

demonstrates that independence of pressure and linearity of van't Hoff plots do not assure the achievement of equilibrium. It leads to a calculated value of the apparent heat of reaction which depends only on the activation energy of the clustering reaction and the functional form of the temperature dependence of mean residence times. As long as applied fields are sufficient to assure the applicability of (XI), the resultant ΔH_a will be independent of instrumental parameters, drift lengths, field strengths, etc., and will differ by approximately -2 kcal/mol from the activation energy for the forward reactions. These factors will, however, affect the intercept of van't Hoff plots and thereby exercise considerable influence on the apparent values of free energies and entropies of reaction. This is consistent with earlier observations.^{6,11}

The present considerations support the thermodynamic parameters reported by Kebarle and co-workers^{3,12,13} and DePaz, *et al.*,¹⁵ and thereby reflect on the probable structure of the hydrated proton.

Theoretical considerations,^{16,26,27} particularly the *ab initio* calculations of Newton and Ehrenson,¹⁶ are in essential agreement with these experimental thermodynamic quantities and suggest that the optimized chain structures of the lower, and chain and branched structures of the higher proton hydrates, are good representation of actual structures, that the central OH bond distance in the dihydrate is considerably greater than in H_3O^+ , and that the addition of further water molecules causes the central OH bond to shorten again gradually.

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Optical Properties of Sugars. II. Vacuum-Ultraviolet Absorption of Model Compounds

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Abstract: Vacuum-ultraviolet absorption spectra of 11 model sugar compounds were measured to 80 kK. The model sugars include three alcohols, four ethers, and four complex cyclic compounds which combine alcohol and ether chromophores. All spectra show absorption bands in the energy region 50 to 65 kK which are attributed to the presence of the oxygen atom. The spectrum due to a hemiacetal group is presented for the first time. Apparently the interaction between alcohol and ether chromophores in this group is strong so that the hemiacetal is best treated as a single chromophore. In contrast, when chromophores are separated by two carbon atoms their interactions appear weak. In this case the low-energy transitions of the simple compounds measured here are additive and can be combined to yield the spectra of the more complex molecules. The as yet unmeasured spectrum of glucose is predicted.

Sugar monomers contain a number of alcohol chromophores as well as an ether chromophore in a tetrahydrofuran or tetrahydropyran ring. These chromophores exhibit degenerate or nearly degenerate transitions so that, in order to understand the electronic transitions of a monosaccharide, it is important to assess the strength of the interactions between these groups. Such an understanding is particularly important to our laboratory since we are conducting circular dichroism studies on sugars in aqueous solution in the vacuum-ultraviolet where Cotton effects associated with at least the first band in these chromophores can be completely determined.³

It might be best to measure the electronic absorption spectra of the sugars themselves in aqueous solution for direct comparison with the circular dichroism spectra.

However, to measure spectra in aqueous solution in the vacuum uv, it is necessary to use extremely short and unknown path lengths to minimize light absorption by the solvent. Such a procedure is reasonable for circular dichroism spectra because the absorption due to the symmetric solvent cancels in the measurement, but clearly the procedure is not applicable to the measurement of absorption spectra where the path length of the sample and the blank must be identical.

As a first step we have measured the spectra of some less complex molecules which are related to sugars. Since they are measured in the vapor phase, the results are not complicated by solvent effects, but of course solvent effects must be considered if the results are generalized to aqueous solution.

The spectra of four complex model sugar compounds (tetrahydrofurfuryl alcohol, 3-hydroxytetrahydrofuran, tetrahydropyran-2-methanol, and 2-hydroxytetrahydropyran) are new in this study, as are the spectra of cyclohexanol and the cyclic ether 2-methyltetrahydropyran. The spectra of two other alcohols (methanol

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and ethanol) as well as the spectra of three other ethers (diethyl ether, tetrahydrofuran, and tetrahydropyran) which were measured previously are presented here to compare with the more complex molecules. (References 4–12 contain alcohol and ether spectra of recent workers and references to earlier work.) We have repeated the spectra of these molecules on our spectrometer for internal consistency using modern dual beam instrumentation and improved pressure measuring methods.

Experimental Section

Procedure. All spectra were measured on a standard McPherson 225 vacuum-ultraviolet spectrometer with a double beam attachment (McPherson Model 665) and logarithmic ratiometer (McPherson Model 782). The spectra were recorded directly in optical density. The 1-m focus tripartite grating (ruled 600 lines mm^{-1}) gave a dispersion of 16 \AA mm^{-1} . Entrance and exit slit widths of 100μ were used for all measurements so that the spectral slit width was 1.6 \AA .

All compounds were studied in the vapor phase and cell path lengths of 1, 10, or 100 mm were appropriately chosen to match the pressure of the compound and its extinction coefficient. Three different methods were used for measuring the pressure of the gases. (1) For compounds with a high vapor pressure and bands of low extinction coefficient the pressure in the cell could be measured directly using a simple U-tube mercury manometer. (2) For compounds with sufficient vapor pressure and bands of high extinction coefficient the pressure was measured in a small calibrated volume. This volume of vapor was expanded in the cell. (3) During the final stages of this work all pressures were measured directly on a Baratron type 144 pressure meter from MKS Instruments, Inc. This allowed measurement of pressures to 0.0030 mm with an accuracy of 1% so that accurate extinction coefficients could be determined for the compounds with very low vapor pressures. All three methods of pressure measurement were compared using ethanol and found to give values within $\pm 2.5\%$.

Materials. The four low-boiling compounds (methanol, ethanol, diethyl ether, and tetrahydrofuran) were all reagent grade and their spectra were found to be unchanged by fractional distillation. All other compounds were purified by gas-liquid chromatography. Compound purity was also monitored by measuring the refractive index.

The 2-hydroxytetrahydropyran was synthesized in our laboratory by acid hydration of dihydropyran following the method of Woods.¹³

Before measurement all samples were outgassed by repeated freezing and thawing under vacuum. Each spectrum was measured at a variety of pressures and at a number of different times. No evidence of photodecomposition was observed. In the cases where spectra had been published previously, they compared favorably with our results.

Results

The spectra are divided into three groups: (1) simple alcohol chromophore; (2) simple ether chromophore, and (3) alcohol and ether chromophore combined. The shape of the spectra seems to be more closely related to the oxygen chromophore (whether it is an alcohol or an ether) than to the hydrocarbon

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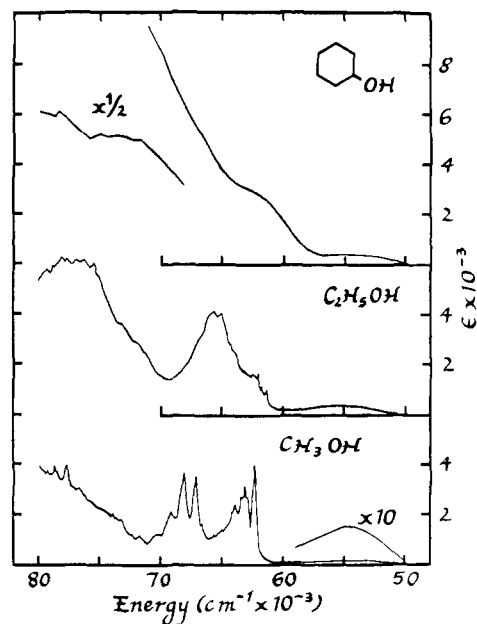


Figure 1. Absorption spectra of simple alcohols.

skeleton, at least below 70 kK.¹⁴ This leads us to devise a simple method to predict the spectra of the more complex compounds and unmeasured sugars. This is developed in the discussion. Here we present the spectra and briefly discuss the features in the low-energy region of the spectrum and their assignments.

The first group consists of methanol, ethanol, and cyclohexanol whose spectra are presented in Figure 1. All the alcohols show a broad, low-intensity band between 50 and 60 kK. Methanol exhibits two sharp and structured bands (ϵ about 4000) at 63 and 68 kK. In ethanol these two bands presumably coincide at about 66 kK. In the case of cyclohexanol only a shoulder appears in this region. These bands have been assigned by many investigators to σ^* type and n-Rydberg type transitions,^{5,8,10–12,15–17} but there is no real agreement and no reason to favor one assignment over another.

The simple ether chromophore is represented in diethyl ether, tetrahydrofuran, tetrahydropyran, and 2-methyltetrahydropyran shown in Figures 2 and 3. The spectra of diethyl ether and tetrahydropyran are strikingly similar. Both have three major peaks centered at almost the same energies (about 53, 59, and 65 kK). These peaks show fine structure which has been studied by Hernandez.⁷ In analogy to the alcohol bands, the low-energy ether bands have been assigned σ^* type and n-Rydberg type transitions,^{4,6,8,10,15–17} but again agreement between investigators is lacking.

The spectra of tetrahydropyran and 2-methyltetrahydropyran are also strikingly similar as would be expected if the low-energy transitions are due basically to the ether chromophore. Both have a highly structured but low-intensity band between 52 and 55 kK which is partially hidden by a more intense structured

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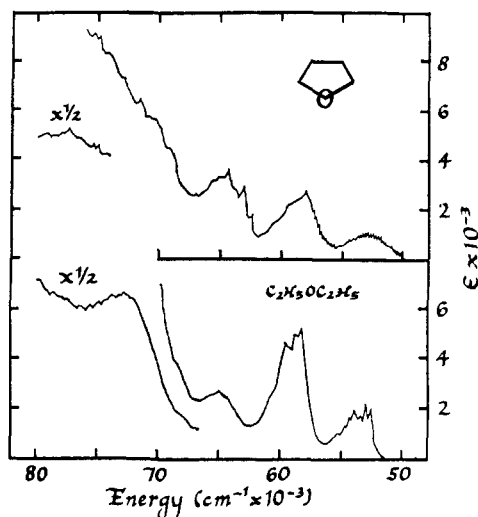


Figure 2. Absorption spectra of simple ethers.

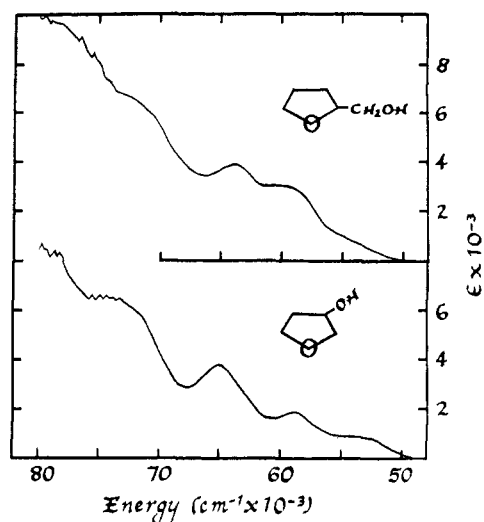


Figure 4. Absorption spectra of tetrahydrofuran chromophore combined with an alcohol chromophore.

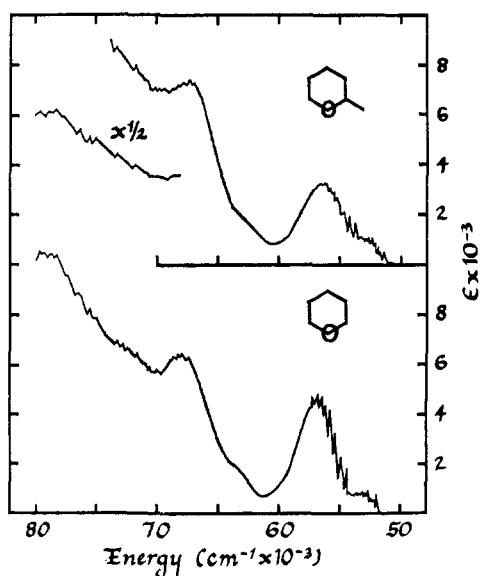


Figure 3. Absorption spectra of simple ethers.

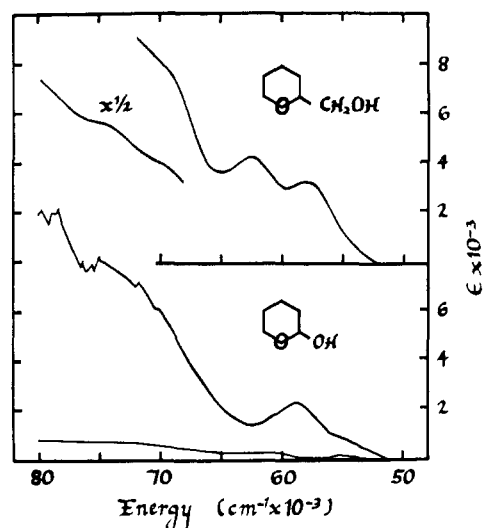


Figure 5. Absorption spectra of tetrahydropyran chromophore combined with an alcohol chromophore. The base line for the 2-hydroxytetrahydropyran represents the contribution of the ring-open form.

band centered at 57 kK. A third peak is evident on top of the background continuum at about 68 kK.

The set of cyclic compounds with both ether and alcohol chromophores consists of 3-hydroxytetrahydrofuran, tetrahydrofurfuryl alcohol, 2-hydroxytetrahydrofuran, and tetrahydropyran-2-methanol, shown in Figures 4 and 5. All these compounds are closely related to simple monosaccharides and their spectra have not been recorded previously. None of these spectra exhibit fine structure. The two tetrahydrofuran derivatives have the OH chromophore separated from the ether chromophore of the tetrahydrofuran ring by two carbon atoms. Although their structures are different their spectra are fairly similar. Both compounds exhibit a weak shoulder between 50 and 55 kK, a more intense band at about 60 kK, and a third peak at about 64 kK.

Tetrahydropyran-2-methanol differs from tetrahydrofurfuryl alcohol only in ring size, since they both have CH_2OH groups attached to the ring at the 2 position. Again the spectra are similar with the two prom-

inent bands red shifted about 1 kK for the six-membered ring while the low-energy shoulder has disappeared.

The 2-hydroxytetrahydropyran differs from all the others in that the ring can open and close. This is similar to the situation in monosaccharides. In order to interpret the lower energy part of the spectrum we must know whether the majority of the molecules in the vapor phase are cyclic or straight chain. We cannot obtain spectral evidence to support either form in the vapor phase, since under the prevailing conditions of temperatures and pressure even a 100% vapor spectrum of the straight chain form would not have shown a detectable $n\pi^*$ transition for the carbonyl bond. In an attempt to estimate the amount of straight chain in the vapor, we measured the absorbance spectrum of a 0.0054 M solution of 2-hydroxytetrahydropyran in cyclohexane. In this solvent the compound shows an extinction coefficient at 2900 Å of 0.45. The minimum extinction coefficient of the pure straight chain $n\pi^*$ transition is about 10, so this corresponds to at worst

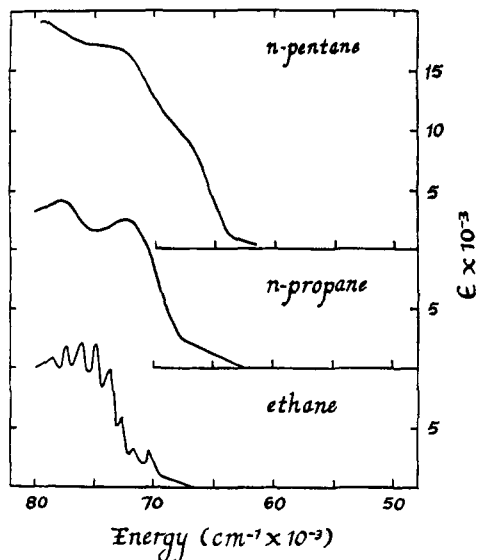
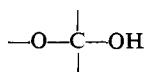


Figure 6. Hydrocarbon absorption spectra from ref 20. The spectrum of cyclopentane is similar to pentane.

4.5% straight and 95.5% ring form. Approximately the same percentages are found in aqueous solution¹⁸ implying that this is probably the percentage in the vapor as well. We have plotted below the spectrum of the 2-hydroxytetrahydropyran a spectrum which is 5% as high as a sum of propionaldehyde¹⁹ and 2-butanol.¹⁷ This represents the maximum contribution to the spectrum of the open form. The sharp peaks in the actual propionaldehyde spectrum have been smoothed here since they are not present in the spectrum of 2-hydroxytetrahydropyran.

The two chromophores in this compound are in close proximity. Since there may be strong interaction between them, we should probably consider them together as the single chromophore



While the low-intensity shoulder between 60 and 55 kK as well as the 59-kK band (typical of the other compounds) are still clear in this spectrum, the third high-energy band usually present at about 65 kK has either blue shifted or disappeared.

Discussion

While workers disagree on the exact assignment of the three low-energy transitions in alcohols and ethers, they do agree that these transitions are due to the presence of the oxygen atom in the molecule and are excitations of the nonbonding electrons on the oxygen to higher energy unoccupied states.^{4-12, 15-17} Further evidence for this can be found by comparing the spectra of some simple alcohols and ethers to those of the corresponding hydrocarbons (Figure 6).²⁰ Such comparisons indicate that alcohols and ethers have three low-energy bands which are due to the presence of the oxygen atom in the molecules. We assume that the prominent low-energy bands in the cyclic com-

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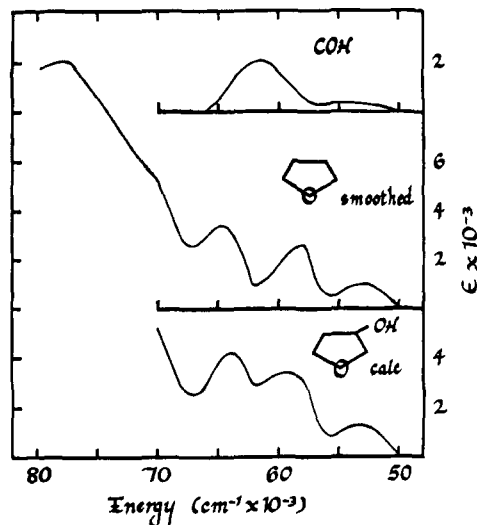


Figure 7. Absorption spectrum of a complex molecule calculated by combining the spectra of the individual chromophores.

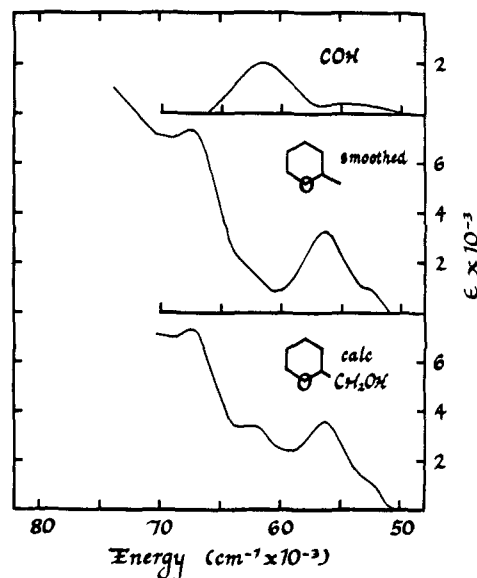


Figure 8. Absorption spectrum of a complex molecule calculated by combining the spectra of the individual chromophores.

pounds with alcohol and ether chromophores combined are also due to the presence of the oxygen atom.

Figures 7 and 8 demonstrate how one can generate the spectra of the more complex compounds. In both cases we combine the spectrum of the simple cyclic compound with the spectrum of the COH chromophore. The COH contribution is found by subtracting the $\sigma\sigma^*$ transitions from the spectrum of cyclohexanol. In Figure 7 the spectrum of 3-hydroxytetrahydrofuran is predicted by combining the smoothed spectrum of tetrahydrofuran with that for the COH group. The predicted spectrum compares rather well with the actual spectrum of the compound (Figure 4). The calculated spectrum also compares to that for tetrahydrofurfuryl alcohol (Figure 4) although this compound has an extra methyl group.

In Figure 8 we combine the spectrum of 2-methyltetrahydropyran which has also been smoothed to eliminate vibrational structure with the spectrum of the

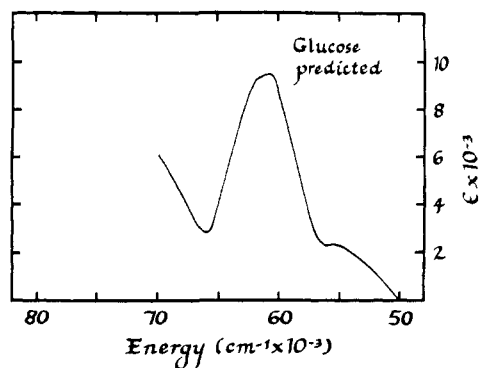


Figure 9. Absorption spectrum of glucose predicted by combining the spectra of the individual chromophores.

COH chromophore. Again the graphically calculated spectrum predicts the measured spectrum of tetrahydropyran-2-methanol (Figure 5) satisfactorily.

The success in constructing spectra in this manner indicates that the COH chromophore is independent and interacts little with the ring oxygen chromophore when the two are separated by at least two carbon

atoms. In contrast, one can try to generate the spectrum of 2-hydroxytetrahydropyran by combining the spectrum of tetrahydropyran with the spectrum of the COH chromophore. The result (similar to the calculated spectrum of tetrahydropyran-2-methanol, Figure 8) does not resemble the measured spectrum of 2-hydroxytetrahydropyran. This indicates that the COH and ring oxygen interact strongly here.

Finally it is of interest to try to predict the as yet unmeasured spectrum of a sugar in the vapor phase. We chose glucose which in our approximation should have an absorption spectrum identical with the other seven diastereomers in their cyclic six-membered ring form. The predicted spectrum, given in Figure 9, is calculated by combining the spectrum of 2-hydroxytetrahydropyran plus the spectra of four COH groups. The $\sigma\sigma^*$ transitions of the saccharides will differ from those of the model compounds in that the saccharides will have more CO and OH transitions and fewer CH transitions. In this case the basic cyclic compound should have been 2-hydroxy-5-methyltetrahydropyran but the spectrum of this compound should not differ markedly from the spectrum of 2-hydroxytetrahydropyran.

Valence Level Studies of $\text{Cr}(\text{CN})_6^{3-}$, $\text{Mn}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, $\text{Co}(\text{CN})_6^{3-}$, and $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ by X-Ray Photoelectron Spectroscopy

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Abstract: The X-ray photoelectron spectra of the valence regions of the molecular ions $\text{Cr}(\text{CN})_6^{3-}$, $\text{Mn}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, $\text{Co}(\text{CN})_6^{3-}$, and $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ have been measured from spectra of salts containing these ions. The results have been compared with the photoelectron spectrum of the cyanide ion itself and with expectations from theoretical studies of the ions. The salient feature in some of the spectra is the $2t_{2g}$ level, arising from metal 3d and half ligand orbitals in $\text{Fe}(\text{CN})_6^{4-}$.

The cyanide complexes of the first transition series have received very large amounts of attention, both theoretical and experimental. This attention is due to the fact that they are relatively simple, symmetrical compounds and that, more importantly, they serve as a model of the low spin, strong crystal field complex.^{1,2}

We have studied the valence electron levels of a number of iron series cyanide complexes, and of a related compound, by X-ray photoelectron spectroscopy. This technique reveals a different aspect of the electronic structure and, we believe, clarifies our understanding of these compounds.

Before discussing our experiments, we remind the reader of some salient features of previous work on the cyanides. We cannot hope to survey so vast an area of research in a short introduction, so we emphasize merely those studies which are germane to the ground-

state electronic structure of the cyanide complexes. In these areas, we emphasize general conclusions and data which may be compared with our results.

Most of the large amount of optical spectroscopic work on cyanides has involved examination of ligand field transitions and, thus, involves moving electrons between occupied and unoccupied orbitals. Some work on ligand-to-metal charge-transfer transitions has appeared, however. In these transitions one moves electrons between two orbitals, both of which may be occupied in the ground state. The data, thus, have some direct relevance to ground-state electronic structure. An extensive discussion of the optical spectra of cyanides, based upon Gaussian analysis of spectra at room temperature and at 77°K and upon approximate calculations, has been given by Gray and Alexander.³

According to them, the first $L \rightarrow M$ charge-transfer

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