Infrared Spectra of BF_3-NO Mixed Solids

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It has been reported that nitric oxide and boron trifluoride form an addition complex at the temperature of liquid N_2.[1] Recently we studied the infrared spectra of BF_3-NO mixed solids, which were deposited from a mixed gas onto a cold CsI window.

When a BF_3-rich mixture is deposited very slowly, the spectrum of Fig. 1 (solid line) is obtained; however, the deposit of the same sample at a higher rate gives the absorption bands of the NO dimers[2] at the same time, as is shown in Fig. 2. Such a difference seems mainly due to the blanket effect[3] in the latter case. The results for NO-rich samples are essentially the same as those of Fig. 2 except that no splitting is observed in the $(NO)_2$ absorption at 1760 cm^{-1}.

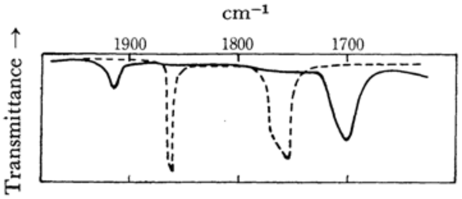


Fig. 1. Solid line; Slow deposit of a BF_3 rich (5 : 1) sample. (65°K) Dotted line; Solid NO. (65°K)

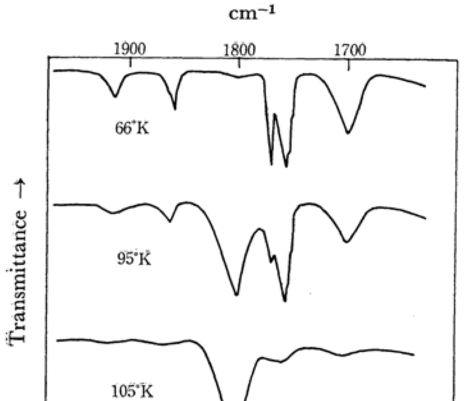
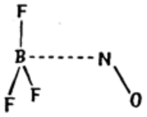


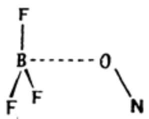
Fig. 2. Fast deposit of a BF_3 rich (5 : 1) sample, and its change by annealing.

When the sample temperature is allowed to rise slowly, an interesting spectral change occurs, as is also shown in Fig. 2. As the temperature goes up, all the bands shown at the top of Fig. 2 gradually lose their intensities, but a new absorption appears at 1800 cm^{-1} and grows up rather quickly. At about 105°K, the initially-observed bands almost disappear, but the new 1800 cm^{-1} absorption holds its maximum intensity at this temperature and is still observable at 130°K, where the individual components are never able to remain on the window. The spectral change is irreversible and common to both BF_3- and NO-rich samples.

As the transient bands at 1915 cm^{-1} and 1700 cm^{-1} are definitely different in frequency from those of gaseous or solid NO, they may be interpreted as due to the complexed states existing in the lattice of excess NO or BF_3, most likely in such a form as:



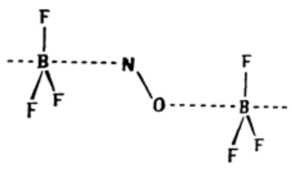
I



II

In either case, donor-acceptor interactions are conceivable between vacant orbitals of BF_3 (A_1' and A_2'') and π-electrons, as well as σ-lone pairs, of NO. Of the two principal resonance structures, $:\ddot{N}::\ddot{O}:$ and $:\ddot{N}^-::\ddot{O}^+:$, the former is more favorable for II, and the latter, for I, in the donation of π-electrons. This suggests that the higher frequency, 1915 cm^{-1}, should be assigned to I, and the lower, 1700 cm^{-1}, to II. The donation of σ lone pairs may be of comparable importance, so the oblique forms, as above, may be most probable.

On the other hand, the 1800 cm^{-1} band may be of a stable complex. The fact that the frequency is nearly equal to the mean value of the transient bands suggests the following n : n structure:



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[1] G. R. Finlay, *J. Chem. Educ.*, **24**, 149 (1947).

[2] NO forms dimers in condensed phases. W. J. Dulmage, E. A. Meyers and W. N. Lipscomb, *Acta Cryst.*, **6**, 760 (1953); A. L. Smith, W. E. Keller and H. L. Johnston, *J. Chem. Phys.*, **19**, 189 (1951).

[3] W. G. Fateley, H. A. Bent and B. Craword, Jr., *ibid.*, **31**, 204 (1959).