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ABSTRACT

The molecular beam method used previously to fix the electronic ground state of lanthanum monoxide has been modified and extended to scandium monofluoride. King furnace equilibrium absorption and emission measurements of the radiance of the green $E^1\Pi - X^1\Sigma^+$ and red $^3\Phi - ^3\Delta$ transitions have given the relative transition probabilities. The ratio of f_{abs} value of the $^3\Phi - ^3\Delta$ to that of the $E^1\Pi - X^1\Sigma^+$ is 0.8 ± 3. From these data the expected relative radiance of the transition in the molecular beam has been calculated assuming no radiative intersystem decay. The relative fluorescent radiance at various molecular beam path lengths indicates that both the $^1\Sigma^+$ and $^3\Delta$ states of ScF persist at least as long as 10^{-4} seconds. A maximum energy separation has been estimated to be 1000 cm^{-1}.

The electronic energy levels of gaseous ScF, TiO and ZrO have been compared using molecular orbitals. The energy of several unobserved levels is predicted in each of these molecules. The contribution of low-lying electronic states to the internal partition function is discussed.

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INTRODUCTION

Diatomic molecules which contain one transition metal atom are of theroetical interest as models to determine the role of d-electrons in chemical bonding (1). The gaseous scandium monofluoride molecule is of particular interest because scandium is the lightest element with a d-electron in its ground-state and because ScF is isoelectronic with the astrophysically important TiO molecule.

Accurate calculation of the thermodynamic free-energy function of a high-temperature diatomic molecule requires a knowledge of not only the electronic ground-state, but the vibrational and rotational characteristics and excitation energies of low-lying electronic states. At moderately high temperatures, where molecules like ScF contribute substantially to the vapor, several electronic states may make appreciable contributions to the electronic partition function. It is possible that low-lying excited electronic states could dominate the internal partition function if their electronic degeneracy is large. Such is the case for the gaseous C_2 molecule where the $^3\Pi_u$ state contributes more to the partition function than the ground-state $^1\Sigma_g^+$ at most temperatures.

$$Q_{int} = \sum_{\substack{\text{all energy} \\ \text{levels}}} g_i \exp(-\varepsilon_i/kT) \tag{1}$$

Q_{int} is the internal partition function for the gaseous molecule, g_i is the degeneracy of the ith energy level and ε_i is the energy of the ith level relative to the lowest accessible internal level of the molecule.

The electronic energy levels of diatomic oxides and halides of transition metals are in general quite incompletely studied. The spectra of lighter diatomic molecules, especially the oxides and halides, have

been analyzed much more completely. Furthermore, semi-empirical models have been proposed which can account for the observed electronic states and predict the energy of unobserved ones and calculation of low-lying energy states is feasible. Self-consistent field calculations based on the method of Roothaan (2) are difficult to perform with the accuracy required to adequately define the internal partition function for molecules with as many electrons as a transition metal oxide. The differences in correlation energy, which are generally of the same order of magnitude as the energy separation of the electronic states for diatomic molecules with one transition metal atom, are difficult to estimate to the desired accuracy even with semi-empirical methods(3).

The absorption spectrum of high-temperature molecules can include absorption from excited states. Most diatomic molecules containing one transition metal atom have several allowed electronic transitions within the visible and near-ultraviolet spectral regions so that weaker transitions are often obscured by overlapping transitions. Oftentimes more than one species will absorb in a spectral region making a complete analysis prohibitively difficult. In principle, a complete spectral analysis including the detection of "forbidden" intercombination lines would characterize the energy levels and give the partition function exactly. In practice, only the stronger electronic bands are generally analysed.

The matrix isolation technique has been successfully applied to many high-temperature species to gain information about the electronic ground-state. "Matrix shifts" of over 1000 cm^{-1} in absorption spectra from rare-gas matrices probably resulting from solute-solvent and solute-interactions

have been reported (4). The origin of the matrix effects is not well-understood and they demonstrate that the species trapped in the matrix is not identical with the gaseous-phase species. In favorable cases, this method will simplify the gaseous-phase spectrum and identify the electronic ground-state, but it will generally not give information about low-lying excited states which may be thermodynamically important.

Other experimental techniques have proved of value in determining the energy of low-lying electronic levels. The $X^3\Delta$ state of TiO was found to be about 581 cm^{-1} below the $a^1\Delta$ state by a study of the temperature dependence of the radiance of two electronic transitions involving these states (5). The energies of the electronic states of the gaseous C_2 molecule were determined by analysis of rotational perturbations (6). The magnetic deflection of a molecular beam has been used to determine the ground state symmetry of LiO and LaO (7). Each of these experimental techniques although limited in accuracy and applicability has been of value in at least one case. Only the matrix isolation technique has been applied to the gaseous ScF molecule (8).

Gaseous phase absorption and thermal emission from ScF have been reported in the visible and near-ultraviolet spectral regions (9) and the results of these studies have been summarized (10). Partial rotational analysis has been completed on transitions involving seven singlet and four triplet electronic states. The lowest observed states of each multiplicity are $^1\Sigma^+$ and $^3\Delta$ and their energy separation was not determined. Absorption is seen at about 2300°K from both the $^1\Sigma^+$ and $^3\Delta$ states which suggests that both states are thermodynamically important.

The absorption spectrum from neon matrices at 4°K has been correlated

with the gaseous phase singlet transitions (3). Although some of the extra

absorption features could not be attributed to either multiple matrix

sites or other fluorides of scandium, no correspondence could be made

with the gaseous phase triplet transitions.

The term energies, T_e, of the three low-lying electronic states aris-

ing from σ^2 ($^1\Sigma^+$) and $\sigma\delta$ ($^3\Delta, ^1\Delta$) molecular orbital configurations have

been calculated for both ScF and TiO (11). An experimental value of the

energy separation of these states is available for TiO (5) so that an es-

timate of the accuracy of these calculations for ScF may be made. The

calculated $^1\Delta{-}^3\Delta$ and $^1\Sigma^+{-}^3\Delta$ energy differences for TiO are 2150 cm^{-1} and

6690 cm^{-1} while the observed values are 580 cm^{-1} and 2290 cm^{-1} respectively.

The ScF $^1\Sigma^+{-}^3\Delta$ separation is calculated is to be -460 cm^{-1} so that within

the corresponding uncertainties associated with TiO, the electronic

ground-state of ScF is not determined unambiguously. It may be con-

cluded, however, that the $^3\Delta$, $^1\Sigma^+$ and probably the $^1\Delta$ have appreciable

contributions to the electronic partition function.

The electronic ground-state of fluorine is $^2P^o$ and the first excited

state is over 100,000 cm^{-1} higher in energy (12). The ground-state of

scandium is ^2D from the $4s^23d$ open-shell configuration. Furthermore

scandium has low-lying electronic levels from the $4s3d4p$ and $4s3d^2$

configurations which may well combine with the $^2P^o$ state of F to give

low-lying molecular states. Figure 1 shows some states of scandium

below 30,000 cm^{-1}. Table 1 lists the molecular states which arise from

the combination of ground-state F with the low-lying states of Sc.

There are eighteen molecular states arising from ground-state atoms

alone and it is difficult to predict _a priori_ which of these states

might be stable. The three molecular states arising from Sc$^+$(^3D) + F$^-$(^1S)

Table 1. Molecular states of ScF from atomic configurations

Sc State	F State	Molecular States of ScF	Multiplicities
^2D	$^2P^\circ$	$\Sigma^+(2)$, Σ^-, $\Pi(3)$, $\Delta(2)$, Φ	1,3
^4F	$^2P^\circ$	Σ^+, $\Sigma^-(2)$, $\Pi(3)$, $\Delta(3)$, $\Phi(2)$, Γ	3,5
^2F	$^2P^\circ$	Σ^+, $\Sigma^-(2)$, $\Pi(3)$, $\Delta(3)$, $\Phi(2)$, Γ	1,3
$^4F^\circ$	$^2P^\circ$	$\Sigma^+(2)$, Σ^-, $\Pi(3)$, $\Delta(3)$, $\Phi(2)$, Γ	3,5
$^4D^\circ$	$^2P^\circ$	Σ^+, $\Sigma^-(2)$, $\Pi(3)$, $\Delta(2)$, Φ	3,5

should also be considered since the large electronegativity difference of Sc and F may cause these ionic molecular states to be quite low in energy.

The near degeneracy of the s and d atomic orbitals and the presence of low-lying p orbitals lead to many molecular states of low energy. It is necessary to clarify the role of these electronic states in order to fix the internal partition.

METHODS

In low resolution a triplet band system of ScF which is easily observed (13) in the visible region is the $A^3\Phi$-$X^3\Delta$ with (0,0) heads at 652.3, 654.0 and 655.8 nanometers (nm). It is red degraded and free of significant overlap from other bands of the same electronic transition. The (0,1) head of the $E^1\Pi$-$X^1\Sigma^+$ transition at 511.5 nm is also strong in low resolution. These two transitions involve the lowest states of each multiplicity, namely the $^1\Sigma^+$ and the $^3\Delta$.

The strengths of these transitions were compared in both a King furnace and in a molecular beam coming from a cell of the same temperature after a transit time of approximately 10^{-4} seconds. Should intersystem radiative decay occur within this time, the effect would be noticeable as an apparent change in relative radiance of the band systems. In this manner the gaseous phase electronic ground-state can be determined experimentally while avoiding many of the temperature dependent errors of other methods.

In Hund's coupling case c the $^3\Delta_1$ to $^1\Sigma^+_0$ is an allowed transition. ScF is a reasonably heavy diatomic molecule and should have a large enough degree of case c coupling to make this transition possible within the time of transit of the molecular beam.

A Steinheil three prism spectrograph with an f/4 aperature was used in an optical arrangement designed for Raman spectroscopy. The reciprocal linear dispersion varied with wavelength from about 3 nm/mm at 500 nm to about 11 nm/mm at 670 nm. The prism positions, slit width and other instrumental adjustments were kept identical throughout the course of this study to allow cancellation of instrumental broadening effects.

A full description of the carbon-tube or King furnace appears elsewhere (14). The graphite tube was lined first with tantalum foil then with tungsten foil to prevent reaction of the graphite with scandium. A current of 1400 amperes provided a uniform temperature of 2100°C within 20° in a zone 150mm in length and 12.5mm in diameter. At the ends of the hot zone, graphite radiation shields with a bore of 6.3mm were used to achieve a sharp temperature gradient to the water-cooled electrodes.

There is an apparent radiance difference at the singlet wavelength (511.5nm) and the triplet wavelength (655.8nm) from the differences in the sensitivity of the photographic plate and the differences in blackbody radiance. A neutral density filter which reduced the radiance by a factor of approximately ten was placed inside the Steinheil in front of the photographic plate such that it covered only the red region of the spectrum. In this manner simultaneous measurements at both the wavelengths of interest could be made.

A series of ScF absorption exposures were taken on a plate at a measured furnace temperature of 2100°C. The same exposure time of three minutes was used for all exposures while different calibrated neutral density filters were used to vary the exposure. Similarly a series of emission exposures were obtained either within the same experiment or in separate runs.

A tungsten strip filament lamp was used as an absorption light source and for determination of the characteristic curve of the photographic plates. It was run at 215 watts which was about double the rated power.

Temperature measurements were made with an optical pyrometer. It has been shown (15) that the temperature measured from the King furnace walls

approximates well the temperature of a blackbody so no corrections were applied for the wall emissivity. Blackbody radiation into the spectrograph from the walls of the furnace was minimized with iris aperture stops.

The molecular beam apparatus, first used by Walsh (16) for studies on gaseous lanthanum monoxide, was modified. A double crucible arrangement was developed which would allow control of the total vapor pressure at one temperature and the vapor composition at a second higher temperature. Calculations based on estimates (17) of the thermodynamic properties of the fluorides of scandium indicate that ScF_3 is the principal vapor species even in the presence of scandium metal. Furthermore, ScF_2 is also an important vapor component. However, the composition of the vapor changes such that ScF becomes a more important constituent as the temperature is increased.

Figure 2 shows the double crucible, the heating element, the heat radiation shielding and the electrodes. In order to prevent leaks due to non-uniform expansion from thermal gradients, the crucible was machined from one piece of tantalum 25 mm in diameter and 80 mm in length. The top portion of the container was 25 mm in both length and diameter with a wall thickness of about 1mm. The bottom portion was 12.5mm in diameter and 55mm in length with a wall thickness of about 2mm. An extension of about 10 mm of the bottom portion went into the top. Thus, liquid scandium could be held in the top part of the crucible at the higher temperature. The cap of the crucible was 6.2mm thick with a circular orifice 1mm in diameter. A large temperature gradient was achieved using this double crucible. In preliminary experiments a Pt vs Pt/10% Rh thermocouple measured 1300°C at the bottom of the crucible with the top at 2100°C.

The heating element was composed of strips of tungsten foil 25mm in width, 0.4mm thick and 150mm in length. These pieces of foil were shaped into concentric touching cylinders and attached to 12.5mm diameter tantalum rod with small force-fitted tantalum tacks. The tantalum rod was fitted into a 25mm diameter molybdenum rod. This in turn was attached to the water-cooled copper electrodes with clamp. In operation, between 25 and 30 amperes were drawn at about 250 volts from the source supply after passage through the variable transformer. So at the heating element about 1200 amperes were being passed and greater than 6 KVA of power was being dissipated. Tantalum foil 0.1mm thick was employed for radiation shielding. The entire assembly including the electrodes was covered with a graphite felt rectangular box containing a circular opening for the molecular beam.

The crucible was supported by a molybdenum rod. A water-cooled copper connection as well as the water-cooled electrodes were all 19mm in diameter and were sealed with rubber seals to provide simultaneous vacuum seals and electrical insulation. All three vacuum inlets were adjustable so that different molecular beam path lengths could be employed with only minor adjustments. The molecular beam chamber was evacuated with a 150mm diffusion pump to a background pressure of less than 5×10^{-6} torr at room temperature.

The light source was a General Electric 120 volt, 650 watt movieflood DWY lamp. The filament was a tungsten coil with iodine vapor inside the quartz envelope. The lamp was operated on 110 volt AC power in an aluminum shield from a variable transformer.

Corning color glass filter 3-72 was used to prevent excitation of wavelengths shorter than that of the singlet transition. In this manner

cascading effects can be avoided. The combined effect of this filter and the heat absorbing glass in the water cooler was equivalent to a neutral density filter of .31 at the triplet wavelength.

Fluorescence was observed at right angles to the exciting light. A 97mm focal length lens focused the fluorescence onto the Steinheil slit. The filament was 150mm from the lens and approximately 245mm from the entrance window. The Steinheil slit was about 112mm from the lens on the exit window.

Temperature measurement was done with the same optical pyrometer used in the King furnace work. A glass prism on the cover of the molecular beam chamber allowed a line of sight directly into the crucible. With this method no corrections for emissivity of the crucible were applied since the cell should approach blackbody conditions. Corrections were applied for the prism.

The slit width, prism positions and other Steinheil adjustments were identical to those used during King furnace exposure. A neutral density filter inside the Steinheil adjusted the light levels so that both the singlet and triplet wavelengths could be viewed simultaneously.

Kodak 103a-F photographic plates were used in all studies. Care was taken to insure duplication of development conditions so that quantitative results could be obtained. Optical density measurements were performed on the photographic plates with a Baird-Atomic Inc. model CB densitometer and were recorded on a Bristol model 560 strip chart recorder. The instrument allows measurement of densities from zero to 2.0. Averages were taken of several independent readings until the density was certain to .02 density units. The graininess of the photographic emulsion caused

an uncertainty of .01 density units. The tungsten strip lamp was used as the light source for calibrating the characteristic curves at the two wavelengths of interest. Since the ScF features are subject to the Eberhard effect (18), these curves are possible sources of error when interpreting ScF features. Constant exposure times were used while varying the exposure with calibrated neutral density filters.

A background radiance is present in both King furnace exposures and in fluorescence exposures from the molecular beam. In the molecular beam exposures a background was added to the part of the photographic plate in order to make the optical density after exposure on the more linear portion of the characteristic curve. This "pre-exposure" results in more accurate determination of the radiance from the characteristic curve.

THEORY

Define a radiance ratio, R, as follows:

$$R = \frac{L(\text{triplet})}{L(\text{singlet})} \quad . \qquad (2)$$

R is the ratio of radiances of any source at two particular wavelengths, namely, the 655.8 nm ScF $^3\Phi$ - $^3\Delta$ (0,0) band head and the ScF $^1\Pi$ - $^1\Sigma$ (0,1) band head (~511.5 nm). All radiances are given in terms of number of quanta per second per square centimeter normal to the source per unit solid angle per unit wavelength interval.

In a high-temperature equilibrium source such as the King furnace, the radiance observed at a particular wavelength after passing light from a lamp at a temperature T_ℓ through a column of gas at a temperature T_g is given by:

$$L_{\text{observed}} = L_{\text{lamp},T_\ell} - L_{\text{abs}}^{\text{lamp}} + L_{\text{em}} - L_{\text{abs}}^{\text{self}} \qquad (3)$$

$L_{\text{abs}}^{\text{lamp}}$ is the radiance coming from the lamp that is absorbed by the gas. L_{em} is the emission radiance of the gas and $L_{\text{abs}}^{\text{self}}$ is the absorption by the gas of the emitted radiance. The self-absorption will be small for small gas densities or path lengths and will be neglected here. Arguments will be presented later to justify this approximation in this work. When a lamp with a brightness temperature equal to the gas temperature is used in the King furnace

$$R_{\text{em},\text{KF},T_g} = R_{\text{abs},\text{KF},T_g} = T_\ell \qquad (4)$$

This is a statement of the reversal condition; $L_{observed}$ is equal to $L_{lamp, Tg = T_{\ell}}$ in Eq. (3) at each wavelength.

At each wavelength, α is the absorption coefficient.

$$\alpha = \frac{L_{abs}^{lamp}}{L_{lamp, T_{\ell}}} \tag{5}$$

If a blackbody at the gas temperature were used as a lamp, then from the reversal conditions for either wavelength:

$$\alpha = \frac{L_{em, KF, T_g}}{L_{BB, T_g}} \tag{6}$$

The relationship between King furnace absorption and emission is now established. Experimentally a lamp at T_{ℓ} is used instead of a blackbody at the gas temperature, but the relationship of lamp radiance at T_{ℓ} to blackbody radiance at T_g is easily calculated from the Planck equation and the emissivity of the lamp filament. Then at each wavelength the following two equivalent relationships may be used to determine the absorption coefficient.

$$\alpha = \frac{L_{abs, KF, T_g}^{lamp}}{L_{lamp, T_{\ell}}} = \frac{L_{em, KF, T_g}}{L_{lamp, T_{\ell}}} \frac{L_{lamp, T_{\ell}}}{L_{BB, T_g}} \tag{7}$$

The ratio of emission radiances is now given from Eq. (6) by:

$$R_{em, KF, T_g} = \frac{\alpha(t) \ L(t)_{BB, T_g}}{\alpha(s) \ L(s)_{BB, T_g}} \tag{8}$$

$$= R_{\alpha} R_{BB, T_g}$$

The letters s and t represent the two wavelengths of interest (665.8

and 551.5 nm). By a similar consideration of Eq. (7), the ratio of α

values may be obtained from King furnace absorption studies.

$$R_\alpha = \frac{R_{abs, KF, T_g}^{lamp}}{R_{lamp,T_\ell}} = \left(\frac{R_{em,KF,T_g}}{R_{lamp,T_\ell}}\right)\left(\frac{R_{lamp,T_\ell}}{R_{BB,T_g}}\right) \qquad (9)$$

It should be noted that the dependence of α upon the absorption

path length and the gas density divides out in the ratio since it depends

only on the system geometry. Thus, the α ratio depends only upon the

relative triplet and singlet transition probabilities.

In the molecular beam, fluorescence is observed at right angles to

the exciting light source. If no significant population change of the

lowest singlet and the lowest triplet occurs during the beam transit time,

then the equilibrium relative radiance measurements of the King furnace

may be applied to determine the expected relative radiance in the beam.

The fluorescent radiance observed depends upon the transition probability

to the upper state of each system and the exciting light radiance at the

wavelength. In addition there is a geometric factor which includes the

differences between the geometry of the beam and that of the King furnace

as well as the fact that fluorescence takes place in all directions. This

geometric factor is the same for singlet and triplet so it will divide

out in the ratio. The ratio of fluorescent radiance (f) in the beam (B)

is given by:

$$R_{f,B,T_g} = \frac{\alpha(t)\ L(t)_{ex}}{\alpha(s)\ L(s)_{ex}} \qquad (10)$$

$$= R_\alpha\ R_{ex}$$

R_{ex} is the ratio of exciting light radiance at the triplet and

singlet wavelengths. This equation assumes that each state fluoresces at

the same wavelength as the absorbing light; corrections for fluorescence

to possible excited electronic and vibrational states will be considered later. The influence of these corrections may be distinguished from change due to intercombination radiative decay by studying relative radiance as a function of the molecular beam path length. Whereas intersystem radiative decay is relatively slow, the fluorescent processes are rapid and will not, in general, be a function of the beam transit time.

Since the triplet transition is more easily observed, the most useful working equation is the prediction of the singlet radiance from the observed triplet radiance.

$$L(s)_{f,B,T_g} = L(t)_{f,B,T_g} \frac{1}{R_\alpha R_{ex}} \tag{11}$$

The experimentally measurable optical density, D, of the photographic plate can be related to the incident light radiance L by a characteristic curve which is an empirical plot of D vs. log L for equal exposure times. In emission studies the radiance due to emission, L_{em}, was found from the radiance at the peak of the feature, L_p, and the intensity at the base of the feature, L_b. The quantities L_p and L_b are obtained from D_p and D_b by means of the characteristic curve and subtracted to get L_{em}. By similar means the fluorescent radiance or the absorption radiance may be obtained from the photographic plate.

The blackbody radiance in quanta per second per square centimeter normal to the source per unit solid angle per unit wavelength interval (in centimeters) is given by the following form of the Planck equation.

$$L = \frac{2c}{\lambda^4} \left[\exp\left(\frac{hc}{\lambda kT} \right) - 1 \right]^{-1} \tag{12}$$

The radiance ratio of a blackbody at T_g to a lamp at T_ℓ may be calculated from Eq. (12) by including the emissivity of the lamp

filament. The one in Eq. (12) has been neglected.

$$\frac{L(\lambda)_{lamp,T_\ell}}{L(\lambda)_{BB,T_g}} = \epsilon(T_\ell,\lambda) \ \exp\left[-\frac{hc \ (T_g - T_\ell)}{\lambda k T_g T_\ell}\right] \quad (13)$$

The temperature of the previously described tungsten strip lamp filament was measured with the calibrated optical pyrometer at a power of 215 watts. The measured brightness temperature at 650 nm was 2839°K within 6° with corrections applied for the optical pyrometer. The true temperature of the lamp may be calculated

$$\frac{1}{T_B} - \frac{1}{T} = \frac{\lambda}{c_2} \ \ln[\tau \times \epsilon(\lambda,T)] \quad (14)$$

T is the true temperature, T_B the brightness temperature, λ the wavelength of observation, c_2 the second radiation constant, τ the transmission factor for the glass of 92% and ϵ (19) the emissivity. Values for the emissivity of a tungsten strip lamp have been reported (20) as a function of the true temperature at various wavelengths. Extrapolation was required for the temperatures used in this work, but the errors should be negligible. The true temperature of the tungsten strip lamp is calculated to be 3235°K with an estimated error of 10°.

For this lamp temperature and a blackbody at 2373°K (the King furnace and molecular beam operating temperature), Eqs. (13) and (7) may be combined to give the working equation for determining R_α from King furnace emission.

$$\alpha(singlet) = 10.31 \ \frac{L(s)_{em,KF,2373}}{L(s)_{lamp,3235}} \quad \text{and}$$

$$\alpha(\text{triplet}) \quad = \quad 4.88 \quad \frac{L(t)_{em,KF,2373}}{L(t)_{lamp,3235}} \qquad \text{or}$$

$$R_\alpha \quad = \quad .473 \quad \frac{R_{em,KF,2373}}{R_{lamp,3235}} \tag{15}$$

The net or apparent absorption radiance which is the observable quantity is related to α. L^{net}_{abs,T_g} is determined from the optical densities of the photographic plate in a manner analogous to the determination of L_{em}.

$$\frac{L^{net}_{abs,T_g}}{L_{lamp,T_\ell}} \quad = \quad \frac{L^{lamp}_{abs,T_g} - L_{em,T_g}}{L_{lamp,T_\ell}}$$

$$= \quad \frac{\alpha L_{lamp,\,T_\ell} - \alpha L_{BB,T_g}}{L_{lamp,T_\ell}}$$

$$= \quad \alpha \left[1 - \frac{L_{BB,T_g}}{L_{lamp,T_\ell}} \right] \tag{16}$$

Applying the calculation used in Eqs. (13) and (15) at these temperatures the working equation for determining R_α from King furnace absorption studies is derived.

$$\frac{L^{net}_{abs,2373}}{L_{lamp,3235}} \quad = \quad .905 \; \alpha(\text{singlet})$$

$$= \quad .795 \; \alpha(\text{triplet}) \qquad \text{or}$$

$$R_\alpha \quad = \quad .878 \; \frac{R^{net}_{abs,KF,2373}}{R_{lamp,3235}} \tag{17}$$

The units of radiance have no absolute meaning since the characteristic curves were plotted on an arbitrary log L scale. This means that all radiances obtained from these curves have unknown absolute values and, most importantly, the log L scales for the two wavelength regions are unrelated. In order to predict the ScF singlet radiance from that of the triplet in the molecular beam, the log L scales must be related. The true radiance may be obtained at each wavelength by multiplying by a constant or by adding a constant to log L

$$\log L(\text{triplet}) = \log L(\text{triplet})_m + k$$
$$\log L(\text{singlet}) = \log L(\text{singlet})_m + k'$$
$$(18)$$

The subscript m denotes the measured value obtained from the measured optical density and the characteristic curve. It should be noted that these constants include the photographic plate sensitivity.

It may be shown that value of R_α measured either from emission or absorption in the King furnace is identical to the true R_α on an absolute scale. In order to apply Eq. (11) to the experimental results the scales must be related. This can be done with the tungsten strip lamp since the relative radiance may be calculated as well as measured from the arbitrarily chosen log L scales. By applying Eq. (18) we get

$$\log R_{\text{lamp},T_\ell} = \log L(t)_{\text{lamp},T_{\ell,m}} + k$$
$$(19)$$

$$- \log L(s)_{\text{lamp},T_{\ell,m}} - k'$$

Using the Planck equation as expressed in Eq. (12) for the experimental conditions used in this study, the value of R_{lamp,T_ℓ} may be calculated.

$$R_{lamp, T_\ell} = \left[\frac{\lambda(t)}{\lambda(s)} \right]^4 \frac{\epsilon(t)}{\epsilon(s)} \exp \left[\frac{hc}{kT_\ell} \frac{(\lambda(t) - \lambda(s))}{\lambda(t) \quad \lambda(s)} \right]$$

$$= .3702 \frac{\epsilon(t)}{\epsilon(s)} \exp \left[\frac{6.190 \times 10^3}{T_\ell} \right] \quad (20)$$

By using the measured lamp temperature the two scales may now be related

$$k - k' = .38 - \log R_{lamp, 3235, m} \quad (21)$$

R_{ex} of Eq. (10) may be found graphically from the data of Studer and Van Beers (21) to be 2.3 in relative number of quanta or log R_{ex} is .36. The experimentally determined value was .39 with an average error less than .01. The experimental value was used in the following calculations.

Combining Eqs. (19) and (11) with the experimental results for R_{ex} gives the working equation for the prediction of the fluorescent radiance of the singlet from that of the triplet in terms of measured quantities.

$$\log L(s)_{f, B, 2373} = \log L(t)_{f, B, 2373} - \log R_\alpha \quad (22)$$

$$- \log R_{lamp, 3235} - .01$$

It should be noted that this equation does not include the correction term for fluorescence discussed in relation to Eq. (11) or the correction for the filter and water cooler employed of .31.

RESULTS

The experimental value of log $R_{lamp,3235,m}$ was 1.21 with an average error of 0.01 for 43 determinations. As shown by Eq. (21), the arbitrary choice of scales for log L on the characteristic curves is quite different from the true radiance ratio. Using this value in Eq. (15) the experimental value of log R_α from log $R_{em,KF,2373}$ was -0.12 ± .05 after correction for neutral density filters. The previously described method of using a neutral density filter inside the Steinheil was employed for some measurements; a Corning color glass filter 3-74 was used outside the instrument in others; a Wratten filter 38 was used similarly in others and a time average of different exposures during the same run was also used to compare the radiance ratio. All methods gave substantially the same value and a total of 32 values were averaged. Absorption experiments were less accurate due to large corrections for gas emission. Equation (17) was applied to the measured log $R_{abs,KF,2373}^{net}$ to give a log R_α of -0.04 ± .08 in 12 measurements. The methods used to obtain these measurements are identical to those used to obtain log $R_{em,KF,2373}$. The agreement of log R_α from absorption and emission results is within experimental uncertainties and the more accurate emission results were used to calculate the expected fluorescence radiance.

Initial observations of fluorescence from the molecular beam showed only the triplet system at 655.8 nm. The application of Eq. (22) with the results of the King furnace showed however that it would be expected that the singlet transition should be weaker.

$$\log L(s)_{f,B,2373} = \log L(t)_{f,B,2373} -0.77 \qquad (23)$$

Table 2. $E^1\Pi-X^1\Sigma^+$ fluorescent radiance as a function of molecular beam path length

Path length (cm)	Transit time (sec)	log $L(s)_{f,B,2373}$ Calc.—Obs.
9.0	8.0×10^{-5}	0.51
9.2	8.2×10^{-5}	0.55
10.2	9.2×10^{-5}	0.59
11.8	1.1×10^{-4}	0.63

Table 2 summarizes the results of measuring the radiance of the head

at 655.8 nm applying Eq. (23) to predict the radiance at 511.5 nm and

comparing that to the observed radiance. It is only the calculated

minus the observed value of the log $L(s)_{f,B,2373}$ that is comparable

at different path lengths due to the experimental variations. The

estimated uncertainty in this number is about 0.10 due to scatter in

densitometer readings and the error associated with the use of the

charactersitic curve. Also included in Table 2 is the transit time of

ScF molecules in the beam calculated using the root mean square velocity

of molecules effusing from the crucible (22).

Self absorption in emission studies and deviation from the linear

curve of growth in absorption studies are potential sources of error in

the determination of R_α. The small ScF density in the molecular beam

would give negligible errors from these sources. The spectrum of rota-

tional lines near the observed heads was calculated from the known spectro-

scopic constants. The apparent spectrum and the true spectrum were

approximated as the sum of triangles. A computer program was written

to add the radiance at intervals of 0.01 cm^{-1} using the Doppler width for

the true spectrum and the instrumental width for the observed spectrum.

By comparison of the peak radiances, which were normalized to identical

area triangles, the true α values were inferred. Both true α values

were less than 7%. This gives (23) a correction of about 0.2 to 0.3%

due to self-absorption. Since interest in this work is in relative

values, the net correction due to self-absorption or deviation from

the linear curve of growth is negligible.

DISCUSSION AND CONCLUSIONS

Both the $E^1\Pi - X^1\Sigma^+$ and $^3\Phi - ^3\Delta$ transitions are observed in fluorescence in the molecular beam. Since cutoff filters in the exciting light prevent excitation of higher energy states, it is concluded that both the $X^1\Sigma^+$ and $^3\Delta$ states persist during the transit time of the molecular beam. A lower limit may be set on the lifetime of the higher energy state. The change of $\log L(s)_{f,B,2373}$ observed over the extremes of path length employed would correspond to a lifetime of the $^1\Sigma^+$ state of 1.1×10^{-4} seconds, but within the experimental uncertainty of $\log L$, there is no decay of the $^1\Sigma^+$ or $^3\Delta$ state. One can not say that intercombination decay has occurred. In Hund's case c where the selection rule $\Delta\Omega = 0, \pm 1$ applies, the transition $^1\Sigma^+ - ^3\Delta_1$ would be allowed.

The relationship among the f_{abs}-value, lifetime (τ) and wavelength (λ) in cm of a transition is well known. (24) (assuming no additional electronic states are lower in energy than the $^1\Sigma^+$).

$$f_{abs}\tau = (mc/8\Pi^2 e^2) \; \frac{g'}{g''} \; \lambda^2$$

$$= 1.499 \; \frac{g(^3\Delta_1)}{g(^1\Sigma^+)} \; \lambda^2 \qquad (24)$$

It is assumed here that the $^1\Sigma^+$ is higher in the energy than the $^3\Delta$ although analogous arguments apply if the reverse is the case. The lower and upper state degeneracies are represented by g" and g' respectively. Exposures taken with no neutral density filter inside the Steinheil show that all three triplet heads appear in molecular beam fluorescence with roughly the same relative radiance as in the King furnace. The degeneracy

of the $^3\Delta_1$ is two for the case c allowed transition. Equation (24) may then be written in terms of the energy separation, ΔE in $cm^{-1} \times 10^{-3}$, of the $^3\Delta$ and $^1\Sigma^+$ for this case.

$$\Delta E = (7.5 \times 10^{-7}/f_{abs}\ \tau)^{1/2} \tag{25}$$

A complete discussion of oscillator strengths of f-values for molecules is beyond the scope of this paper (25). The strength of one rotational line is well-defined, but the measurements made here involve a band or sequence of bands so Franck-Condon factors must be accurately known. Experimental disagreements for atoms are common (26) and the data for molecules are sparse (25). An estimate of the f-value for the $^1\Sigma^+-^3\Delta_1$ transition may be obtained by analogy to other molecules and a consideration of the coupling expected for ScF. The f-value of interest here is for an electronic transition as a whole including all vibronic transitions.

The f-value of the $B^3\Pi_{0_u^+} - X^1\Sigma_g$ transition of I_2 has been calculated from observed lifetimes (26) to be approximately 10^{-2} assuming a mean wavelength of 800 nm. An analysis of the mixing of states of different multiplicity in ScF has not been done, but it has been suggested that there are reasonably large effects (11). It would seem that in view of the large number of observed and predicted low-lying electronic states that a high degree of configuration interaction should occur. This would give substantial "triplet character" to the singlets and vice-versa resulting in a high f-value for the intercombination transition. It should be noted that additional symmetry restrictions in a homonuclear molecule like I_2 would prevent mixing of states which could mix in an isoelectronic

heteronuclear molecule. Thus I_2 may be too restrictive a case for determining what the upper limit of the f-value might be in ScF.

The degree to which a molecule approaches Hund's coupling case c from cases a or b may be estimated in part by its molecular weight as shown by the increasing case c character of diatomic molecules formed from second and third row elements as molecular weight increases. The $^3\Pi-^1\Sigma$ transitions have been observed and analyzed in AlBr and AlCl (27). The molecular weight of AlCl is close to that of ScF and the molecules are somewhat analogous in electronic structure. The observation in this case of a forbidden transition is a strong indication that AlCl has a significant degree of case c coupling. The d-orbitals of Sc lead to a large number of low-lying atomic energy levels (see Fig. 1) which implies that ScF should have a much larger effect due to configuration interaction than AlCl. Thus, ScF should have an f-value considerably larger than that of AlCl.

An indication of case c character is the difference in spectroscopic constants of the case a multiplet sublevels (28). In ScF the three rotational constants of the $^3\Delta$ differ by about two percent. This may be taken as an indication of departure of the coupling from case a.

The scandium atom transition $z^2D_{5/2}-a^2D_{5/2}$ (630.567 nm) has a gf value of 0.033 while the $z^4D_{5/2}-a^2D_{5/2}$ (625.896 nm) has a value of 0.01 (29). This difference of a factor of three between the "allowed" and "forbidden" transitions in scandium suggests that the $\Delta S=0$ selection rule might also be easily violated in ScF as well. The gf values for the $z^2D_{3/2}-a^2D_{3/2}$ (621.068 nm) and the $z^4D_{3/2}-a^2D_{3/2}$ (623.978 nm) differ only by a factor

of two. These four transitions were among those seen in absorption, emission and fluorescence.

Additional strong evidence for a relatively strong ScF intercombination transition is the observed (30) absorption from the $^1\Sigma$ ground state of GaF to both the $^1\Pi$ and $^3\Pi$ states. This gives a direct indication of comparable transition probabilities to the "allowed" and "forbidden" states. The molecular weight of GaF is only slightly greater than that of ScF and there are similarities in bonding.

These considerations indicate that the "forbidden" $^1\Sigma^+$ - $^3\Delta$ transition of ScF should be within an order of magnitude of the "allowed" transitions. Using an f-value of 10^{-2} and the experimentally determined limit on the lifetime of 10^{-4} seconds, Eq. (25) limits the energy separation to 850 cm^{-1} (rounded to 1000 cm^{-1}). If the apparent decay of the $^1\Sigma^+$ as a function of molecular beam path length is real, the $^3\Delta$ is the gaseous phase electronic ground state contrary to the suggestion of matrix isolation studies. Due to the experimental uncertainites and the uncertainty of the intercombination f-value, the electronic states of ScF are probably best represented for the calculation of an absolute entropy by considering the $^3\Delta$ and $^1\Sigma^+$ states as accidentally degenerate. A full discussion of estimated contributions to the internal partition function will be presented later.

As previously discussed, the corrections for self-absorption are less than one percent. Furthermore, the Boltzmann factors should be similar for the $^1\Sigma^+$ and $^3\Delta_1$ states. The (0,0) R-head of the $^3\Phi_2$ - $^3\Delta_1$ occurs at about $J = 28$ and the (0,1) R-head of the $^1\Pi$ - $^1\Sigma^+$ at about $J = 12$. There-

fore, the experimental value of R_α represents a ratio of f_{abs} values within experimental uncertainities and the uncertainty of relative population. It is concluded that the ratio of the $^3\Phi$ - $^3\Delta$ f_{abs} value to that of the E $^1\Pi$ - $X^1\Sigma^+$ is 0.8 ± 3.

Relative absorption radiance in the molecular beam may be calculated from Eq. (23). The relative fluorescence radiance would be identical to that in absorption in the beam if all the light in the upper states fluoresced to the same energy level from which it was originally absorbed. In the molecular beam work account must be taken of the Franck-Condon factor from the initial state of fluorescence: the v = 0 levels of the $^1\Pi$ and $^3\Phi$. The internuclear distance of v = 0 of the $^1\Sigma^+$, $^1\Pi$, $^3\Delta$ and and $^3\Phi$ states using the rotational constants of Barrow (10) are calculated to be 1.79, 1.87, 1.86 and 1.90 Å respectively. Since the change in internuclear distance for the singlet (0,0) transition is greater than that for the triplet (0,0), it would be expected that the $^3\Phi$ - $^3\Delta$ (0,0) transition would have the larger Franck-Condon factor. Furthermore the Franck-Condon factor for the $^3\Phi$ - $^3\Delta$ transition should be larger than that for the $^1\Pi$ - $^1\Sigma^+$ (0,1) since the v = 0 level of the $^1\Pi$ should have comparable overlap with several v". The neglect of the Franck-Condon factor should result in a calculated singlet fluorescent radiance based on the observed triplet fluorescent radiance that is larger than observed. In confirmation Table 2 shows that the singlet radiance is a factor of three smaller than the calculated value neglecting the Franck-Condon factors.

If there are additional allowed electronic transitions, further reduction of the fluorescent radiance from that expected is possible.

It will be shown that there is an unobserved $^3\Pi$ state below the $^3\Phi$ (see Fig. 3). The transition is forbidden between these states (31) by the case a selection rule $\Delta\Lambda = 0, \pm 1$. It would also be at an unfavorable energy relative to the allowed $^3\Phi-^3\Delta$ transition. Therefore, the $^3\Phi-^3\Pi$ should take a very small portion of the light away from the $^3\Phi-^3\Delta$ transition. There are no other triplet transitions to be expected.

On the other hand, a $^1\Pi-^1\Delta$ transition is allowed and this transition could considerably reduce the observed singlet fluorescent radiance from that calculated. The data of Table 2 show that the $^1\Pi-^1\Delta$ transition cannot be much stronger than the $^1\Pi-^1\Sigma^+$ transition. Both the $C^1\Sigma^+$ and $B^1\Pi$ (see Fig. 3) have allowed transitions with the $E^1\Pi$, but their wavelengths are less favorable. No apparent effect was observed from these two states.

Scandium fluoride, titanium oxide and zirconium oxide are isoelectronic in valence electrons and it would be expected that their molecular orbitals are comparable and that their electronic spectra should show similarities. The electronic spectrum of TiO has been of interest to astrophysicists for some time and its spectrum has been well-studied. The ZrO molecule is also of astrophysical interest although its spectrum is less studied.

The assignment of the known states of these three molecules to molecular orbital configurations has proven useful. It now seems possible to predict with reasonable accuracy the energies of unobserved electronic states and the approximate spectral region of allowed transitions. Further-

TABLE 3.

Observed and estimated electronic energy levels
of ScF, TiO, and ZrO, in $cm^{-1} \times 10^{-3}$

Molecular Orbital Configuration	Molecular State	ScF	TiO	ZrO
$s\sigma^2$	$^1\Sigma^+$	0.0	2.8	0.0
$s\sigma$ $d\delta$ $d\pi$	$^3\Delta$	0.0	0.0	1.0
	$^1\Delta$	2	0.6	5.0
$s\sigma$	$^3\Pi$	8	9	8
	$^1\Pi$	10.7	11.9	11
$d\delta$ $d\pi$	$^3\Phi$	15.3	14.1	16.7
	$^3\Pi$	18.3	16.2	18.7
	$^1\Phi$	19	18.4	20
	$^1\Pi$	20.3	19	21
$s\sigma$ $d\sigma$	$^3\Sigma^+$	14	13	14
	$^1\Sigma^+$	16.1	15	16
$d\delta$ $d\sigma$ $p\pi$	$^3\Delta$	21.9	19.3	22.5
	$^1\Delta$	24	22	24.3
$s\sigma$	$^3\Pi$	24	22	25
	$^1\Pi$	26.8	25	27
$d\delta$ $p\pi$	$^3\Phi$	27.2	25	27
	$^3\Pi$	31	29	31
	$^1\Phi$	32	30	32
	$^1\Pi$	34.9	33	35

more it will better define the internal partition function for these three molecules. It should also provide a basis for the prediction of states of other molecules which contain a transition metal atom, but where the spectrum is not well-studied.

A population analysis (11) of the 9σ molecular orbital in the lowest energy $^3\Delta$ state shows it is 93.0% Sc 4s in ScF and 91.0% Ti 4s in TiO. The 1σ orbital is exclusively metal 3d. It may be expected that to the accuracy of this approximation the electronic transitions of these molecules would be analogous to the atomic transitions of the transition metal atom. The d metal electron yields δ, π and σ molecular orbitals and the p electron yields π and σ orbitals. The nomenclature suggested by the population analysis has been adopted here to distinguish orbitals of the same symmetry. The results are summarized in Table 3 and Fig. 3.

For ScF the $X^1\Sigma^+$ and $^3\Delta$ should both be at zero energy. The un-observed $A^1\Delta$ is put at 2000 cm^{-1} which represents a compromise between the calculated (11) 4400cm^{-1} and the comparable splitting in TiO which has been experimentally determined (5) to be about 600 cm^{-1}. The $B^1\Pi$ is put (10) at 10,700 cm^{-1} although it may be lower (13) since the observed band having this origin may not be the (0,0). The $^3\Pi$ state from the same molecular orbital configuration has not been seen in ScF,TiO or ZrO. It is put at 8,000 cm^{-1} since from Hund's rules it is lower in energy than the $^1\Pi$. The $A^3\Phi$ is put at 15,300 cm^{-1} which is an average of the observed (10) sublevel splittings. Since no $^3\Sigma$ states have been observed for ScF, TiO, or ZrO, the sublevel splittings are not accurately known. The $C^1\Sigma^+$, $E^1\Pi$, two other $^1\Pi$ states, $^3\Pi$ and $^3\Phi$ are all known (10). A $^1\Phi$ is put at 19,000 cm^{-1} since it is assumed to be the fourth state of the $d\delta$ $d\pi$ configuration and the three other states

are known. A $^3\Sigma^+$ state is put 2,000 cm^{-1} below the known C$^1\Sigma^+$ state on the assumption that both are sσ dσ. Barrow has observed (10) a transition at 21,927 cm^{-1} which has the appearance of a $^3\Delta$ - X$^3\Delta$. As can be seen in Fig. 3 this is the expected energy of such a transition by analogy to the TiO and ZrO α systems. The $^1\Delta$ from the same molecular orbital con - figuration (dδ dσ) is put at 24,000 cm^{-1} since it should be higher in energy than $^3\Delta$ and by analogy to the energy of the d$^1\Delta$ in ZrO. A $^3\Pi$ state is put at 24,000 cm^{-1} or about 2,800 cm^{-1} below the $^1\Pi$ which is assumed to come from sδ pπ. The $^3\Pi$ at 31,000 cm^{-1} and the $^1\Phi$ at 32,000 cm^{-1} are assumed to be from the dδ pπ configuration and are put between the known $^3\Phi$ and $^1\Pi$ states which are also assumed to be from this con- figuration.

Absorption features observed when TiO was deposited in rare gas mat- rices have been attributed to the α system, the γ system and the γ'_b system of TiO (32). The lower state of all three systems in the X$^3\Delta$ state. The a$^1\Delta$ state is put at 581 cm^{-1} from studies of the temperature dependence of the relative strengths of the α (c$^3\Delta$ - X$^3\Delta$) and the β(c$^1\Phi$-a$^1\Delta$) system (5). Since the a$^1\Delta$ and X$^3\Delta$ states presumably come from the sσ dδ molecular orbital configuration, it would be expected that the $^3\Delta$ would be lower in energy. Calculations (11) indicated that this separa- tion is about 4,400 cm^{-1}. Assuming the a$^1\Delta$ is 581 cm^{-1} above the X$^3\Delta$, the β system fixes the energy (33) of the c$^1\Phi$ at 18,421.60 cm^{-1}; the ϕ system fixed the energy (33) of the b$^1\Pi$ at 11,853.77 cm^{-1}; the δ system fixes the energy (34) of the d$^1\Sigma^+$ at 2,799.77 cm^{-1}; the α system (35) puts the

$C^3\Delta$ at about 19,300 cm^{-1} and the γ system (36) puts the $A^3\Phi$ at about 14,100 cm^{-1}. Three unassigned systems of Rosen and Lemaitre (37) are designated as γ'_c (or system I), γ'_b (system II) and system III. The γ'_b system was seen in absorption from the rare gas matrices (32) and is at the energy expected for the $B^3\Pi$ - $X^3\Delta$ transition by analogy to ScF and the α system of ZrO. The appearance of the γ'_b system is consistent with this assignment (38) so the $B^3\Pi$ is put at about 16,200 cm^{-1}. A $^3\Pi$ state is put at 9,000 cm^{-1} and is assumed to come from the same configuration (sδ dπ) as the b$^1\Pi$. A $^1\Pi$ state is put at 19,000 cm^{-1} by analogy to the E state of ScF (dδ dπ). The $^3\Sigma^+$ and $^1\Sigma^+$ states from sσ dσ were put at 13,000 and 15,000 cm^{-1} respectively by analogy to ScF. A $^1\Delta$ state from dδ dσ is expected to be above the $C^3\Delta$ state from the same configuration and is put at 22,000 cm^{-1}. The $^3\Pi$ and $^1\Pi$ from sσ pπ are not known and are put at 22,000 and 25,000 cm^{-1} by analogy to ScF. The $^3\Phi$, $^3\Pi$, $^1\Phi$ and $^1\Pi$ from dδ pπ are not known so that it is difficult to make as accurate an estimate of their energies as for the other unobserved states. They are put at slightly lower energies than the corresponding ScF state since the observed states of TiO generally fall somewhat lower than those of ScF. The γ'_c system (system I of Rosen and Lemartre) appears to have both R and Q heads suggesting a transition with $\Delta\Lambda = \pm 1$. The spacing of the heads is about that expected if the lower state were the $X^3\Delta$. However this system is not seen in absorption from the rare gas matrices and has the appearance of a singlet transition (30). Vibrational constants for the a$^1\Delta$ are not known, but it might be expected that they would be similar to the $X^3\Delta$ since both states come from the sσ dδ configuration. If the a$^1\Delta$ state is the lower state of the γ'_c system then

the upper state is most likely the $^1\Pi$ state from dδ pπ since it is the only $^1\Pi$ or $^1\Phi$ state expected near this energy (~16,700 cm^{-1}). Since this is somewhat lower than would be expected for the $^1\Pi$ state, clarification of the γ'_c system must await further experimental evidence.

Only two singlet systems of ZrO have been assigned and they have no common state. The A bands correspond to b$^1\Sigma^+$ - x$^1\Sigma^+$ and the B bands to d$^1\Delta$ - c$^1\Delta$. Since the absorption spectrum from rare gas matrice corresponds to the A bands (32) the x$^1\Sigma^+$ state is put at zero energy, and the b$^1\Sigma^+$ at 27,144.71 cm^{-1} (39). As is expected by the molecular orbital analogy and by the correspondence of observed ZrO states to those of ScF and TiO, the X$^3\Delta$ state must be extremely low in energy if not the electronic ground state in the gaseous phase. The X$^3\Delta$ is put at 1,000 cm^{-1}. The lower state of the B band the c$^1\Delta$ is put at 5,000 cm^{-1} since it it should be above the X$^3\Delta$ if both states come from sσ dδ. Furthermore, the d$^1\Delta$ is then (40) at 24,272.55 cm^{-1} and it is from dδ dσ. This puts d$^1\Delta$ state somewhat above the c$^3\Delta$ which is assumed to be of the same configuration. The original assignment of the A and B bands (39) was in doubt as $^1\Sigma$-$^1\Sigma$ could not be distinuished from $^1\Delta$-$^1\Delta$ in either transition. Absorption was seen in rare gas matrices at an energy nearer the B bands than the A bands. Weltner and McLeod favor the assignment of the $^1\Sigma^+$ to the lower state of the A bands, however it does not seem possible to entirely exclude the reverse assignment. Assuming the X$^3\Delta$ is at 1,000 cm^{-1} the γ system (41,42) fixes the A$^3\Phi$ state at about 16,700 cm^{-1}; the β system (42,43) fixes the B$^3\Pi$ at about 18,700 cm^{-1} and the α system (41,42) fixes the c$^3\Delta$ at about 22,500 cm^{-1}. The $^3\Pi$ and $^1\Pi$ from sσ dπ are put at 8,000 and 11,000 cm^{-1} by analogy to ScF and

TiO. The $^1\Phi$ and $^1\Pi$ from dδ dπ are put at 20,000 and 21,000 cm^{-1} since they come from the same configuration as the A and B states. The $^3\Sigma^+$ and $^1\Sigma^+$ from sσ dσ are put at 14,000 and 16,000 cm^{-1} by analogy to ScF. The $^3\Pi$ and $^1\Pi$ from sσ and pπ are not known and are put at 25,000 and 27,000 cm^{-1} and the reported δ system (44) is about the expected energy for the $^3\Pi$-X$^3\Delta$ transition. However there is another expected $^3\Pi$ from the dδ pπ which may be closer to the energy of the δ system. The $^3\Phi$, $^3\Pi$, $^1\Phi$ and $^1\Pi$ from dδ pπ are included for completeness and their energies cannot be predicted accurately.

The b$^1\Sigma^+$ at 27,144.71 has not been accounted for with the molecular orbitals used. The $^3\Sigma^-$, $^1\Gamma$ and $^1\Sigma^+$ from the dδ^2 configuration have not been used and the b state of ZrO may be from this configuration. No $^3\Sigma^-$ or $^1\Gamma$ state has been observed in ScF, TiO or ZrO and has been calculated to be very high in energy (11). Promotion of an electron from the 3π molecular orbital which has been considered here as a closed shell will give a multitude of molecular electronic states including a $^1\Sigma^+$. In view of the population analysis of the sσ and dδ orbitals, the correspondence of the observed states to the expected molecular orbitals and the expectation that the $^1\Sigma^+$ will not be the lowest energy state from configurations involving 3π^3, this alternative seem less likely.

There are not enough known states of ZrO to allow accurate predictions of the states involved in the ϕ system (44) or the system at about 6000 Å of Rosen and Lemaitre (37).

It would be of considerable interest to locate exactly the lowest $^1\Delta$ states and the unobserved $^3\Pi$ states in each of these molecules. It might also be fruitful to examine some of the perturbations observed in the ScF spectrum (13) to see if the precise value of the separation of

the $^3\Delta$ and $^1\Sigma^+$ states may be determined.

The partition functions of gaseous scandium monofluoride, titanium oxide and zirconium oxide can now be better defined. Calculation of the free-energy function or absolute entropy of these molecules is possible to an accuracy sufficient for many calculations.

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FIGURES

1. Electronic energy levels of the scandium atom.

2. The molecular beam heating assembly with radiation shields.

3. Known transitions of ScF, TiO, and ZrO and estimates of the
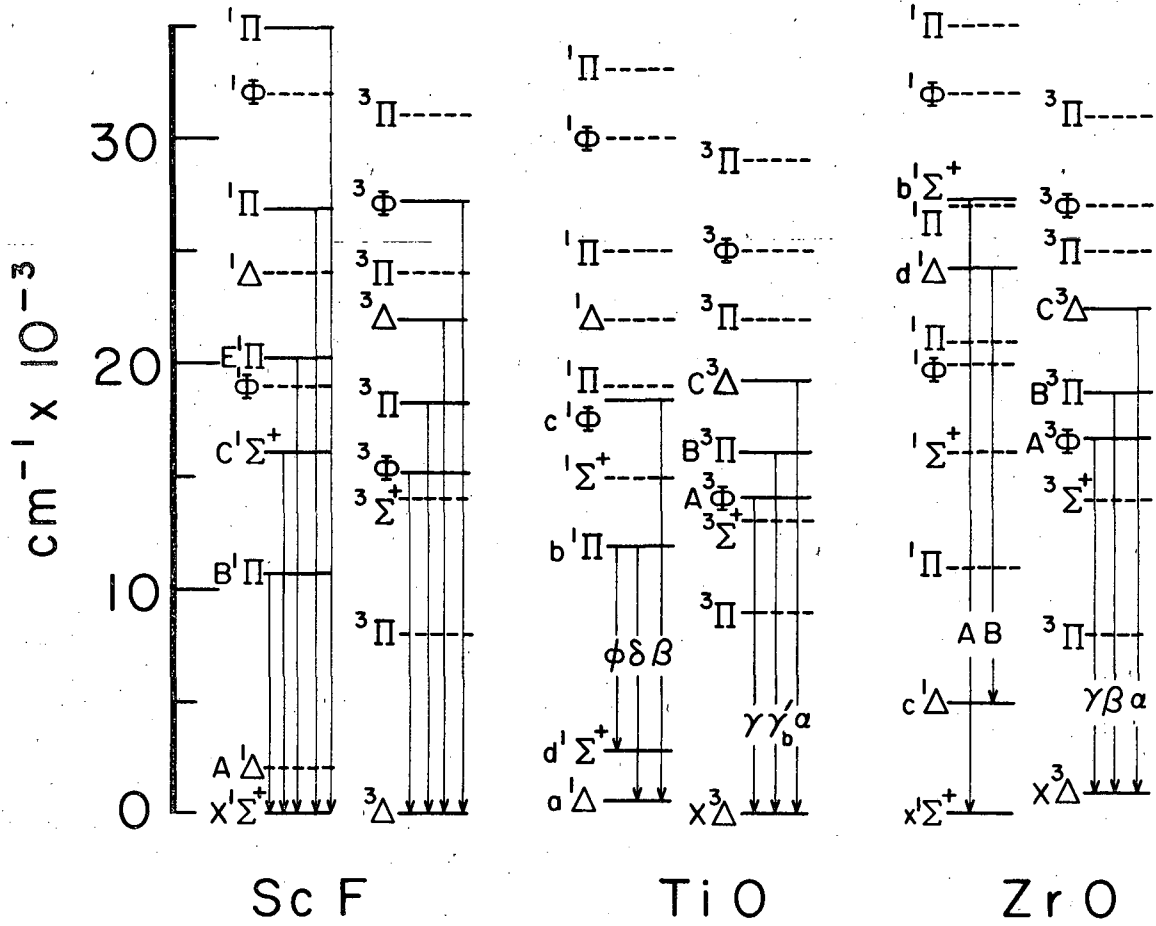   absolute energy of the electronic states.
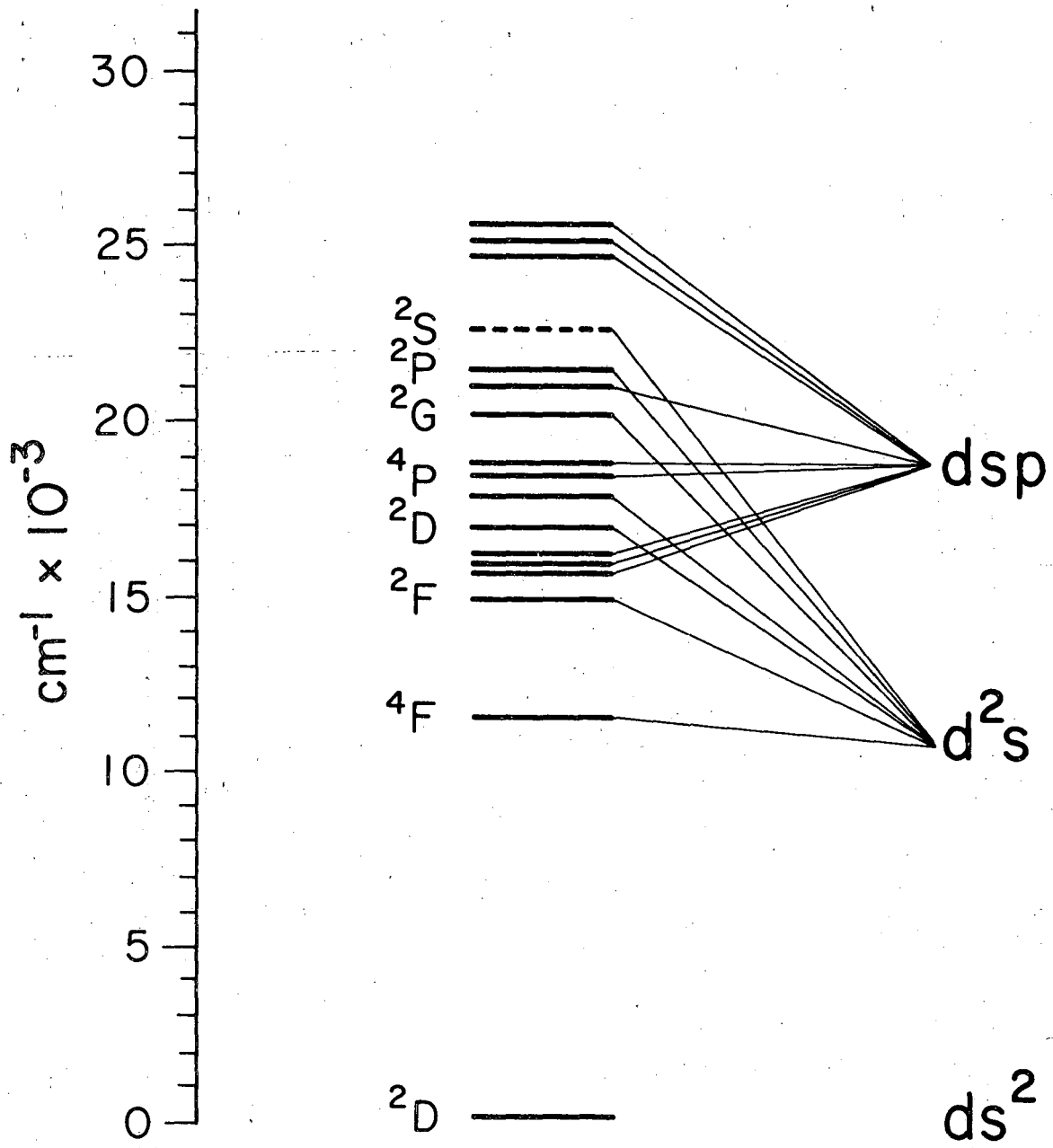
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Fig. 1

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Fig. 2

Fig. 3