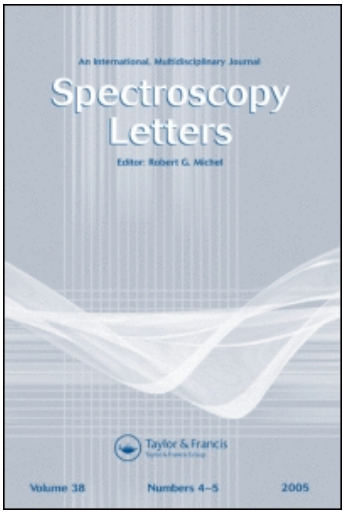

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Raman Spectrum of the Split ν_4 Mode of $CO^{=}_3$ Ions in Aragonite

V. Rives-arnau[a]; G. Munuera[a]; J. M. Criado[a]
[a] Departamento de Química Inorgánica Facultad de Química, Universidad de Sevilla, Sevilla, Spain

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RAMAN SPECTRUM OF THE SPLIT ν_4 MODE OF $CO_3^=$ IONS IN ARAGONITE

Key words: Raman spectra, Splitting modes, Aragonite

V. Rives-Arnau, G. Munuera and J. M. Criado

Departamento de Química Inorgánica
Facultad de Química
Universidad de Sevilla
Sevilla(Spain)

INTRODUCTION

Infrared and Raman spectra of $CO_3^=$ ions are different in the two crystallographic forms of $CaCO_3$ — Calcite and Aragonite — owing to their different site symmetries. Due to this fact, i.r. has been used to assess the reversible Calcite ⇌ Aragonite transformation which occurs upon grinding of $CaCO_3$, and much work has been done in this field in the last few years[1-4]. In the present paper data are reported on Raman spectra of Calcite and Aragonite forms of $CaCO_3$ produced by the above mechanical procedure.

EXPERIMENTAL

The samples studied were the same previously used by Criado et al.[5], and correspond to $CaCO_3$ (D'Hemio AnalaR), ground for periods of 2 to 24 h in a planetary mill. Samples ground for 0, 4.5 and 8 h were selected since X-ray analysis[5] showed that the unground sample was rich in Calcite, the sample ground for 8 h was rich in Aragonite, and the sample ground for 4.5 h contained a mixture of both.

The Raman spectra were recorded using a triple monochromator laser-Raman Cary 82 spectrophotometer coupled to a Spectra-Physics 165-03 Argon ion laser tube; the line at 514.5 nm, with a power of ca. 800 mW at the tube output, was used with the following recording conditions: spectral bandwidth 3 cm^{-1}, scan speed 0.3 cm^{-1} s^{-1}, pen period 10 s, sensitivity 2 Kcps/f.s.d., with expanded abscissa scale.

For comparison, i.r. spectra were recorded using KBr discs containing ca. 2% $CaCO_3$ and a Perkin-Elmer 621 double beam spectrophotometer under standard conditions, giving a resolution better than 2 cm^{-1}.

RESULTS AND DISCUSSION

Fig. 1 shows the i.r. and Raman spectra of the three samples in the range 800-600 cm^{-1}, where the ν_4 mode of $CO_3^=$ ions appears. The Calcite-rich specimen (a) gives a single band at 715 cm^{-1} in Raman which coincides with the i.r. band at

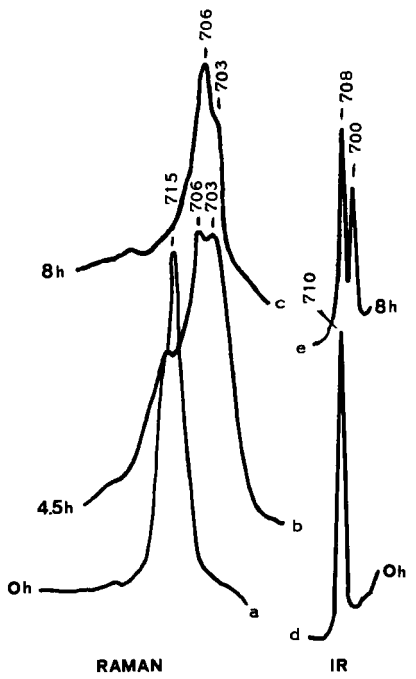

FIG. 1. Raman and i.r. spectra of unground (a, d) and ground (b, c, e) Calcium Carbonate. Spectra a and d correspond to a Calcite-rich sample, spectra c and e to an Aragonite-rich sample and spectrum b corresponds to a sample containing a mixture of both.

710 cm^{-1}. The Aragonite-rich specimen (c) produces a split mode at 706 and 703 cm^{-1} that corresponds to the two bands at 708 and 700 cm^{-1} in the i.r. spectrum of this sample. Sample (b), formed by a mixture of Calcite and Aragonite, gives spectra which are intermediate between those of samples (a) and (c).

Site group analysis predicts that the site symmetry of the $CO_3^=$ ion in Calcite and Aragonite must be respectively D_3 and C_s, while symmetry in the free ion is D_{3h} [6]. The correlation chart for D_{3h}, D_3, and C_s in Fig. 2 shows how the existence of

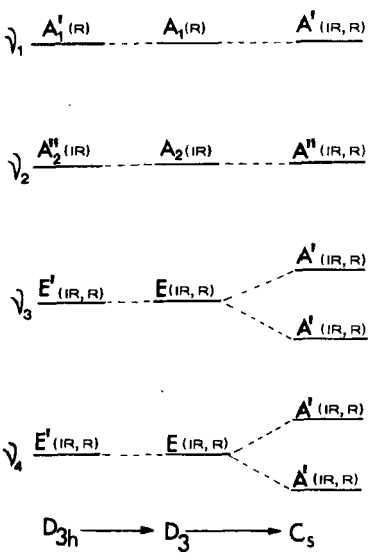

FIG. 2. Correlation chart for D_{3h} (free $CO_3^=$ ion), D_3 (Calcite) and C_s (Aragonite). IR and R stand for infrared and Raman active modes, respectively.

Aragonite (C_s symmetry) and/or Calcite (D_3 symmetry) in a specimen of $CaCO_3$ can be ascertained from the number of bands in the i.r. or Raman spectrum of the sample. In particular, splitting of the ν_4 mode is of diagnostic value for qualitative detection of Calcite and/or Aragonite.

Fig. 3 collects data of i.r. and Raman recently compiled by Nakamoto[7] for the vibrational modes of the free $CO_3^=$ ion, Calcite, and Aragonite. In the i.r. spectrum of Aragonite, this author reports a split band at 1504 and 1492 cm^{-1}, corresponding to the ν_3 mode, and another split band at 711 and 706 cm^{-1}, which corresponds to the ν_4 mode. On the contrary, for Raman spectra of the same compound, this author does not report

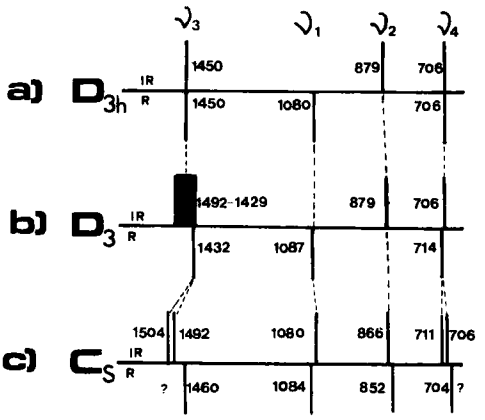

FIG. 3. Position of the infrared and Raman bands for (a)free $CO_3^{=}$ ion, (b)Calcite, and (c)Aragonite. (Data from ref. 7).

any splitting in either of the two modes (i.e., only single bands at 1460 and 704 cm^{-1} are reported), in spite of the prediction from the correlation chart above that both modes should be split and i.r. and Raman actives.

Raman spectra in Fig. 1 show that, in agreement with the X-ray data[5], the original Calcite-rich sample only shows a single band at 715 cm^{-1} (spectrum a) corresponding to the ν_4 mode, which coincides with the i.r. band at 710 cm^{-1} (spectrum b) and values in the literature[7] (i.r.:706 cm^{-1};Raman:714 cm^{-1}). When the sample is ground for 4.5 h additional bands at 706 and 703 cm^{-1} develop which must be ascribed to the new Aragonite phase detected by X-ray. After 8 h of grinding, the bands at 706 and 703 cm^{-1} were the only ones present in the spectrum, while X-ray indicated an almost complete transformation of the specimen into Aragonite. These two bands must be ascribed to the two A' modes of the Aragonite arising from the ν_4 mode,

that was originally degenerated both in the free $CO_3^{=}$ ion (D_{3h}) and in the Calcite form (D_3). This is confirmed by the i.r. spectrum included in Fig. 1 (spectrum e), where the original band at 710 cm^{-1} has disappeared and two bands at 708 and 700 cm^{-1} are now recorded, which closely matches the i.r. data reported in the literature[7] (711 and 706 cm^{-1}).

Although Nakamoto[7] and Rao[4], among others, have previously reported the split ν_4 mode in the i.r. spectra of Aragonite (pure and doped), to the authors' knowledge, the Raman spectrum of the split ν_4 mode is here reported for the first time.

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