g, 70% yield), mp 270–271° (sealed tube). *Anal.* Calcd for $C_2H_{11}B_{10}F$: C, 14.76; H, 6.83; B, 66.63; F, 11.68; mol wt 162.22. Found: C, 14.84; H, 6.67; B, 66.42; F, 11.63; mol wt 162 (by low-voltage mass spectrometry).

An infrared spectrum of the compound showed absorption bands (cm^{-1}) at 3050 (m), 2580 (vs), 1280 (vs), 1210 (w), 1135 (w), 1100 (m), 1025 (m), 1010 (w), 980 (m), 728 (m), 710 (m), and 678 (m).

Preparation of 3-Bromo-*o*-carborane.—$[(CH_3)_3NH][o\text{-}B_9C_2H_{12}]$ (10 g, 0.052 mol) was treated with butyllithium (50 ml of 2.1 *M* C_4H_9Li in hexane, 0.11 mol) to yield $Li_2[o\text{-}B_9C_2H_{11}]$ according to the procedure described above. This intermediate was treated with boron tribromide (15 g, 0.062 mol) in 50 ml of ethyl ether. Recrystallization of the crude solid product from hexane gave 3-bromo-*o*-carborane (3 g, 26% yield), mp 121–122°. *Anal.* Calcd for $C_2H_{11}B_{10}Br$: C, 10.77; H, 4.97; B, 48.45; Br, 35.81; mol wt 223.13. Found: C, 11.52; H, 5.06; B, 49.50; Br, 35.0; mol wt 223 (by low-voltage mass spectrometry).

The infrared absorption bands (cm^{-1}) of $o\text{-}B_{10}C_2H_{11}Br$ are 3050 (w), 2550 (s), 1200 (w), 1140 (m), 1020 (w), 995 (w, sh), 970 (vs), 945 (w), 910 (w), 840 (s), and 720 (s, b).

Preparation of 3-Diphenylamino-*o*-carborane.—The intermediate $Li_2[o\text{-}B_9C_2H_{11}]$ was prepared by treating $[(CH_3)_3NH][o\text{-}B_9C_2H_{12}]$ (132.3 g, 0.68 mol) with butyllithium (730 ml of 2.1 *M* C_4H_9Li in hexane, 1.53 mol) in 1200 ml of ethyl ether. Diphenylaminodichloroborane (17 g, 0.68 mol) in 300 ml of ethyl ether was then added to $Li_2[o\text{-}B_9C_2H_{11}]$ in the same manner as described above. The crude product was recrystallized twice from hexane to give 3-diphenylamino-*o*-carborane (128 g, 60% yield), mp 124–126°. *Anal.* Calcd for $C_{14}H_{21}H_{10}N$: C, 53.99; H, 6.80; B, 34.71; N, 4.50; mol wt 311.44. Found: C, 53.68; H, 7.08; B, 34.69; N, 4.31; mol wt 311 (by low-voltage mass spectrometry).

An infrared spectrum showed absorption bands (cm^{-1}) at 3030 (vw), 2550 (vs), 1580 (s), 1480 (vs), 1450 (m), 1430 (m), 1370 (w), 1330 (m, sh), 1300 (vs), 1250 (m), 1210 (w), 1175 (w), 1090 (w), 1065 (w), 1020 (m), 980 (m), 750 (s), 725 (w, b), 700 (vs), and 690 (m).

Preparation of 2-Fluoro-*m*-carborane.—$Li_2[m\text{-}B_9C_2H_{11}]$ was prepared by treating $[(CH_3)_3NH][m\text{-}B_9C_2H_{12}]$ (10 g, 0.052 mol) in 50 ml of ethyl ether with butyllithium (50 ml of 2.1 *M* C_4H_9Li in hexane, 0.11 mol) as described above. It was then treated with boron trifluoride etherate (15 ml. 0.094 mol) as described before. The product was purified by recrystallization from hexane to yield 2-fluoro-*m*-carborane (5.5 g, 65%), mp 259–260° (sealed tube). *Anal.* Calcd for $C_2H_{11}B_{10}F$: C, 14.76; H, 6.83; B, 66.63; F, 11.68; mol wt 162.22. Found: C, 14.66; H, 6.63; B, 66.59; F, 11.82; mol wt 162 (by low-voltage mass spectrometry).

Infrared absorption bands (cm^{-1}): 3080 (vw), 2590 (s), 1350 (m), 1310 (s), 1275 (s), 1150 (m), 1115 (m), 1060 (s), 1025 (m), 985 (m), 730 (s), 716 (m), and 690 (m).

Preparation of 2-Diphenylamino-*m*-carborane.—$Li_2[m\text{-}B_9C_2H_{11}]$ was obtained from the reaction between $[(CH_3)_3NH][m\text{-}B_9C_2H_{12}]$ (40 g, 0.21 mol) in 600 ml of ethyl ether and butyllithium (275 ml of 1.6 *M* C_4H_9Li in hexane, 0.44 mol). It was then treated with diphenylaminodichloroborane (52 g, 0.21 mol) according to the procedure described above. The crude product from the organic layer, however, was purified by fractional distillation under vacuum to obtain a fraction boiling at 136–146° (0.05 mm). The distillate solidified on cooling to room temperature and was further recrystallized from hexane to yield 3 g of 2-diphenylamino-*m*-carborane, mp 115–117°. *Anal.* Calcd for $C_{14}H_{21}B_{10}N$: C, 53.99; H, 6.80; B, 34.71; N, 4.50; mol wt 311.44. Found: C, 54.30; H, 6.77; B, 34.65; N, 4.37; mol wt 311 (by low-voltage mass spectrometry).

The infrared absorption bands of the compounds are (cm^{-1}) 3050 (vw), 2600 (s), 1590 (m), 1500 (s), 1430 (m), 1300 (s), 1250 (m), 1180 (vw), 1160 (vw), 1150 (w), 1115 (w), 1080 (vw), 1070 (m), 1060 (m), 1025 (m), 992 (w), 752 (m), 725 (w, b), 705 (s), and 690 (w).

Pyrolysis of 3-Fluoro-*o*-carborane.—$o\text{-}B_{10}C_2H_{11}F$ (3 g, 0.0185 mol), sealed in a 1-in. od heavy-walled Pyrex test tube under an atmosphere of nitrogen, was heated to 395–400° in a furnace for 18 hr. When the tube was opened, 2.7 g of white solid was obtained which, according to a vapor-phase chromatographic analysis, was a mixture of two components at a ratio of 2:1. Separation of the mixture on a basic aluminum oxide chromatographic column, using hexane as an eluting agent, yielded 1.7 g (60%) of the major component and 0.1 g of the second component.

The major component had an infrared spectrum and a melting point which were identical with those of 2-fluoro-*m*-carborane prepared by the insertion reaction as described above.

The second component, mp 263–265° (sealed tube), had a different infrared spectrum from either that of the starting material or that of 2-fluoro-*m*-carborane. Mass spectral and elemental analysis showed it to be $B_{10}C_2H_{11}F$.

Pyrolysis of 3-Diphenylamino-*o*-carborane.—The 3-diphenylamino-*o*-carborane (3 g, 0.0185 mol) was isomerized by the same procedure and under similar conditions as those described above. The pyrolysis product was dissolved in ethyl ether and then filtered to remove the insoluble materials. The filtrate was evaporated to dryness to yield 2.2 g of brown, sticky liquid. Analysis of the product by vapor-phase chromatography with a QF-1 (fluoroalkylsiloxane polymer) column showed one main component (95%) and two minor components. The major component, however, was separated into two isomers on the basic alumina chromatographic column, using hexane as an eluting agent. The first isomer (0.3 g) was identical in melting point and infrared spectrum with 2-diphenylamino-*m*-carborane prepared from the reaction between diphenylaminodichloroborane and $Li_2[m\text{-}B_9C_2H_{11}]$.

The second isomer (1.2 g), mp 68–70° (sealed tube), was similar to the starting material only in mass spectral and elemental analysis. However, it was quite different from both the starting material and the first isomer in an infrared absorption spectrum and a melting point.

Anal. Calcd for $C_{14}H_{21}B_{11}N$: C, 53.99; H, 6.80; B, 34.71; N, 4.50; mol wt 311.44. Found: C, 54.01; H, 6.70; B, 34.99; N, 4.48; mol wt 311 (by low-voltage mass spectrometry).

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Intensity as a Criterion in Assigning Electronic Transitions in Metal Complexes

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It is characteristic of transition metal complexes that their absorption spectra generally consist of bands of widely varying intensities with oscillator strengths (f) typically $\sim 5 \times 10^{-6}$–5×10^{-4} ($\epsilon_{max} \sim 1$–100) for the weakest to $f \approx 10^{-1}$ ($\epsilon_{max} \gtrsim 10{,}000$) for the strongest.[1] These limiting cases usually pose no problem when it comes to identification. The weak bands

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[1] T. M. Dunn, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 4.

are well explained by crystal or ligand field theory as forbidden d → d transitions of the central ion which gain intensity through odd vibrations in centrosymmetric cases and additionally through orbital mixing if there is no center of symmetry.[2] The strong bands are assigned as fully allowed transitions which involve either charge transfer between metal and ligand orbitals, intraligand excitations, or d → p transitions on the central metal ion. The theory for these is not as comprehensive as for the d → d bands and detailed assignments are not known. On the whole, the general outlines are reasonably well understood.[3]

Absorptions having oscillator strengths in the intermediate range ($f \approx 10^{-3}$–10^{-2}; $\epsilon_{\max} \sim 500$–5000) present a less clear picture. There is a general reluctance to assign bands with $\epsilon > 500$ as d → d transitions in centrosymmetric systems, and these medium-strong bands are usually regarded as weak charge-transfer transitions.[4] Recently it has been suggested by more than one author[5–7] that certain relatively intense bands are in fact d → d transitions despite extinction coefficients of up to 9000. The basis for these identifications has usually been the discovery that the *energies* of the transitions agree very closely with those predicted by a crystal field calculation.

Experimental methods exist which in principle enable us to determine the nature of a transition. For example, we may cool the sample to low temperature either as a crystal or in a glass-forming solvent and hope that the vibronic structure of the band develops. Characteristically, a parity-forbidden transition may then be identified by a very weak origin line (0 → 0) followed by a progression in the totally symmetric mode superimposed upon one quantum of an odd vibration. If a 0 → 0 line is not detected, however, it may be difficult to distinguish between this pattern and that expected for an allowed transition, namely, a 0 → 0 origin followed by a progression in the totally symmetric mode. A second technique which has recently become available as a result of the development of fast-response detection systems is the measurement, at low temperature, of the fluorescence from the state involved. The emission spectrum will be an approximate mirror image of the absorption spectrum with the origins superimposed. Thus the first vibronic component of an allowed transition will have absorption and emission spectra which overlap whereas a forbidden transition with a "virtual" origin as discussed above will exhibit a gap between the two spectra due to the forbidden 0 → 0 line. A third method is to study the oscillator strength of the band as a function of temperature. An allowed transition will sharpen as the molecules are cooled into the vibrational ground state but will maintain the same total intensity (provided there is no change in electronic wave functions with temperature—for example due to a change in crystal field with lattice contraction). The oscillator strength of a vibronically allowed transition, on the other hand, decreases according to the hyperbolic cotangent law (eq 1) upon cooling[2,8] where $f(0)$ is

$$f(T) = f(0) \coth (h\nu/2kT) \qquad (1)$$

the oscillator strength at 0°K and ν is the electronic ground-state frequency of the intensity-producing normal mode. (Lohr[8] has recently emphasized that eq 1 is independent of the form of the excited-state potential energy curve but does require the ground state to be a harmonic oscillator.)

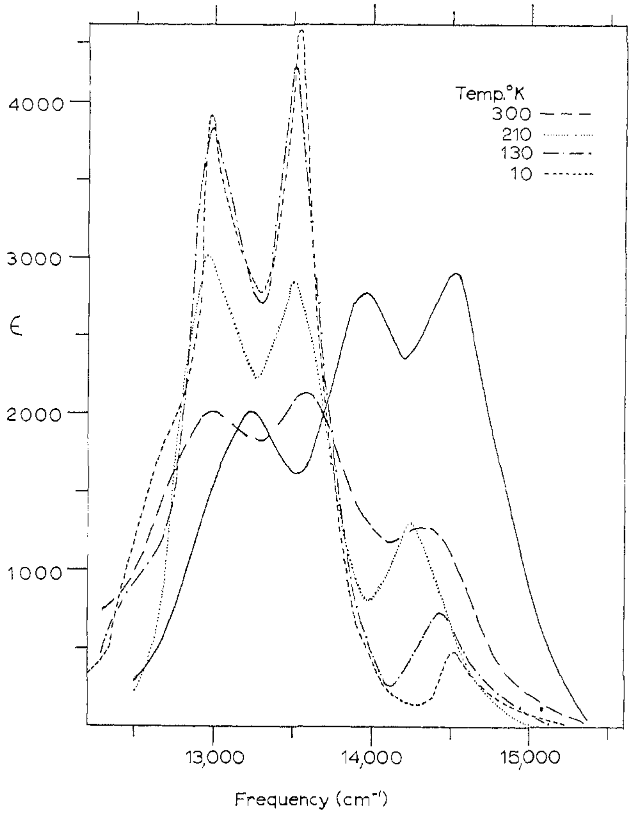

Figure 1.—Absorption spectrum of $IrBr_6^{2-}$. ϵ is the molar extinction coefficient. The solid curve is for $((C_4H_9)_4N)_2IrBr_6$ in CH_2Cl_2 solution at 300°K; the broken curves are for $(NH_4)_2$-$SnBr_6$–Ir^{4+} at the indicated temperatures. *Note well:* the concentration of Ir^{4+} is not known in the crystal and hence the crystal spectra have been arbitrarily normalized so that $\epsilon_{\max}$ values for solution and crystal at 300°K coincide for the 13,000-cm^{-1} band. This has no effect on *ratios* involving the crystal at different temperatures but does mean that crystal and solution spectra cannot be compared quantitatively.

In this note we utilize this latter technique to identify a forbidden transition in a group of bands having solution extinction coefficients in the range 2000–3000. These results will show that the room-temperature intensity data may be very misleading.

Figure 1 shows the absorption spectrum of $IrBr_6^{2-}$ in dichloroethane solution at room temperature and

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(2) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(3) C. K. Jørgensen, "Halogen Chemistry," Vol. 1, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, p 265 ff.

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(5) P. B. Dorain, H. H. Patterson, and P. C. Jordan, *J. Chem. Phys.*, **49**, 3845 (1968); P. C. Jordan, H. H. Patterson, and P. B. Dorain, *ibid.*, **49**, 3858 (1968); P. B. Dorain and R. G. Wheeler, *ibid.*, **45**, 1172 (1966).

(6) M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc., A*, 540 (1967).

(7) G. Dyer and D. W. Meek, *J. Am. Chem. Soc.*, **89**, 3983 (1967).

(8) L. L. Lohr, Jr., *J. Chem. Phys.*, **50**, 4596 (1969).

doped in the cubic lattice $(NH_4)_2SnBr_6$ at several temperatures between 300 and 10°K. Note first that the strongest band in solution (14,500 cm^{-1}) is in fact the weakest in the 300°K crystal spectrum indicating a substantial contribution to the observed intensity from solvent perturbations. As the temperature is lowered, this band undergoes a striking reduction in intensity while the ϵ_{max} of the other two bands (13,000 and 13,600 cm^{-1}) increases markedly. Gaussian fitting and numerical integration of the data indicates that the oscillator strength of the 14,500-cm^{-1} band in the crystal is reduced by a factor of ~5.5 while the sum of the oscillator strengths of the 13,000- and 13,600-cm^{-1} bands actually shows a monotonic increase[9] of ~40–50% upon cooling to 10°K.

Using intensity data at 300, 210, 166, 143, 130, 79, and 10°K for the 14,500-cm^{-1} band assuming a single activating vibration, one obtains a quite reasonable fit of eq 1 with $\nu \sim 80$ cm^{-1}. Only the two t_{1u} fundamentals of $IrBr_6^{2-}$ appear to have been reported[10] ($\nu_3 \sim 230$ cm^{-1}, ν_4 82 cm^{-1}), but in analogy with $ReBr_6^{2-}$,[11] $PtBr_6^{2-}$,[12] and WBr_6^{2-},[13] the t_{2g} (ν_5) and t_{2u} (ν_6) fundamentals probably also occur in this region as well as several lattice modes. Furthermore, there is no *a priori* reason for assuming a single activating frequency,[2] and we make no attempt here to decide which vibrations are involved.

The $(NH_4)_2SnBr_6$ lattice has the cubic K_2PtCl_6 structure at room temperature[14] with the Sn (and hence presumably the substituted Ir) at a site of O_h symmetry. It is known from the nuclear quadrupole resonance data[15] that this structure persists at least down to 201°K, but no quadrupole resonance signal at all was observed at liquid nitrogen temperature,[15] and it is known from heat capacity measurements[16] that there is a λ point at 145°K and some sort of phase transition covering a range of ~90°. However, our intensity data for the 14,500-cm^{-1} band vary smoothly with temperature through this region and there seems no doubt that we are observing the behavior characteristic of a vibronically allowed transition.

We have also studied the system K_2SnBr_6–Ir^{4+} where the K_2SnBr_6 lattice is a slight tetragonal modification of the K_2PtCl_6 structure.[17] The behavior of this same band system is very similar, the sum of the intensities of the two lower frequency components increasing by about 10% and the intensity of the vibronically allowed component decreasing by about a factor of 5 as the temperature is lowered to 11°K. We shall discuss the absorption and MCD spectra of the $IrBr_6^{2-}$ ion in detail at a later date.[18]

These experiments indicate that absorption bands in the intermediate intensity range must be approached with a considerable degree of caution. We have clearly demonstrated that a forbidden transition may have substantial oscillator strength at room temperature. Our example also shows that these bands of intermediate intensity may be allowed transitions, and we feel that it is very desirable to differentiate by experiment rather than to rely heavily on the agreement of band positions with a crystal field calculation. In addition, it should be emphasized that vibronically allowed bands can arise from forbidden charge-transfer transitions as well as from d → d transitions.

Finally, Table I emphasizes the sensitivity of eq 1 to the numerical value of the activating frequency. We see that a given vibronically allowed transition at room temperature may vary in intensity over a sizable range depending upon the frequency of the activating vibration (or vibrations). Thus for metals with heavy ligands (and hence low vibrational frequencies) it may be very difficult on the basis of room-temperature intensity measurements alone to distinguish forbidden vibronic transitions from fully allowed charge-transfer transitions, particularly in solution where solvent interactions may also enhance the intensity. In the example cited in this note, a band with $\epsilon_{max} \sim 3000$ in solution at room temperature has been shown rather conclusively to be due to a forbidden (vibronically allowed) transition.

TABLE I

RATIO OF ROOM-TEMPERATURE TO LOW-TEMPERATURE (0–10°K) OSCILLATOR STRENGTH AS A FUNCTION OF ACTIVATING FREQUENCY (ν)

ν, cm^{-1}	$f(300°K)/f(0–10°K)$	ν, cm^{-1}	$f(300°K/f(0–10°K)$
≥1250	1.00	200	2.24
700	1.07	100	4.25
500	1.20	80	5.28
300	1.62	40	10.5

Acknowledgments.—This work was supported by a grant from the National Science Foundation.

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(9) Similar behavior has been noted recently for several bands of $OsBr_6^{2-}$: B. D. Bird, P. Day, and E. A. Grant, *J. Chem. Soc.*, *A*, 100 (1970). We shall argue elsewhere that the two strong bands (13,000 and 13,600 cm^{-1}) in $IrBr_6^{2-}$ are Jahn–Teller components of the first $E_g'' \rightarrow U_u'$ charge-transfer transition.

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New Chromyl Compounds

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New chromyl compounds, CrO_2X_2 (where X = CF_3CO_2, $ClCF_2CO_2$, and $CF_3CF_2CF_2CO_2$) have been

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