Absolute Infrared Intensities of Solid Chloroform

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Recently, a number of studies of the absolute infrared intensities of the fundamental absorption bands of molecules in the solid state have appeared.[1-3] These studies have attempted to compare the intensities in the solid state with those in the gaseous state; the intensities may be classified into three groups:

(1) Hydrocarbons (unsaturated), C_6H_6, C_2H_4, and C_2H_2,[1]

(2) Linear triatomic molecules, CO_2, CS_2, *etc.*,[2] and

(3) Hydrogen halides.[3]

Large intensity changes have been observed in the first group. For benzene and ethylene the intensities of the C–H stretching bands decrease going from the gaseous to the solid states, while those of the other fundamental bands increase. The intensity changes observed for the second group are relatively small and may be interpreted as the field effects. The third group, like the first, shows large intensity changes, arising from the effect of hydrogen bonding. Although the importance of the vibronic contribution from the π-electron system to the intensity has been suggested to explain the intensity changes observed for benzene,[4] the observed intensity changes have not yet been fully understood. Further experimental studies will be required to develop this problem theoretically.

In the present work we have studied solid chloroform and compared its intensity behavior with that of benzene and ethylene.

The technique for obtaining the spectrum was the same as that described in the literatures.[1-3] The sample was deposited from the gas phase onto the KRS-5 window in a cold cell, which was kept at the temperature of liquid nitrogen. The film thickness was determined from the interference fringes. The film thus obtained was well annealed until the spectrum no longer showed any change. The spectra were obtained using a Jasco DS-402G spectrometer.

TABLE 1. ABSOLUTE INFRARED INTENSITIES OF CHLOROFORM (in darks)

Mode	Solid		B(gas)[a]	B(liquid)
	ν_{max}(cm^{-1})	B(solid)*		
$\nu_1(A_1)$	3007	1400	44	—
$\nu_4(E)$	1225 1210 1206	3100	4200	—
$\nu_5(E)$	765 750 738	25600	27000	28600[b]
$\nu_2(A_1)$	673	1800	600	—

* Calculated using 16.2 mol/*l* as the value of the concentration and 1.61 as the index of refraction.

a) J. Morcillo, J. Herranz and J. F. Biarge, *Spectrochim. Acta*, **15**, 110 (1959).

b) From ATR measurements; A. C. Gilby, J. Burr, Jr., W. Krueger and B. Crawford, Jr., *J. Phys. Chem.*, **70**, 1525 (1966).

The results obtained are summarized in Table 1, together with the intensity values for gaseous and liquid states.

When the gas condenses to a solid, the intensity of the ν_1 band increases remarkably and that of the ν_2 band increases appreciably, while those of the ν_4 and ν_5 bands decrease slightly, as may be seen from Table 1. For the ν_4 and ν_5 bands the intensity ratios between gas and solid states are found to be about the same as those observed for the second group. The fact that the ν_1 and ν_2 bands, belonging to A_1 species of the free molecule, increase considerably in intensity may be interpreted as the effect of the very weak hydrogen bonding. The intensity increase of the C–H stretching band is in contrast with the intensity behavior observed for benzene and ethylene. These results may support the idea that the intensity changes observed for benzene and ethylene are mainly due to π-electron interaction between neighboring molecules.

More detailed findings on solid chloroform will be published in the near future.

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[1] J. L. Hollenberg and D. A. Dows, *J. Chem. Phys.*, **37**, 1300 (1962); *ibid.*, **39**, 495 (1963); G. M. Wieder and D. A. Dows, *ibid.*, **37**, 2990 (1962); D. A. Dows, *Spectrochim. Acta*, **22**, 1479 (1966).

[2] H. Yamada and W. B. Person, *J. Chem. Phys.*, **40**, 309 (1964); *ibid.*, **41**, 2478 (1964); **43**, 2519 (1965).

[3] H. B. Friedrich and W. B. Person, *ibid.*, **39**, 811 (1963); H. B. Friedrich, H. Yamada and W. B. Person, *ibid.*, **43**, 4180 (1965); J. M. P. J. Verstegen, H. Goldring, S. Kimel and B. Katz, *ibid.*, **44**, 3216 (1966).

[4] T. L. Brown, *ibid.*, **43**, 2780 (1965).