electron–magnon coupling.[14] Our experiments are consistent with this conclusion.

Turning our attention now to the maximum at 30,200 cm^{-1} in the spectrum of $NiCl_2$ we note that it is completely absent in $CdCl_2$–Ni^{2+}. On the surface this would tend to indicate an absorption process which is similar to that observed for the $^3A_{2g} \rightarrow {}^1A_{1g}$ absorption band. Indeed Kozielski, *et al.*,[4] have concluded that such is the case. Two phenomena dictate against this being either a short- or a long-range magnetic exchange process, however. The first is the total absence (in $CdCl_2$–Ni^{2+}) of the transition even though the weaker (in $NiCl_2$) $^1T_{1g}$ and $^1A_{1g}$ bands are present. Since the concentration of Ni^{2+} is 10% in the $CdBr_2$–Ni^{2+} spectrum shown and 7% in the $CdCl_2$–Ni^{2+} spectrum, considerable numbers of pairs should be present. It follows then that a pairwise interaction would produce a band at 30,200 cm^{-1}. Second, the band is observed even at 113°K. This is some 63°K above the Neel temperature of $NiCl_2$ and would seem to be much too high a temperature for even moderate-range order to exist. This suggests that this maximum arises from the presence of a cooperative interaction of a type other than a magnetic one. Because of a lack of polarization it is not possible to determine the exact nature of the interaction.

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Structure of Tungsten Oxytetrafluoride[1]

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Single-crystal X-ray intensity measurements on WOF_4 have been interpreted in terms of ordered tetrameric units with oxygen atoms assigned to the bridging positions.[2] The infrared spectrum of the solid showed a strong band at approximately 1050 cm^{-1} which the authors interpreted in terms of a W–F stretching frequency due to an abnormally short W–F bond. It has been pointed out that this assignment is inconsistent with vibrational assignments in similar transition metal oxyfluoride compounds[3] and alternate disordered structures containing fluorine bridges have been suggested for this material.[4] Unfortunately the X-ray measurements are not sufficiently accurate to distinguish between the various proposed models.

We have made infrared and nmr measurements on the solid phase which lend convincing support to a model containing fluorine at the bridging positions in the tetramer.

Infrared Data.—Oxygen-18-substituted WOF_4 was prepared by the reaction of WF_6 with $H_2{}^{18}O$ in the presence of HF and purified by sublimation. The composition of the material was established by single-crystal precession techniques. The infrared measurements were taken on a Perkin-Elmer 521 spectrometer from samples sublimed onto a CsCl window at liquid nitrogen temperature. The resulting spectrum shows the same structure in the region 500–750 cm^{-1} as do the previously published spectra.[2] In addition a strong peak appears at 997 cm^{-1} with a smaller peak at 1054 cm^{-1}. These peaks are, therefore, obviously due to W–^{18}O and W–^{16}O stretching frequencies, respectively.

Nuclear Magnetic Resonance.—A polycrystalline nmr sample was prepared by the same reaction and sealed in a polypropylene tube. At room temperature the ^{19}F resonance is dominated by a motionally narrowed line with a width of 200 mG; this is an indication of molecular motion at a rate in excess of 10^4 Hz. A spectrum without the narrowing is obtained at lower temperatures (−58 and −114°). The line recorded in the *CW* mode is 8 G wide and symmetric. Another line could be recorded only in the fast-passage mode because of extremely long spin–lattice relaxation time T_1 of between 3 and 4 min. In contrast, the first line has an estimated T_1 of 0.1 sec, three orders of magnitude shorter. From these observations we conclude that there are fluorine nuclei located in vastly different sites insofar as librational motion of WOF_4 is concerned; this is not consistent with a tetramer with all fluorines in terminal positions, no matter how chemically dissimilar those sites may be.

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Emission Lifetimes of Tungsten Carbonyl Complexes

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The behavior of excited states of coordination compounds has been investigated by studying photophysical processes, such as energy transfer[2–5] and radiative decay[6] as well as photochemistry.[7] However, development of models for structure–reactivity relationships has been slow because of the lack of absolute rate data. For example, variations in quantum yields for a measurable process may be due either to an increase in the rate constant for that process or to a decrease in the rate constant for some competitive process. The

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