generate the following irreducible representation:<sup>9</sup>

$$\Gamma_{D_{3d}} = 3A_{1g} + A_{1u} + 3A_{2u} + 3E_g + 4E_u$$

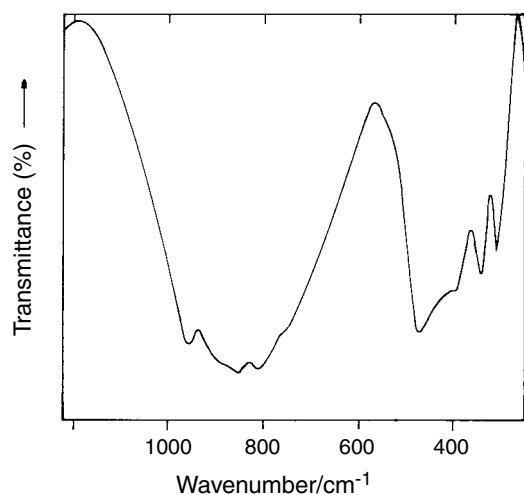
in which phonons with *g*-parity are only Raman active whereas those with *u*-parity present only IR activity, except  $A_{1u}$ , which is inactive. The distribution of the vibrational modes between these different symmetry species is presented in Table 1.<sup>9</sup> In the crystal lattice the symmetry of the anion is reduced to  $C_{2h}$  and also the factor group presents identical symmetry, with only one  $\text{As}_2\text{O}_7^{4-}$  anion in the spectroscopic unit cell. As a result, under this factor group symmetry, the symmetry species are transformed as also shown in Table 1.

The IR spectrum of  $\text{Cd}_2\text{As}_2\text{O}_7$  in the spectral range between 1200 and 300  $\text{cm}^{-1}$  is shown in Fig. 1 and the corresponding Raman spectrum in Fig. 2. The proposed assignment is presented in Table 2.

**Table 1.** Factor group analysis of the  $\text{As}_2\text{O}_7^{4-}$  vibrations in the  $\text{Cd}_2\text{As}_2\text{O}_7$  lattice [ $C2/m(C_{2h}^3)$  and  $Z = 2$ ]<sup>a</sup>

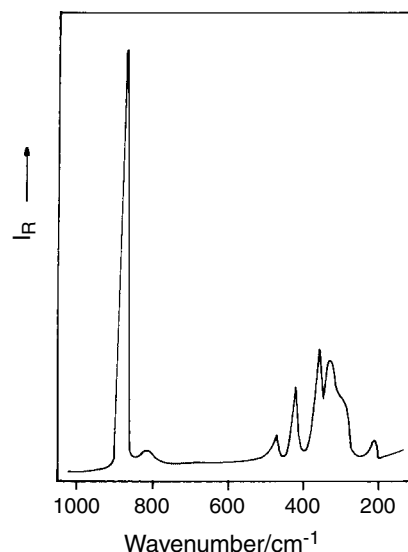
Vibrational mode	'Free ion' / $D_{3d}$	Factor group / $C_{2h}$
Symmetric $\text{AsO}_3$ stretching	$A_{1g} + A_{2u}$	$A_g + B_u$
Antisymmetric $\text{AsO}_3$ stretching	$E_g + E_u$	$A_g + B_g + A_u + B_u$
Symmetric bridge stretching	$A_{1g}$	$A_g$
Antisymmetric bridge stretching	$A_{2u}$	$B_u$
Symmetric $\text{AsO}_3$ bending	$A_{1g} + A_{2u}$	$A_g + B_u$
Antisymmetric $\text{AsO}_3$ bending	$E_g + E_u$	$A_g + B_g + A_u + B_u$
Bridge bendings	$E_g + E_u$	$A_g + B_g + A_u + B_u$
Torsions	$A_{1u} + E_u$	$2A_u + B_u$

<sup>a</sup> Activity under factor-group symmetry:  $A_u, B_u$ , IR-active;  $A_g, B_g$ , Raman active.

**Figure 1.** FTIR spectrum of  $\text{Cd}_2\text{As}_2\text{O}_7$ .

As can be seen, both spectra are relatively simple, presenting a reduced number of bands, in good agreement with the factor group predictions. The IR spectrum is similar to that measured for  $\text{Mn}_2\text{As}_2\text{O}_7$ ,<sup>2</sup> but somewhat different from that of  $\text{Ca}_2\text{As}_2\text{O}_7$ ,<sup>10</sup> although both compounds are isostructural with  $\text{Cd}_2\text{As}_2\text{O}_7$ .

As in these two previously investigated cases, the highest energy IR band ( $953\text{ cm}^{-1}$ ) is assigned to the antisymmetric bridge stretching, which in agreement with the analysis of Table 2 is inactive in the Raman effect, supporting the existence of a linear bridge conformation. This behaviour shows that linear diarsenates behave in a similar way to related disilicates and digermanates in which also the highest wavenumber band is assigned to the  $\nu_{\text{as}}(\text{X}-\text{O}-\text{X})$  mode.<sup>11,12</sup>

**Figure 2.** Raman spectrum of  $\text{Cd}_2\text{As}_2\text{O}_7$ .**Table 2.** Wavenumbers and assignment of the vibrational spectra of  $\text{Cd}_2\text{As}_2\text{O}_7$ <sup>a</sup>

IR, $\nu/\text{cm}^{-1}$	Raman, $\nu/\text{cm}^{-1}$	Assignment
953 m		$\nu_{\text{as}}(\text{As}-\text{O}-\text{As})$
c. ~890 sh	880 vs	$\nu_{\text{s}}(\text{AsO}_3)$
854 vs, 812 vs	810 vw	$\nu_{\text{as}}(\text{AsO}_3)$
472 vs, 393 s	489 w, 358 s	$\delta_{\text{as}}(\text{AsO}_3)$
	423 m	$\nu_{\text{s}}(\text{As}-\text{O}-\text{As})$
341 s	323 s	$\delta_{\text{s}}(\text{AsO}_3)$
310 s	294 sh, 216 vw	See text

<sup>a</sup> s, Strong; m, medium, w, weak; v, very; sh, shoulder.

The corresponding antisymmetric mode could not be identified with certainty. In diarsenates with bent angles this vibration is found at around  $550\text{ cm}^{-1}$ .<sup>7,13</sup> However, it is known that in case of  $\text{X}_2\text{O}_7^{n-}$  anions the separation between the two bridge modes increases with increasing bridge angle.<sup>12,14–16</sup> Consequently, it is expected that in the present case, the  $\nu_{\text{s}}(\text{As}-\text{O}-\text{As})$  mode may be displaced to lower wavenumbers. On the basis of this argument, and although its relatively low intensity cannot be clearly explained, we have assigned the Raman signal at  $423\text{ cm}^{-1}$  to this vibration. The assignment is also supported by the fact that this line does not have an IR counterpart, in agreement with the factor group analysis.

The bridge bendings are probably located below  $200\text{ cm}^{-1}$ , as usual for most of the  $\text{X}_2\text{O}_7^{n-}$  anions.<sup>15,17</sup>

In the case of the stretching vibrations of the terminal  $\text{AsO}_3$  groups, the symmetric mode originates the strongest Raman line and is seen only as a weak shoulder in the IR spectrum. For the corresponding antisymmetric mode, the two expected IR components can be clearly visualized as very strong IR bands, whereas in the Raman spectrum only one, very weak, signal is found in this region.

In the lowest energy region  $\delta_{\text{as}}(\text{AsO}_3) > \delta_{\text{s}}(\text{AsO}_3)$  in a similar way as found for other diarsenates and also in the case of arsenates.<sup>7,14</sup> The number of observed IR and Raman bands is in total agreement with the factor group expectations.

The last observed bands (cf. Table 2) are probably related to some of the expected torsional modes, probably coupled with external (lattice) vibrations.

As also seen in Table 2, corresponding IR and Raman bands show somewhat different wavenumbers, in agreement with their different phononic origins.

To conclude, the presented spectroscopic analysis of  $\text{Cd}_2\text{As}_2\text{O}_7$  is in excellent agreement with the factor analysis, derived from the crystal structure, and reports for the first time good quality Raman data for a thortveitite-type diarsenate.

This study also confirms the linearity of the As—O—As bridge in this compound. The vibrational disorder of the bridge O atom is not very important and does not have spectral consequences of the type found in  $\text{Ca}_2\text{As}_2\text{O}_7$ , in which the bridge oxygen presents a very large vibrational amplitude<sup>3</sup> and both bridge vibrations become Raman and IR active.<sup>10</sup>

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