

Infrared Longitudinal Bands in Crystalline Carbon Dioxide

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Recently two absorption peaks at 678.3 cm^{-1} and 2383.0 cm^{-1} were reported for the cubic crystal of carbon dioxide. They appeared at non-normal incidence and disappeared at normal incidence.¹⁾ An attempt^{1,2)} has been made to interpret them as the longitudinal modes of ν_2 and ν_3 vibrations by means of the Haas-Hornig equation.³⁾ Assignment of these bands, however, still seems uncertain, because of the uncertainty of the value $d\mu/dQ$ used in the Haas-Hornig equation.

We have remeasured the absorption spectra of polycrystalline CO_2 films deposited fairly rapidly (60~90 sec) at liquid nitrogen temperature, the thickness being $1.8\text{--}2.8\text{ }\mu$. Spectra of each film were run at normal incidence, 0° , and at angles up to 30° from

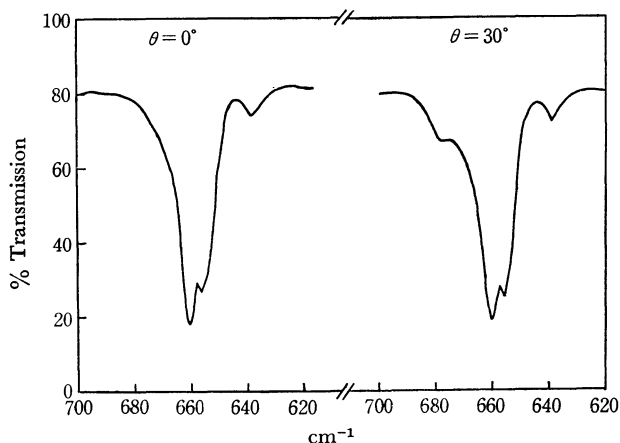


Fig. 1. Infrared absorption spectra of CO_2 crystal in the ν_2 region, at normal and non-normal incidence (unpolarized).

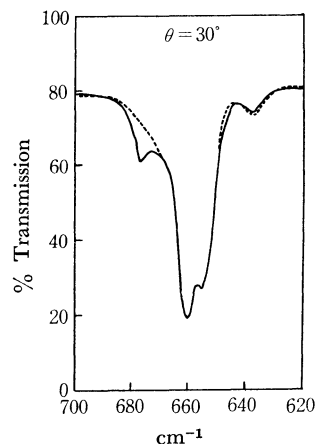


Fig. 2. Polarized absorption spectra of CO_2 crystal in the ν_2 region at non-normal incidence;
— p -polarized, ---- s -polarized.

normal. The results are completely in agreement with those reported by Parker and Eggers.¹⁾ The peaks at 678.0 cm^{-1} and 2379 cm^{-1} are angle-dependent, but the others do not shift or change significantly with the angle of incidence. We have further tried to confirm the longitudinal modes by a direct polarization measurement at non-normal incidence. As shown in Figs. 1 and 2, the peak at 678.0 cm^{-1} in the ν_2 region observed at non-normal incidence appears strongly in the p -polarized component of the radiation, where the electric vector is parallel to the incident plane, disappearing in the s -polarized radiation where the electric vector is perpendicular to the incident plane. The absorption curve observed at normal incidence shows no difference in p - and s -polarizations. The same holds for the peak at 2379 cm^{-1} in the ν_3 region.

Since the peaks occur only in the p -polarization, this strongly supports their assignment to the longitudinal optical modes.

1) M.A. Parker and D. F. Eggers, *J. Chem. Phys.*, **45**, 4354 (1966).

2) D. C. McKean, *ibid.*, **52**, 6451 (1970).

3) C. Haas and D. F. Hornig, *ibid.*, **26**, 707 (1967).