

Identification of Li-O bands in the infra-red spectra of simple lithium compounds containing LiO₄ tetrahedra

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THE infra-red spectrum of lithium carbonate exhibits an unexpected group of fairly strong bands in the medium frequency region (500–390 cm⁻¹). These bands are missing in the spectra of the other alkali carbonates and it is clearly impossible to assign them to vibrational modes of the CO₃²⁻ anion.

The spectroscopic study of the isotopic species ⁶Li₂CO₃ and ⁷Li₂CO₃ shows that these bands must be assigned to Li-O bonds. The observed frequencies are collected in Table 1. No significant shift is found for the high frequency bands ($\nu > 700$ cm⁻¹), whose assignment to the CO₃²⁻ vibrational modes has been recently discussed [1]; but the low frequency bands are shifted by an amount considerably higher than experimental errors (Table 1 and Fig. 1).

These results definitely prove that the low frequency bands must be assigned to Li-O vibrations or, more precisely, to the valence frequency of LiO₄ tetrahedra (all the lithium is four-fold co-ordinated in Li₂CO₃ [2]).

Table 1

Observed frequencies (cm ⁻¹)		Isotopic shift
⁶ Li ₂ CO ₃	⁷ Li ₂ CO ₃	
1505	1501	(-4) *
1443	1441	(-2) *
1087	1089	(+2)
866	866	0
845	846	(+1)
738	738	0
531	497	-34
469	435	-34
447	416	-31
414	397	-17

* Broad bands

This investigation has been extended to a series of solid inorganic compounds of lithium containing either LiO₄ tetrahedra or LiO₆ octahedra (about twenty compounds in all), and the actual results may be summarized as follows:

(1) The spectra of compounds with six-fold co-ordinated lithium (LiO₆ octahedra) are not significantly altered in the 2000–300 cm⁻¹ region by the isotopic ⁶Li–⁷Li replacement. It is inferred that the fundamental frequencies of LiO₆ octahedra should lie below 300 cm⁻¹. It should be pointed out, however, that only three compounds of this type have been investigated.

(2) All compounds, the structure of which contains LiO₄ tetrahedra, give spectra which are significantly altered by the ⁶Li–⁷Li replacement. The observed changes are of 2 types:

(a) a few bands of the 400–500 cm⁻¹ region are displaced by 20–30 cm⁻¹, an order of magnitude which is in accordance with a rough estimation for the ν_3 mode of ⁶LiO₄ and ⁷LiO₄ tetrahedra. This implies that these vibrations are essentially free from interactions with the vibrations of neighbouring groups.

(b) in some cases, the ⁶Li–⁷Li replacement may bring out rather complex changes in the frequencies and relative intensities of a number of bands in the 350–600 cm⁻¹ region. These bands are clearly related to complex vibrations, where the ν_3 mode of LiO₄ tetrahedra is strongly coupled with vibrations of neighbouring groups.

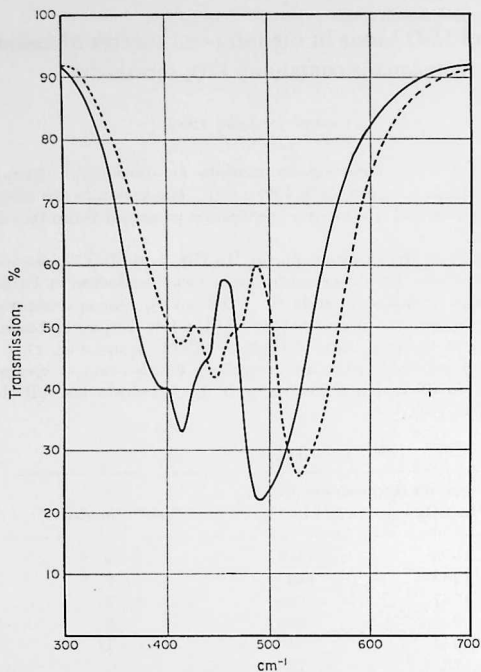


Fig. 1. Isotopic shift in the IR spectrum of Li_2CO_3 in the low frequency region.

Curve — : ${}^7\text{Li}_2\text{CO}_3$

Curve - - - : ${}^6\text{Li}_2\text{CO}_3$

In both *a* and *b* cases, important spectral changes in the 400–550 cm^{-1} region are always related to the occurrence of LiO_4 tetrahedra, whereas no such changes are observed with structures containing LiO_6 octahedra only.

These data provide an efficient method for determining the co-ordination of lithium in a compound of unknown structure, or the cation distribution in spinels such as LiCrGeO_4 [3]. This may have important applications in the crystal chemistry of lithium compounds, because the precise location of lithium by the conventional X-Ray methods is rather difficult. Finally, it should be pointed out that the differences in the spectroscopic behaviour of LiO_4 tetrahedra and LiO_6 octahedra are in accordance with the previous results given by a number of other four-fold or six-fold co-ordinated groups [4,5].

The detailed results will be published in the near future.

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